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KINETICS AND MECHANISMS OF ELECTRON TRANSFER REACTIONS OF METAL COMPLEXES.

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KINETICS AND MECHANISMS OF ELECTRON TRANSFER REACTIONS OF METAL COMPLEXES

by

Ormond Jerry Parker

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
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DOCTOR OF PHILOSOPHY

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Approved:

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Iowa State University
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1968

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INTRODUCTION

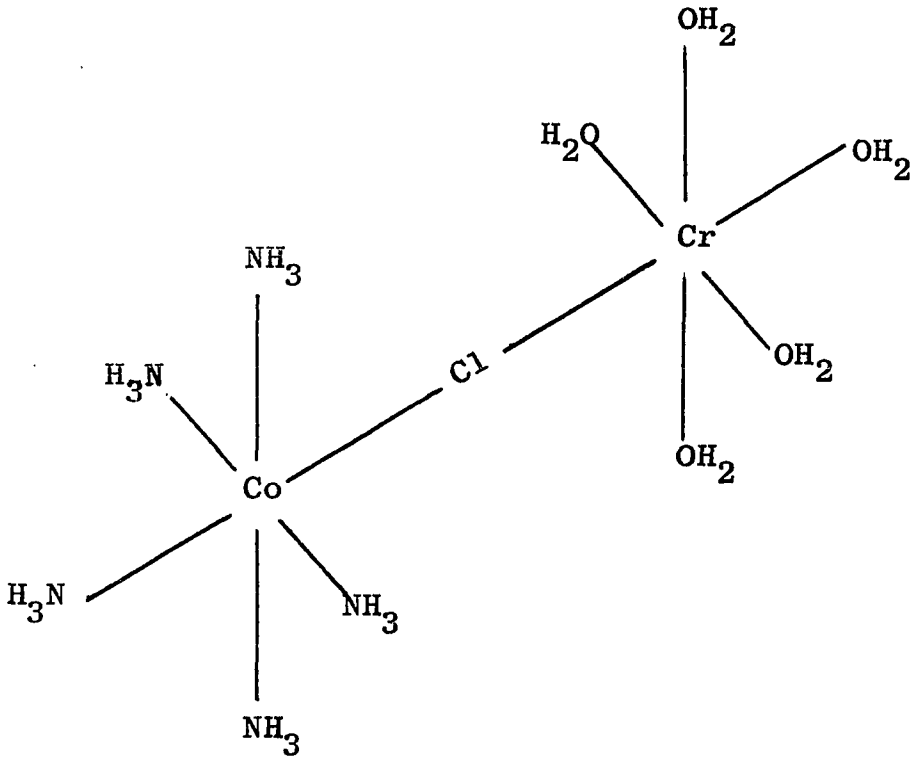
The rates of electron transfer reactions between metal ion complexes in solution have been widely studied recently (1-20). Taube (1) has pointed out that mechanisms of oxidation-reduction reactions of transition metal ion complexes can be separated into two classes; inner-sphere and outer-sphere, depending upon whether or not the first coordination spheres of the two metal ions have a ligand in common at the time of electron transfer.

Taube and Myers (2) have shown that reaction 1 proceeds by an inner-sphere mechanism.

$$Co(NH_3)_5Cl^{2+} + Cr^{2+} + 5H^+ = Co^{2+} + CrCl^{2+} + 5NH_4^+ \qquad (1)$$

In this case chloride ion is the bridging ligand in the transition state as shown in the diagram on the following page.

After completion of the electron transfer and dissociation of the activated complex, the bridging ligand remains bound to the least labile of the product metal ions, for a time governed by the solvation rate characteristic of the particular metal ion complex. In this particular example, the proof of the inner-sphere mechanism was the demonstration of transfer of the bridging ligand from one metal to the other. This proof is possible only when the reactant complex containing



the bridging ligand is inert to substitution while the other metal ion is labile. After electron transfer, relative labilities of the products must be opposite those of the reactants and the inert product must be sufficiently inert to be detectable as a metal complex containing the bridging ligand. With reference to Equation 1, Cr^{2+} and Co^{2+} are labile to ligand substitution and exchange, whereas the reactant $Co(NH_3)_5Cl^{2+}$ and the product $Cr(OH_2)_5Cl^{2+}$ are inert to these processes.

Failure to demonstrate ligand transfer does not, however, eliminate the possibility of an inner-sphere mechanism. Ligand transfer cannot be demonstrated unless both the

reactant and the product containing the bridging groups can be identified and unless replacement of the bridging ligand by solvent on both the reactant and the product is negligible during the oxidation-reduction reaction. Thus, inner-sphere mechanisms cannot be demonstrated by the ligand transfer method when both reactants or both products are labile.

Indirect evidence is often invoked to support conclusions regarding the reaction mechanism. The variation (or lack of variation) in reaction rate upon reacting the same metal complexes except for the identity of the bridging ligand is cited (3,4) as evidence for an inner-sphere (or outer-sphere) mechanism. The rates of inner-sphere reactions are more dependent on the identity of the bridging ligands than outer-sphere reactions are on the identity of nonbridging ligands (3-8). An especially informative pair are the ligands H_2O and OH^-. With inner-sphere reactions the rates with OH^- as the bridging ligand are much higher than those with H_2O as the bridging group. Another pair of ligands that have proven useful are N_3^- and NCS^-. The rates noted for N_3^- bridged reactions are normally considerably greater (3) than the rates for NCS^- bridged reactions that are otherwise identical. In using the latter criteria, care must be exercised with regard to whether or not the sulfur-bonded thiocyanate ion is the stable configuration of the product. Another line of indirect evidence that has been used to establish mechanisms

has been obtained from nonbridging ligand effects (9-13). Nonbridging ligand effects for inner-sphere reactions have also received theoretical consideration by L. Orgel (14). The prediction of the relative reactivities of cis and trans isomers of the type MA_4XY^{n+} (M=Cr(III) or Co(III)), where Y is the bridging ligand, depends upon the relative crystal field strengths of A and X. If X has a smaller crystal field than A, the trans isomer should react more rapidly than the cis isomer, whereas the reverse holds if X has the larger crystal field. As an example, the reaction of cis and trans-$Co(en)_2Cl_2^+$ with Fe^{2+} has been studied by Benson and Haim (10). The trans complex is observed to have the higher reaction rate by a factor of 20, leading to the hypothesis that the reaction follows an inner-sphere mechanism. Other indirect evidence that has been used to establish mechanisms has been obtained from variations in entropies of activation (4,15,16,17), volumes of activation (8) and isotope effects on reaction rate (18,19).

The proof of an outer-sphere mechanism is very simple in a limited number of cases. If both the oxidized and reduced form of a metal complex are substitutionally inert and all of the ligands are incapable of electron transfer, the outer-sphere mechanism must be operative. For example, when $Co(NH_3)_5Cl^{2+}$ is reduced by the substitutionally inert reducing agent $Ru(NH_3)_6^{2+}$, the electron transfer process occurs without

disruption of the first coordination sphere of the ruthenium complex, as evidenced by the fact that the substitutionally inert $Ru(NH_3)_6^{3+}$ is the only ruthenium product (6). Indirect evidence often invoked (3-8) for outer-sphere mechanisms is the small dependence of the rate on the identity of ligands bound to the reactants, notably such ligands as H_2O and OH^-. Evidence such as non-bridging ligand effects and others mentioned in connection with inner-sphere mechanisms are also cited in support of outer-sphere mechanisms.

In the absence of complexing anions, copper(I) is thermodynamically unstable with respect to disproportionation (Equation 2). The

$$2Cu^+ = Cu^{2+} + Cu^0 \qquad (2)$$

equilibrium quotient for reaction 2 is 1.3×10^6 $\underline{M}^{-1}$ (20) at 25° at ionic strength 1.96×10^{-2} $\underline{M}$ in the presence of perchlorate anions. Copper(I) in such salts as Cu_2SO_4 rapidly disproportionates in water to give copper metal and the cupric salt (21).

Although copper(I) is thermodynamically unstable in an aqueous medium, it should not be assumed that the rate of the disproportionation reaction is necessarily rapid. A feature of major interest in this work is the use of appropriate one-electron reducing agents to generate quantitative yields of Cu^+ in perchlorate solution. Such metastable solutions

($\leq$ 0.01 M) can, moreover, be used for some time without appreciable disproportionation. Altermatt and Manahan (22,23) have recently published an electrochemical procedure for generating aqueous solutions of copper(I) perchlorate, and have shown that Cu^+ solutions may be prepared by the careful dissolution of the freshly precipitated hydroxide in perchloric acid. The interest in reactions producing metastable copper(I) arose from several factors: (1) the uniqueness in producing Cu^+_{aq} in a metastable situation in perchlorate solution, (2) the questions posed of inner-sphere or outer-sphere reaction mechanisms, (3) the subsequent studies allowed on the reaction mechanisms of copper(I), and (4) direct information on the role of copper(I) in reactions catalyzed by copper(II).

The rate of electron transfer between copper(II) and vanadium(II) (Equation 3) has not been previously measured.

$$Cu^{2+} + V^{2+} = Cu^+ + V^{3+} \qquad (3)$$

This reaction and the similar reduction of copper(II) with chromium(II) (Equation 4) may be utilized to generate the

$$Cu^{2+} + Cr^{2+} = Cu^+ + Cr^{3+} \qquad (4)$$

metastable species Cu^+_{aq} (24) in perchlorate solution. The question of inner-sphere or outer-sphere mechanism is of interest in these reactions. In view of recent attempts (1-20,24) to understand the details of the mechanisms of electron transfer reactions of metal complexes, data on new

systems are especially useful. Thus the production of Cu^{+}_{aq} and the subsequent studies allowed on the reduction mechanisms of copper(I) with various oxidizing agents promised to aid in the understanding of electron transfer processes. An earlier attempt was made by Endicott and Taube (6) to study the rate of some rapid Cu^{+} - Co(III) (where the Co(III) compounds were $Co(NH_3)_6^{3+}$, $Co(NH_3)_5OH_2^{3+}$, and $Co(NH_3)_5Br^{2+}$) reactions. Their study generated very small concentrations of Cu^{+} by the reverse of reaction 2; the exceptionally small concentrations involved led these workers to report some rate constants that are apparently quite incorrect.

Since an e_g electron is lost by Cu^{+}_{aq} as in the case of Cr^{2+}_{aq}, it is expected that the mechanisms of reaction for the two reducing agents would be similar. The Cr^{2+}_{aq} reduction of cobalt(III) complexes has been shown to be inner-sphere by the ligand transfer criteria (2).

The studies to be described here are a series of measurements of the rate of oxidation of Cu^{+} by; Fe^{3+}, <u>trans</u>-$Co(en)_2Cl_2^{+}$, $Co(NH_3)_5Br^{2+}$, $Co(NH_3)_5Cl^{2+}$, <u>cis</u>-$Co(en)_2Cl_2^{+}$, $Co(NH_3)_5N_3^{2+}$, $Co(NH_3)_5NCS^{2+}$, $Co(NH_3)_5F^{2+}$, <u>trans</u>- $Co(NH_3)_4(OH_2)$-CN^{2+}, $Co(NH_3)_5CN^{2+}$, $Co(NH_3)_5OH_2^{3+}$ and $Co(en)_3^{3+}$ (where en = ethylenediammine).

The catalytic effect of Cu^{2+} on a wide variety of reactions is well documented (25-31). One example of particular relevance to this work is the catalysis of the reaction of

$Fe^{3+} + V^{3+}$ by Cu^{2+} (Equation 5), which has been studied by

$$Fe^{3+} + V^{3+} \xrightarrow{Cu^{2+}} Fe^{2+} + V(IV) \qquad (5)$$

Higginson and Sykes (32). It has been postulated that the catalytic activity resulted from the production of Cu^{+}_{aq} in steady-state concentrations. The independent production of Cu^{+}_{aq} and subsequent studies with it promise to yield significant information about the detailed mechanism and characteristic properties of the proposed intermediate Cu^{+}_{aq}. The reaction of V^{3+} and Cu^{2+} has been studied further here utilizing the catalysis of the reaction of V^{3+} and $Co(NH_3)_5Br^{2+}$ by Cu^{2+}.

Ogard and Taube (33) found that a number of strong oxidizing agents catalyzed net aquation of the pentaaquochloro-chromium(III) cation, $(H_2O)_5CrCl^{2+}$ (Equation 6). The proposed mechanism consisted of oxidation of $CrCl^{2+}$ to Cr(IV) followed

$$(H_2O)_5CrCl^{2+} + H_2O = Cr(H_2O)_6^{3+} + Cl^{-} \qquad (6)$$

by reduction back to Cr(III). Since Cr(IV) is presumably labile to substitution, chloride ion was readily released at this stage. This suggests that a parallel catalysis effect on chromium(III) substitution should be noted in the presence of reducing agents. The chromium(II) so formed would release the bound chloride ion and would then be reoxidized in a second step. Using this model, a system was selected involving metal ions where the oxidation-reduction reaction between the aquo

ions had been studied and where the equilibrium position of the Cr(III) substitution process was known. The reaction selected was that of V^{2+} and $CrCl^{2+}$ (Equations 7 and 8).

$$V^{2+} + CrCl^{2+} \underset{2}{\overset{1}{\rightleftharpoons}} V^{3+} + Cr^{2+} + Cl^{-} \qquad (7)$$

$$V^{3+} + Cr^{2+} \xrightarrow{3} V^{2+} + Cr^{3+} \qquad (8)$$

$$\text{net:} \quad CrCl^{2+} = Cr^{3+} + Cl^{-} \qquad (9)$$

The kinetics and mechanism of the reaction of V^{3+} and Cr^{2+} (Equation 8) have been studied previously (34), and the equilibrium quotient for aquation of $CrCl^{2+}$ (Equations 6 and 9) is known (35). According to the principle of microscopic reversibility, the reaction of V^{3+} and Cr^{2+} would show catalysis by chloride ion in a reaction forming the complex $CrCl^{2+}$. A detailed kinetic study has been carried out on each step contributing to the reaction scheme.

Complications arose in the kinetics of the reaction of V^{2+} and $CrCl^{2+}$ that could not be resolved in terms of a two-step mechanism (Equations 7 and 8) satisfying the steady-state approximation. It became apparent that the Cr^{2+} and V^{3+} so produced were not reacting in a second step at a rate high enough to ensure the validity of the steady-state expression. A detailed consideration of the nonsteady-state kinetics was undertaken.

EXPERIMENTAL SECTION

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 $\leq 1 \times 10^{-6}$ ohm^{-1}.

Perchloric acid

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

Nitrogen

Nitrogen gas was purified by passage through a series of five gas-washing bottles equipped with gas dispersion 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.

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.* 4 *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 purified and analyzed in the same manner as lithium perchlorate.

Barium perchlorate

Barium perchlorate was prepared from barium carbonate and analyzed in the same manner as lithium perchlorate.

Barium chloride

Reagent grade barium chloride was recrystallized twice and analyzed in the same manner as lithium perchlorate.

Hydrochloric acid, hydrobromic acid and hydrofluoric acid

Dilutions of the concentrated acid were used without further purification. Solutions were titrated directly with standard sodium hydroxide to a phenolphthalein endpoint.

Sodium azide

Reagent grade sodium azide was dissolved in conductance water, filtered and recrystallized twice. The azide solutions were analyzed by oxidation with cerium(IV) and titration of the excess cerium(IV) with iron(II).

Copper(II) perchlorate

Copper(II) perchlorate was obtained from two independent procedures. Reagent grade (G. F. Smith) copper(II) perchlorate was dissolved in conductance water, filtered and recrystallized

twice. Reagent grade copper(II) carbonate was dissolved in a slight excess of concentrated perchloric acid, followed by boiling to expel CO_2. The resulting copper(II) perchlorate was recrystallized twice in conductance water. Stock solutions of copper(II) were analyzed by two different methods. The total cation content of the solution was analyzed by passing aliquots of the solution through a column of Dowex 50W-X8 cation-exchange resin in the hydrogen ion form, followed by titration of the washings with sodium hydroxide to a phenolphthalein endpoint. The concentration was calculated by assuming that each copper ion released two hydrogen ions from the resin column. Solutions of copper(II) were also analyzed by the standard volumetric procedure in which potassium iodide is added and the liberated iodine titrated with sodium thiosulfate using starch indicator. The analysis of copper(II) and of total cation content always agreed to within 1%.

Cobalt(II) perchlorate

Cobalt(II) was produced by the reduction of cobalt(III) complexes such as $Co(NH_3)_5Br^{2+}$, $Co(NH_3)_5Cl^{2+}$ and $Co(NH_3)_5N_3^{2+}$. The cobalt(II) so produced was analyzed spectrophotometrically as the thiocyanate complex (0.1 g/ml of ammonium thiocyanate) in 50-vol % acetone. The molar absorptivity is 1837 $\underline{M}^{-1}$ cm^{-1} at 623 nm.

Vanadyl perchlorate

Stock solutions were prepared from reagent vanadyl sulfate and a very slight excess of recrystallized barium perchlorate. The precipitated barium sulfate was removed by centrifugation.

Vanadium(II) perchlorate

Vanadium(II) solutions were prepared by reduction of V(IV) solutions containing added perchloric acid with amalgamated zinc. Alternatively, the solution was reduced electrolytically at a mercury cathode. A further independent source of vanadium(II) was provided by the electrolytic reduction of a slurry of vanadium pentoxide in perchloric acid. To prevent appreciable oxidation of vanadium(II) by perchloric ion (36), the stock solutions were stored in a refrigerator at -10°. The solutions were periodically tested for chloride ion by adding excess iron(III), then silver(I); negative tests ($\leq 10^{-3}$ M Cl^-) were obtained. Solutions of vanadium(II) were analyzed by two different methods. Vanadium(II) was added to an excess of $Co(NH_3)_5Br^{2+}$ in perchloric acid and allowed to react for 10-20 min under a nitrogen atmosphere. The cobalt(II) so produced was analyzed spectrophotometrically as the thiocyanate complex. The second method determined the total vanadium concentration by oxidizing all the vanadium species present to VO_2^+. The vanadium(V) was analyzed spectrophotometrically with hydrogen peroxide in sulfuric acid solution (ε 203 $\underline{M}^{-1}$ cm^{-1} at 400nm). Details of the procedure have been published (34).

Vanadium(III) perchlorate

Solutions of vanadium(III) perchlorate were prepared from approximately equimolar amounts of V(II) and V(IV) perchlorate, with a slight excess of the former. Stock solutions were stored in a refrigerator and tested periodically for chloride ion (36) in the same manner as vanadium(II) solutions. The method of analysis was the same as the two methods described in the analysis of vanadium(II). The vanadium(III) concentration was calculated as the difference between the total vanadium concentration and the vanadium(II) concentration as determined with $Co(NH_3)_5Br^{2+}$.

Chromium(III) and chromium(II) perchlorate

Doubly recrystallized chromium(III) perchlorate was reduced either electrolytically or with amalgamated zinc. The detailed procedures of preparation, handling, and analysis of these solutions have been described previously (34). The analytical procedure for chromium(II) was based on its reduction of a slight excess of $Co(NH_3)_5Cl^{2+}$. The cobalt(II) so produced was analyzed spectrophotometrically with thiocyanate ion in a 50 vol % acetone. The total chromium content was measured spectrophotometrically as CrO_4^{2-} after oxidation with alkaline peroxide (37). The chromium(II) solutions reduced with amalgamated zinc contained less than 1 % chromium(III).

Iron(III) perchlorate

Hydrated iron(III) perchlorate was prepared from solutions of the chloride in perchloric acid, by heating to remove HCl. After the solution failed to produce a visible precipitate in a test with silver ion, two successive crystallizations were done. Iron(III) perchlorate solutions were analyzed spectrophotometrically in 0.3-0.6 M perchloric acid using the peak of aquoiron(III) at 240 nm with a molar absorptivity of 4230 M^{-1} cm^{-1} (38). The perchloric acid content of the iron(III) perchlorate solutions was determined by passing samples through a column of Dowex 50W-X8 cation exchange resin in the hydrogen ion form and titrating the washings with sodium hydroxide. The hydrogen ion concentration was calculated from the base in excess of that required for the three moles of hydrogen ion displaced per mole of iron(III).

Chlorochromium(III) ion, $(H_2O)_5CrCl^{2+}$

Chlorochromium(III) ion was synthesized from chlorine and chromium(II) in perchloric acid solution (2). An alternate preparation of $(H_2O)_5CrCl^{2+}$ was the addition of a trace of chromium(II) catalyst to a deoxygenated solution of chromium(III) chloride-6-hydrate (39). The latter compound contains the ion trans-$(H_2O)_4CrCl_2^+$ (40-42). The major product of each reaction was the desired monochloro complex, which was separated and purified by cation exchange using Dowex 50W-X8 resin and elution with 1 F perchloric acid.

Cobalt(III) complexes[1]

trans-$[Co(en)_2Cl_2]Cl$[2] The chloride salt of this complex was prepared by the method of Bailar (43).

cis-$[Co(en)_2Cl_2]Cl$ The trans form was converted to the cis form by evaporating a neutral solution of the trans form to dryness on a steam bath. This procedure was repeated only once because of the undesirable aquation products produced by this procedure (44).

$[Co(NH_3)_5CO_3]NO_3 \cdot H_2O$, $[RCO_3]NO_3 \cdot H_2O$[3] This compound was prepared as a starting material for many of the pentaammine-cobalt(III) complexes. It was prepared by the method of Basolo and Murmann (45).

$[Co(NH_3)_5Br]Br_2$, $[RBr]Br_2$[3] The bromide salt was prepared by the method of Diehl, Clark and Willard (46). The bromide salt was converted and recrystallized as the perchlorate by the following procedure. The bromide salt was added to water previously heated to 70°. Lithium perchlorate crystals were added to this solution until $[Li^+] \sim 4$ M. The solution

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[1]The author is very grateful to Dr. J. H. Espenson and Mr. L. A. Berge who generously allowed him to use several cobalt complexes prepared by them.

[2]Prepared by Dr. J. H. Espenson.

[3]Prepared by Mr. L. A. Berge.

was then cooled to 0°C and the purple crystals filtered, washed with 95% alcohol and then with anhydrous ether, and air-dried. The recrystallization was repeated twice.

$[Co(NH_3)_5Cl]Cl_2$, $[RCl]Cl_2$ [3] Concentrated hydrochloric acid was added to a solution of the pentaamminecarbonatocobalt (III) nitrate. The solution was heated on a steam bath for two hours. The reddish-violet crystals were filtered and washed with 95% alcohol. The chloride salt was converted to the perchlorate salt and recrystallized as such by dissolving the complex in water and precipitating it by adding concentrated perchloric acid. The recrystallization was repeated twice.

$[Co(NH_3)_5N_3](ClO_4)_2$, $[RN_3](ClO_4)_2$ The chloride salt of this complex was prepared in semi-darkness by the method of Linhard and Flygave (47). The salt was recrystallized twice using concentrated perchloric acid.

$[Co(NH_3)_5NCS](ClO_4)_2$, $[RNCS](ClO_4)_2$ [2] This complex was prepared from the pentaamminecarbonatocobalt(III) complex by the following procedure. A solution of 5 g $[Co(NH_3)_5CO_3]NO_3 \cdot H_2O$ in *ca.* 80 ml H_2O was prepared at 90° using conductance water. After the addition of 16 g NaNCS, 25 g $NaClO_4$ and 10 ml concentrated CH_3COOH, the solution was heated for *ca.* 30 min on a steam bath. The red crystals were filtered, washed and recrystallized from conductance water with lithium perchlorate.

$[Co(NH_3)_5F](ClO_4)_2$, $[RF](ClO_4)_2$ [2] The nitrate salt of this complex was prepared by the method of Basolo and Murmann (48). The nitrate was converted and recrystallized as the perchlorate by dissolving the nitrate in conductance water and reprecipitating it as the perchlorate by the addition of concentrated perchloric acid. The pentaamminefluorocobalt(III) was recrystallized twice.

$[Co(NH_3)_5OH_2](ClO_4)_3$, $[ROH_2](ClO_4)_3$ This complex was prepared directly by the slow addition of concentrated perchloric acid to a saturated solution of pentaamminecarbonatocobalt(III) nitrate. After separation of the orange crystals, the complex was recrystallized twice using concentrated perchloric acid.

trans-$[Co(NH_3)_4(OH_2)CN](ClO_4)_2$, trans-$[CoA_4(OH_2)CN](ClO_4)_2$ [2] The chloride salt of this complex was prepared by the method of Siebert (49). Conversion to the perchlorate resulted in a large loss of the complex. The chloride salt of the complex was dissolved at 50°C and reprecipitated by adding $NaClO_4$. The recrystallization with $NaClO_4$ was repeated.

$[Co(NH_3)_5CN](ClO_4)_2 \cdot 0.5\ H_2O$, $[RCN](ClO_4)_2 \cdot 0.5\ H_2O$ [2] The perchlorate was prepared by the method of Siebert (49).

$[Co(en)_3](ClO_4)_3$ [4] The salt of this complex was prepared by the method of Bjerrum and McReynolds (50). Conversion and recrystallization of the perchlorate salt was repeated twice using perchloric acid to reprecipitate the salt each time.

Solutions of the cobalt(III) complexes were made by carefully weighing the amount of complex added. The solutions were analyzed for cobalt content by reaction with excess chromium(II) solution. The Co^{2+} produced was analyzed spectrophotometrically as the thiocyanate complex. The purity of the complexes was indicated by quantitative agreement of the visible spectra with published values. Spectral data is given in Table 2: the molar absorptivity is calculated from the cobalt analysis in each case. The per cent cobalt calculated and found is presented in Table 1. Three of the complexes probably had small amounts of at least one other reagent present. These three impurities however would be innocuous and would not alter the kinetic results. Because of the method of recrystallization, $[Co(NH_3)_5Br](ClO_4)_2$ would be expected to have small amounts of $LiClO_4$ present as an impurity. The starting material for $[Co(NH_3)_5N_3](ClO_4)_2$ is $[Co(NH_3)_5OH_2](ClO_4)_3$ and small amounts of this may not have been removed by the three recrystallizations. The aquo complex would not be accounted for in the cobalt analysis because of its slow reaction with chromium(II). The complex

[4] Prepared by Mr. D. E. Binau.

Table 1. Analysis of the cobalt content in the cobalt(III) complexes

Anal. Calcd. for $[Co(NH_3)_5Br](ClO_4)_2$:	Co, 13.9. Found: Co, 13.0
Calcd. for $[Co(NH_3)_5Cl](ClO_4)_2$:	Co, 15.6. Found: Co, 16.1
Calcd. for $[Co(NH_3)_5F](ClO_4)_2$:	Co, 16.3. Found: Co, 16.1
Calcd. for $[Co(NH_3)_5OH_2](ClO_4)_3$:	Co, 12.8. Found: Co, 12.7
Calcd. for $[Co(NH_3)_5N_3](ClO_4)_2$:	Co, 15.3. Found: Co, 14.2
Calcd. for $[Co(NH_3)_5NCS](ClO_4)_2$:	Co, 14.7. Found: Co, 14.2
Calcd. for $[Co(NH_3)_5CN](ClO_4)_2 \cdot 5H_2O$:	Co, 15.6. Found: Co, 15.3
Calcd. for $[Co(NH_3)_4(OH_2)CN](ClO_4)_2$:	Co, 15.9. Found: Co, 15.7
Calcd. for trans-$[Co(en)_2Cl_2]Cl$:	Co, 20.6. Found: Co, 19.9
Calcd. for cis-$[Co(en)_2Cl_2]Cl$:	Co, 20.6. Found: Co, 19.4

cis-$[Co(en)_2Cl_2]Cl$ prepared by heating a solution of the trans complex to dryness probably contained some unreacted trans complex. Because of its extremely high rate of reaction with copper(I), the trans complex was a more desirable impurity in preparation of cis than was cis-$[Co(en)_2(OH_2)Cl]Cl_2$. The aquation of cobalt(III) complexes is very slow and it did not compete with the reduction of the complexes. The published rates are presented in Table 3. In two cases the aquation rates are high enough to convert significant amounts of the complex during the course of an experiment on the stopped-flow apparatus. The most unfavorable case is the cis-$[Co(en)_2Cl_2]Cl$ which aquates at a rate such that 15 to 20%

Table 2. Absorption spectra of Cobalt(III) complexes[a]. Wavelengths (nm), and molar absorptivities ($\underline{M}^{-1}$ cm^{-1})

Complex	Max. (ε)	Min. (ε)	Max. (ε)	Min. (ε)	Ref.
RBr^{2+}	550 (52)	429 (11)			
	551 (53)	428 (8)			51
	550 (55)				52
RCl^{2+}	531 (50)	418 (9)	362 (46)		
	533 (49)	417 (6)	362 (44)		51
	532 (51)		363 (48)		52
RF^{2+}	511 (45)	406 (8.5)	352 (40)		
	509 (44)	404 (7)	352 (39)		51
ROH_2^{3+} b	492 (49)	401 (9)	345 (46)	287 (6)	
	492 (47)		345 (44.5)		52
	490 (47)				5
RN_3^{2+}	516 (225)	442 (55)	302 (7832)	246 (660)	
	517 (265)	442 (54)			51
	520 (262)		302 (7874)		53
RCN^{2+}	440 (57)	373 (11.5)	327 (53)		
	440 (58)	372 (11)	326 (53)		51
	440 (58)		327 (53.5)		54
	441 (56.2)		327 (52.5)		49
$CoA_4[OH_2]CN^{2+}$	446 (68)	375 (14)	330 (55)		

Table 2. (Continued)

Complex	Max. (ε)	Min. (ε)	Max. (ε)	Min. (ε)	Ref.
trans-$Co(en)_2Cl_2^+$	619 (39)	525 (6)			
	620 (41)				11
	615 (43)				10
	620 (41)				55
cis-$Co(en)_2Cl_2^+$	534 (74)	450 (18)			
	535 (91.5)	528 (89)			11
	535 (95.5)				10
	536 (89)				55
$Co(en)_3^{3+}$ [c]	465 (90)	387 (8.4)	338 (82)	287 (5)	
	465 (89)	387 (9)	338 (79)	287 (5)	51
	465 (87)				
$RNCS^{2+}$	497 (180)	422 (42)	307 (1550)		51
	497 (180)	422 (42)			5
	497 (192)				

[c]Molar absorptivity determined by weight in this case only.

Table 3. Rate constants[a] for aquation of cobalt(III) complexes

Complex	k(sec^{-1})	Ref.
cis-$[Co(en)_2Cl_2]^+$	2.44×10^{-4}	56
trans-$[Co(en)_2Cl_2]^+$	3.53×10^{-5}	56
$[Co(NH_3)_5Br]^{2+}$	6.5×10^{-6}	57
$[Co(NH_3)_5N_3]^{2+}$	1.2×10^{-8} [b]	53,58
$[Co(NH_3)_5Cl]^{2+}$	1.7×10^{-6}	59
$[Co(NH_3)_5F]^{2+}$	2.1×10^{-5} [c]	60
$[Co(NH_3)_5NCS]^{2+}$	2.8×10^{-9}	61

[a] 25°.

[b] Original data by Lalor and Moelwyn-Hughes reinterpreted by Swaddle and King. Swaddle and King data have been extrapolated to 25°. Rate constant given is for $[H^+] = 0.20$ M, $k_{app} = a + b[H^+]$, $a = 1.1 \times 10^{-8}$ sec^{-1}, $b = 6.0 \times 10^{-9}$ M^{-1} sec^{-1}.

[c] $k_{app} = c + d[H^+]$, $c = 8.7 \times 10^{-8}$ sec^{-1}, $d = 1.07 \times 10^{-4}$ $[H^+]$, rate constant given is for $[H^+] = 0.20$ M.

of the complex is aquated during a typical experiment (10-15 min). In order to minimize this effect, Cu(I) was always the reagent in excess by a ratio of ≥ 6, thereby rendering unnecessary an exact value for the initial Co(III) concentration. The complex trans-$[Co(en)_2Cl_2]Cl$ aquates at a rate of 3.53×10^{-5} sec^{-1}, consequently some 3% of the complex was aquated during a typical experiment (15 min). All other aquation rates are very low and did not interfere.

Equipment

Kinetics experiments were studied by two different methods. Conventional spectrophotometric rate measurements were made with a Cary Model 14 recording spectrophotometer. Fast reactions were studied using a stopped-flow technique.

Conventional rate measurements were made with the spectrophotometer cells immersed in a water-filled thermostated cell holder which had been made water tight by fastening a quartz plate over each end window. Constant temperature was maintained during reaction by circulating constant temperature water through the jacket of the thermostated cell holder. The temperature was constant to within ± 0.01°. 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. Absorbance readings larger than 2.0 could be compensated for by placing light screens (of absorbance ~ 0.5, 1.0 and 1.3) in the rear compartment of the spectrophotometer, at the expense, however of wider slits and greater noise levels. A detailed description of these techniques has previously been published (62).

The rapid kinetic measurements were made by a stopped-flow technique. The stopped-flow apparatus was based on the

design of Dulz and Sutin (63). A motor-driven block equipped with a slip clutch pushed a pair of syringes, driving reactants through an eight-jet Teflon mixing chamber into a 3 mm ID quartz observation tube and finally into a stopping syringe. The transmittance of the solution, which remained stationary on filling the stopping syringe, was measured spectrophotometrically. A Beckman model DU monochromator was used. The light intensity was measured by connecting the signal from a photomultiplier tube (EMI 6256B), via filtering and amplifying circuit, to the A input of a Tektronix 564 oscilloscope. The photomultiplier bias voltage was varied between 400 and 1000 volts, with the monochromator slit width at 2.0 mm. An oscilloscope trace was electronically initiated shortly before the stopping syringe was filled and was photographed with a Polaroid camera.

Absorbance changes were kept less than 0.1 so that absorbance and transmittance were always linearly related. The time scale of the oscilloscope was checked with a time mark generator, Tektronix Model 181. A more detailed description of the stopped-flow system has been published (38).

Conventional Spectrophotometric Rate Measurements

The reaction vessels in the conventional rate measurements were cylindrical spectrophotometric cells (1, 2, 5 and 10 cm length) capped with rubber serum caps. Reaction solutions,

complete except for air sensitive reagents were flushed with nitrogen, were brought to temperature by immersion in a constant temperature water bath prior to injection of the last reagents with a calibrated syringe. In experiments with air sensitive reagents the air oxidizable reagent was the last one added except for vanadium(II) in the chlorochromium(III) study. The stock solution of chlorochromium(III) ion was flushed with nitrogen and this reagent was added last. In the vanadium(III) and chromium(II) study where both are air sensitive, the chromium(II) was always added last.

Stopped-Flow Experiments

A typical stopped-flow experiment with copper(I) was done in the following way. Each of the two reactant solutions was prepared complete but for the copper(I) and cobalt(III) complex. The flask that was to receive the complex was positioned in the water bath, the other was always left at room temperature until the preparation of copper(I) was complete. Each reactant flask contained a glass tube with a male ground glass taper for attachment to the corresponding female taper pointing downward from the 3-way stopcock. Each reactant flask contained a second glass tube for introduction of deoxygenated nitrogen. The top of each flask was covered with Parafilm and nitrogen was bubbled vigorously for 30 minutes. Chromium(II) was added to the flask containing copper(II) and allowed sufficient time

to react. The time necessary for the reaction to proceed to 99% completion was calculated from the data of Shaw and Espenson (24). A limited study at various ionic strengths was made in the course of this work in order to be able to make a more accurate calculation of the time. Typical times involved from 5 to 35 minutes. A marginal factor of 5 to 10 minutes was added. A fresh stock solution of the cobalt(III) complex was prepared and added to its reaction flask 15 minutes before the data were taken. The complex was carefully weighed in order to make stock solutions of known concentration. Later a conventional cobalt(II) analysis of the stock solution was obtained to provide precise Co(III) concentrations. Air initially in the pathways from reactant flasks to reactant syringes was prevented from entering the syringes by drawing air only to the syringe tips, changing the 3-way stopcocks and forcing the air through the mixing chamber. This process was continued in a cyclic manner until the air was removed. The reactant syringes were partially filled and emptied three times before data were recorded. Four or five duplicate photographs were made for each set of solutions. Immediately before and after each series of photographs the copper(I) solution was sampled (using a calibrated syringe with a long Teflon needle) for analysis. The analysis used from 1 to 10 ml of copper(I) solution which was added to a measured excess of $Co(NH_3)_5Br^{2+}$. The decrease in absorbance was measured at

253.0 nm where the molar absorptivity is 16700 $\underline{M}^{-1}$ cm^{-1}. Endicott and Taube report a molar absorptivity of 16400 at 252.5 nm (20). None of the other reagents absorb significantly in comparison to $Co(NH_3)_5Br^{2+}$ at this wavelength (Cu^{2+}, ε = 18; Cr^{3+}, ε = 4).

Typical oscilloscope traces are shown in Figure 1.

Stoichiometry Experiments

The stoichiometry of the reaction V(II) and Cu(II) was determined by observing the disappearance of Cu(II) spectrophotometrically at 750 nm. Copper(II) made the main contribution to the absorbance (Cu(II), ε = 11.0; Cu(I), $\varepsilon \sim 0$; V(II), ε = 1.20; V(III), ε = 1.65).

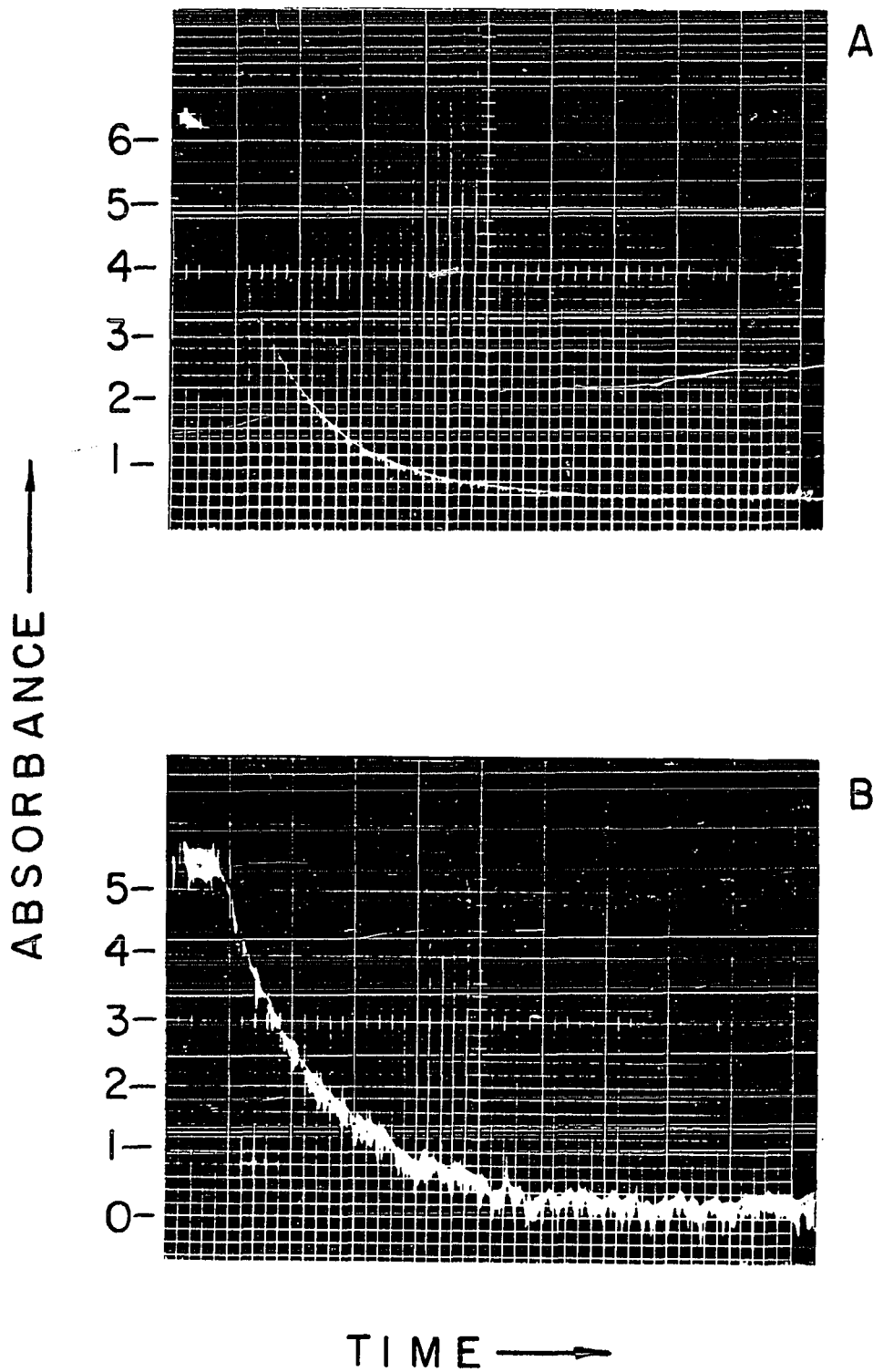
The stoichiometry of the Cu(II) catalyzed reaction of V(III) and RBr^{2+} was determined by spectrophotometric analysis of Co^{2+} (described in the section on reagents) produced when a trace (1.0×10^{-4} $\underline{M}$) of Cu(II) was added to the reaction mixture.

The stoichiometry of the oxidation of Cu(I) by RBr^{2+}, RCl^{2+}, RN_3^{2+} and Fe^{3+} was determined by analyzing the decrease in concentration of the oxidizing agent when it was brought into reaction with an insufficient quantity of Cu^{+}. These analyses were performed at the following wavelengths: RBr^{2+}, 253 nm, ε = 16700 $\underline{M}^{-1}$ cm^{-1}; RCl^{2+}, 260, ε = 1750; RN_3^{2+}, 302, ε = 7874; Fe^{3+}, 240, ε = 4230.

Figure 1. Typical stopped flow oscillograms

A. 5.00×10^{-5} M $Co(NH_3)_5N_3^{2+}$, 1.07×10^{-3} M Cu^+, 0.179 M H^+, μ = 0.200 M, 25.0°; 360 nm, 0.5 sec/cm sweep speed; $k_{RN_3} = 1520\ M^{-1}\ sec^{-1}$

B. 3.19×10^{-5} M Fe^{3+}, 1.16×10^{-4} M Cu^+, 0.350 M H^+, μ = 1.00 M, 1.6°; 240 nm, 0.1 sec/cm sweep speed; $k_{app} = 6.91 \times 10^4\ M^{-1}\ sec^{-1}$


A
6
5
4
3
2
1
B
5
4
3
2
1
0
ABSORBANCE
TIME

Rate Procedures

The reaction kinetics of V(II) and Cu(II) were followed spectrophotometrically by observing the increase in absorbance in the ultraviolet region (225-235 nm) corresponding to the formation of Cu^+ as shown in Figure 2. In all cases the reactions were carried out in a medium in which perchlorate ion was the only anion present, with perchloric acid and lithium perchlorate added to maintain ionic strength 1.00 M.

The Cu(II) catalyzed reaction of RBr^{2+}, RCl^{2+} and trans-$Co(en)_2Cl_2^+$ with V(III) was monitored spectrophotometrically utilizing the charge transfer bands of the various cobalt(III) complexes (255-360 nm). The reaction medium consisted of perchloric acid and/or lithium perchlorate with μ = 3.00 M. A medium of perchloric acid and/or sodium perchlorate at μ = 3.00 M was also used. A limited number of experiments were done with μ = 1.00 M maintained with perchloric acid and lithium perchlorate.

The oxidation of Cu(I) by Fe(III) was followed spectrophotometrically in the ultraviolet region (240-300 nm) where both Fe(III) and Cu(I) have a high absorbance (ε = 4230, $\varepsilon \sim 450$, at 240 nm). The medium consisted of perchloric acid and/or lithium perchlorate with μ = 1.00 M.

The reduction of the various cobalt(III) complexes by copper(I) was in a medium of ionic strength 0.200 M maintained with perchloric acid and/or lithium perchlorates. Two types

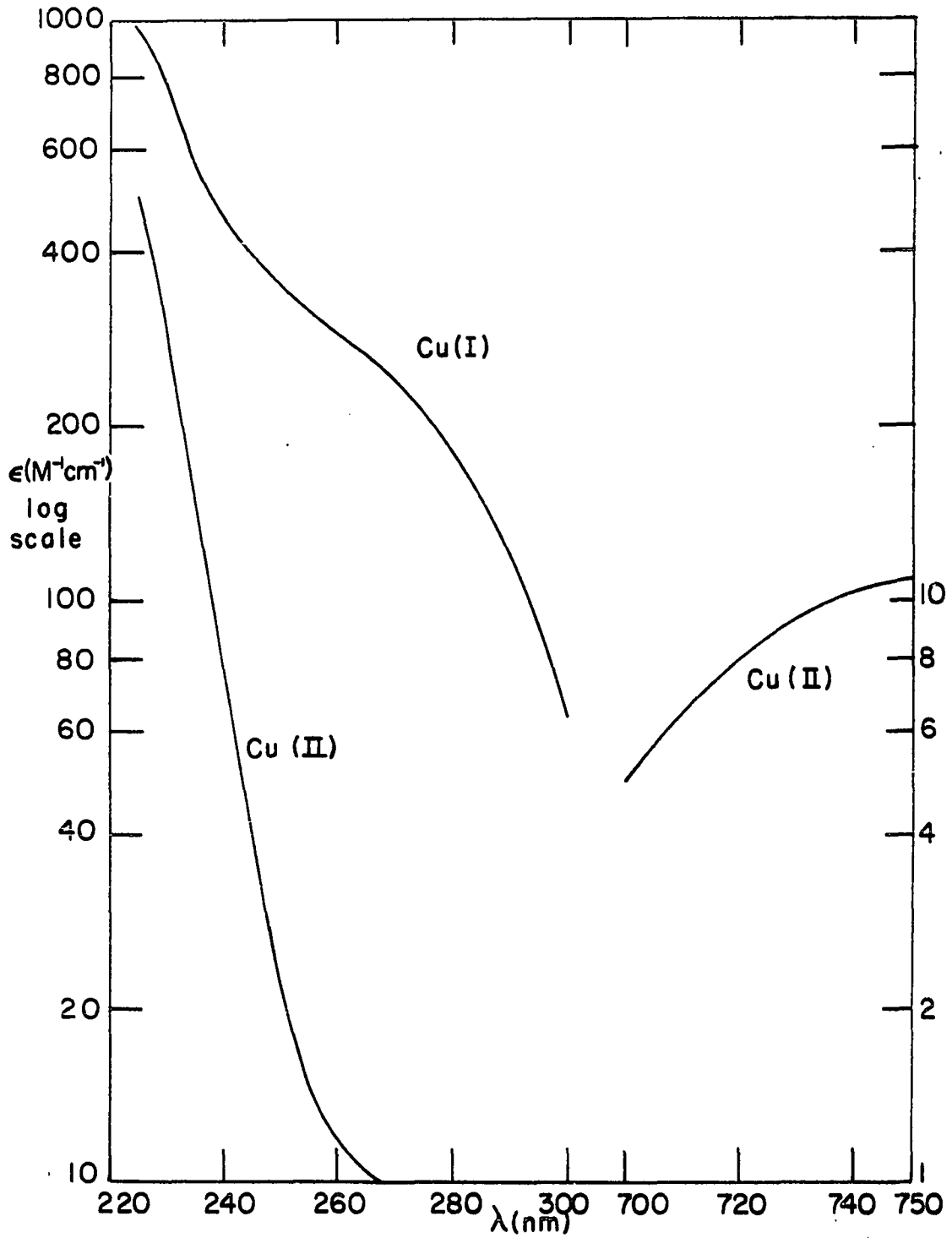


Figure 2. Molar absorptivity of Cu(II) and Cu(I)

of experiments were used in the kinetic rate studies. The rapid reactions, trans-$Co(en)_2Cl_2^+$, RBr^{2+}, RCl^{2+}, cis-$Co(en)_2Cl_2^+$ and RN_3^{2+}, utilized the charge transfer band of the cobalt(III) complexes except in the case of RN_3^{2+} (302-350 nm). In most cases copper(I) was the reagent in excess and the analysis and stopped-flow procedures used were the same as those discussed in the section on stopped-flow experiments. The slow reactions, $RNCS^{2+}$, RF^{2+}, ROH_2^{3+}, $CoA_4(OH_2)CN^{2+}$, RCN^{2+} and $Co(en)_3^{3+}$, were monitored in the ultraviolet region (260-300 nm) utilizing primarily the absorbance of copper(I). The production of Cu(I) by Cr(II), previous to the addition of the complex, was conveniently observed in this region. The reaction of Cu(I) with the complex was initiated immediately after observing the completion of the Cu(II) and Cr(II) reaction.

The reaction of V(III) and Cr(II) was studied as a function of chloride ion concentration. The progress of the reaction was followed at 574 and 250 nm. These runs were relatively rapid; under conditions chosen here, they were followed for times of 30-300 sec. The catalyzed aquation of chlorochromium(III) ion is somewhat slower, and typical reaction times were 10-40 min. For reasons considered later in some detail, a number of the aquation experiments were carried out in the presence of added V(III) or Cr(II). Such runs were studied generally at 440 nm, whereas experiments with only V^{2+} and $CrCl^{2+}$ were studied primarily at 609 nm.

In any given experiment at 574 nm the observed change in absorbance was dependent upon the relative amounts of chlorochromium(III) and aquochromium(III) formed. The resulting dependence of the value of $\Delta\epsilon$ upon $[Cl^-]_0$ was taken into account in computing rate constants from absorbance data. All the rate studies refer to a medium of ionic strength 2.50 M, and a univalent anion concentration of 2.00 M consisting of 0.50 M divalent cations and 1.00 M univalent cations (H^+, Li^+)

Equilibrium Measurements

A few studies were carried out to evaluate the equilibrium quotient for chlorochromium(III) formation under the conditions of the present study: 25.0° and ionic strength 2.50 M. All experiments were done with $[V^{2+}] = 0.0200$ M in order to hasten the approach to equilibrium. The equilibrium concentration of chlorochromium(III) in duplicate samples was determined after air oxidation of vanadium(II) by the quantitative separation of $CrCl^{2+}$ on a cation exchange column. The $CrCl^{2+}$ was analyzed spectrophotometrically as CrO_4^{2-} after oxidation with peroxide in alkaline solution (37). The equilibrium concentrations of Cr^{3+} and Cl^- were calculated from the starting concentrations and the value determined for $[CrCl^{2+}]_{eq}$.

Data Treatment

Treatment of the kinetic data for reaction of V(II) and Cu(II) involved the use of a nonlinear least-squares

program[5] and an IBM 360 computer. The program is written so that first-order and/or second-order data may be treated (Equation 10)

$$-d[A-x]/dt = k_2[A-x][B-x] + k_1[C][A-x] \qquad (10)$$

As an example, second-order data may be treated by fixing the parameter, k_1, and setting the value equal to zero. For this system both the first and second-order parts were used when appropriate. First-order plots of $\ln|D_t - D_\infty|$ versus time were also made as a check. The following definitions are used throughout:

D_o = absorbance at time equal zero,

D_t = absorbance at time equal t, and

D_∞ = absorbance at the completion of an experiment.

No significant difference between the computer and graphical method was noted.

The data for the V(III) and Cu(II) system were treated in a similar manner with the computer program. All data was treated by using only that part of the expression for a first-order process. Graphical analysis was also performed on several experiments with no significant difference in the evaluated rate constant.

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[5]The author is grateful to Dr. T. W. Newton of Los Alamos Scientific Laboratory for supplying the computer programs. The programs are based on a report by Moore and Zeigler (Reference 64).

Data from stopped-flow experiments involving Cu^+ and various oxidizing agents were treated in the following manner. If the excess reagent was present initially at a 10 fold or greater excess, the data were treated as pseudo-first-order with plots of $\ln|D_t - D_\infty|$ versus time. The evaluated rate constant was equal to the second-order rate constant times the average concentration of the reagent in excess. Second-order data were treated by using the following equation

$$\ln \frac{1 - \frac{B_0}{A_0} \cdot \left[\frac{D_t - D_0}{D_\infty - D_0}\right]}{\left[1 - \frac{D_t - D_0}{D_\infty - D_0}\right]} = - k[A_0 - B_0]t \qquad (11)$$

Values for D_0 and D_∞ were read directly from the oscillograms. Although the initial values did not represent the true D_0, the flow rate was high enough so that these corrections had a negligible effect on the evaluated rate constant.

Data from conventional kinetic measurements involving Cu^+ and various oxidants were treated in the same manner as the data from stopped-flow experiments. Because of the low rates of reaction, reliable values of D_0 were available from extrapolation of the initial spectrophotometer readings. The data from the reaction of Cu^+ and $Co(NH_3)_4(OH_2)_2CN^{2+}$ were treated by using the nonlinear least-squares computer program.

Activation parameters were calculated from the absolute rate theory expression, Equation 12, assuming $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$

(κ = 1) are independent of temperature.

$$k = \kappa (k_B T/h) \exp (\Delta S^{\ddagger}/R - \Delta H^{\ddagger}/RT) \qquad (12)$$

The parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ refer to a standard state of 1 mole/liter concentration for a hypothetical ideal solution with μ equal to the particular ionic strength used in the study.

RESULTS

Reactions Producing Copper(I)

Reduction of Cu^{2+} with V^{2+}

Rate equation and stoichiometry Copper(II) is reduced to copper(I) by reaction with vanadium(II) in dilute perchloric acid (24). Provided an insufficient amount of vanadium(II) is added, the stoichiometry of the reaction corresponds to the simple 1-equivalent reduction given in Equation 13.

$$V^{2+} + Cu^{2+} = V^{3+} + Cu^{+} \qquad (13)$$

Kinetic measurements were carried out over a wide range of starting concentrations, $8 \times 10^{-5} \leq [Cu^{2+}]_0 \leq 9 \times 10^{-3}$ M and $1.4 \times 10^{-5} \leq [V^{2+}]_0 \leq 1 \times 10^{-3}$ M. In experiments where $[Cu^{2+}]$ was in large excess over $[V^{2+}]$ the appropriate pseudo-first-order plots of the absorbance data, according to Equation 14, were linear for at

$$\ln (D - D_\infty) = \ln(D_0 - D_\infty) - k't \qquad (14)$$

least 3 half-lives. In several such experiments at varying $[Cu^{2+}]_0$, values of $k'/[Cu^{2+}]_{av}$ were found to be constant, suggesting the following rate equation

$$-d[V^{2+}]/dt = k[V^{2+}][Cu^{2+}] \qquad (15)$$

In experiments where the excess of copper(II) was smaller, vanadium(II) concentrations were computed from the fractional charge in absorbance, D:

$$[V^{2+}]_t = [V^{2+}]_0 \ (D_t - D_\infty)/(D_0 - D_\infty) \qquad (16)$$

Concentrations of copper(II) were then computed from the initial concentrations, assuming the stoichiometry given in Equation 13:

$$[Cu^{2+}]_t = [Cu^{2+}]_0 - [V^{2+}]_0 + [V^{2+}]_t \qquad (17)$$

The appropriate rate plots were then made according to the equation

$$\ln[Cu^{2+}]/[V^{2+}] = \ln [Cu^{2+}]_0/[V^{2+}]_0 + k([Cu^{2+}]_0 - [V^{2+}]_0)t \qquad (18)$$

These plots were consistently linear, and values of k so obtained were in excellent agreement with the values from the pseudo-first-order runs. In practice, all runs regardless of the $[Cu^{2+}]_0/[V^{2+}]_0$ ratio were fit to the integrated second-order rate equation using a least-squares computer program (64). Two typical experiments with the computer output are listed in Table 4. The rate constants so obtained generally reproduced the absorbance values during each run to within $\pm$ 0.002 absorbance units; the standard deviation of each rate constant, based on the internal fit of each run, was usually $\leq \pm$ 2%. The standard deviation of the unweighted mean rate

Table 4. Typical computer output, Cu(II) and V(II)

Exp. 6			Exp. 21		
D_0=0.576, D_∞=1.022			D_0=0.024, D_∞=0.539		
k=26.9±.7, % react. 82			k=26.5±.2, % react. 86		
$[V^{2+}]_0$=1.26x10^{-4}, Δt=11.5			$[V^{2+}]_0$=1.725x10^{-4}, Δt=8.2		
$[Cu^{2+}]_0$=5.015x10^{-4}			$[Cu^{2+}]_0$=19.9x10^{-4}		
Times	Obs. Abs.	Calc. Abs.	Time	Obs. Abs.	Calc. Abs.
0.0	0.641	0.639	0.0	0.205	0.203
10.	0.684	0.685	2.5	0.242	0.243
20.	0.723	0.725	5.0	0.277	0.278
30.	0.758	0.759	7.5	0.309	0.309
40.	0.787	0.789	10.	0.336	0.336
50.	0.813	0.815	12.5	0.359	0.360
60.	0.840	0.837	15.	0.379	0.381
70.	0.860	0.857	17.5	0.400	0.400
80.	0.876	0.875	20.	0.414	0.416
90.	0.890	0.890	22.5	0.430	0.430
100.	0.905	0.904	25.	0.443	0.443
110.	0.918	0.916	27.5	0.457	0.454
120.	0.927	0.927	30.	0.469	0.464
130.	0.936	0.937			
140.	0.943	0.946			

constant at 25.0° was 3%. The rate constants for the individual runs at 25.0° are summarized in Table 5.

Two independent sources of copper(II) (prepared from $CuCO_3$ and $Cu(ClO_4)_2$) and vanadium(II) (zinc reduced $VO(ClO_4)_2$ and electrolytically reduced V_2O_5) were used in these experiments. It can be seen from the tabulated data that the rate constant

Table 5. Kinetic data for the reaction of Cu(II) and V(II)

Conditions: 25.0°, $[H^+]$ = 0.993 ± 0.005 M, except as noted; μ = 1.00 M ($LiClO_4$)

Exp.	$10^4[V^{2+}]_0$	$10^4[Cu^{2+}]_0$	λ(nm)	k(M^{-1} sec^{-1})[a]
1	0.630	0.802	225	29.0
2	0.630	2.01	225	28.1
3	0.630	5.02	225	(29.9)[b]
4	1.24	5.02	230	26.7[c]
5	1.26	5.02	235	26.1
6	1.26	5.02	230	26.9
7	1.26	5.02	225	27.1
8	1.26	5.02	230	26.8
9	1.26	10.0	230	27.6
10	1.27	10.0	230	26.5[c]
11	1.26	20.1	235	25.0
12	1.35	20.0	235	25.9[d]
13	1.35	20.0	231	26.6[d]
14	1.35	20.0	231	25.0
15	1.35	20.0	231	25.9[e]
16	1.35	20.0	230	26.1[e]
17	1.35	20.0	231	26.3[d]
18.	1.54	10.0	230	26.5[f]
19	1.54	10.0	230	25.0[g]
20	1.54	10.0	230	27.8[h]

[a] k_{calc} = 26.4 ± .15, calculated from the activation parameters given in Table 6.

[b] Omitted from average; value exceeded 3 standard deviations.

[c] V^{2+} prepared by electrolysis.

[d] Cu^{2+} prepared from $CuCO_3$.

[e] $[Cr^{3+}]_0$ = 2.0 x 10^{-3} M.

[f] $[H^+]$ = 0.500 M.

[g] $[H^+]$ = 0.100 M.

[h] $[H^+]$ = 0.040 M.

Table 5. (Continued)

Exp.	$10^4[V^{2+}]_0$	$10^4[Cu^{2+}]_0$	λ(nm)	$k(\underline{M}^{-1}\ sec^{-1})^a$
21	1.725	19.9	231	26.5[d]
22	1.725	20.1	231	25.1
23	2.00	10.3	231	(31.1)[b,i]
24	2.00	10.3	235	25.1 [i]
25	2.32	10.0	235	27.6 [j]
26	2.32	10.0	235	28.3 [j]
27	2.32	10.0	235	25.7 [j]
28	2.51	5.02	230	25.5
29	2.49	10.0	230	24.1 [c]
30	2.51	20.1	235	26.7
31	2.51	50.1	240	27.0
32	3.02	35.1	238	26.3
33	3.76	7.62	750	26.8
34	3.76	7 62	750	28.9
35	3.76	7.62	750	29.2
36	4.71	5.02	230	(32.3)[b]
			Av. k	26.6±1.2 [k]

[i] $[Cu^+]_0 = 4.7 \times 10^{-4}$ M, $[Cr^{3+}]_0 = 4.7 \times 10^{-4}$ M.

[j] $[V^{3+}]_0 = 5.8 \times 10^{-4}$ M.

[k] Uncertainty represents standard deviation.

is not a function of which source of Cu^{2+} or V^{2+} was used, proving the reaction is independent of Zn^{2+}, which was introduced with V^{2+} in most of the runs. The lack of variation in values of k with added Cu^{+} or V^{3+} establishes that the products are not exerting an influence on the rate that escaped detection in runs where they were not added at the start. Finally, the variation of wavelength had no effect on the rate constant.

Reaction stoichiometry Close agreement of rate constants at high ratios of $[Cu^{2+}]_0/[V^{2+}]_0$ with those in experiments where the ratio was ≤ 4 was noted. When, for example, it is assumed that the reaction produced quantitative yields of Cu^0_{aq}, as shown in Equation 19, the

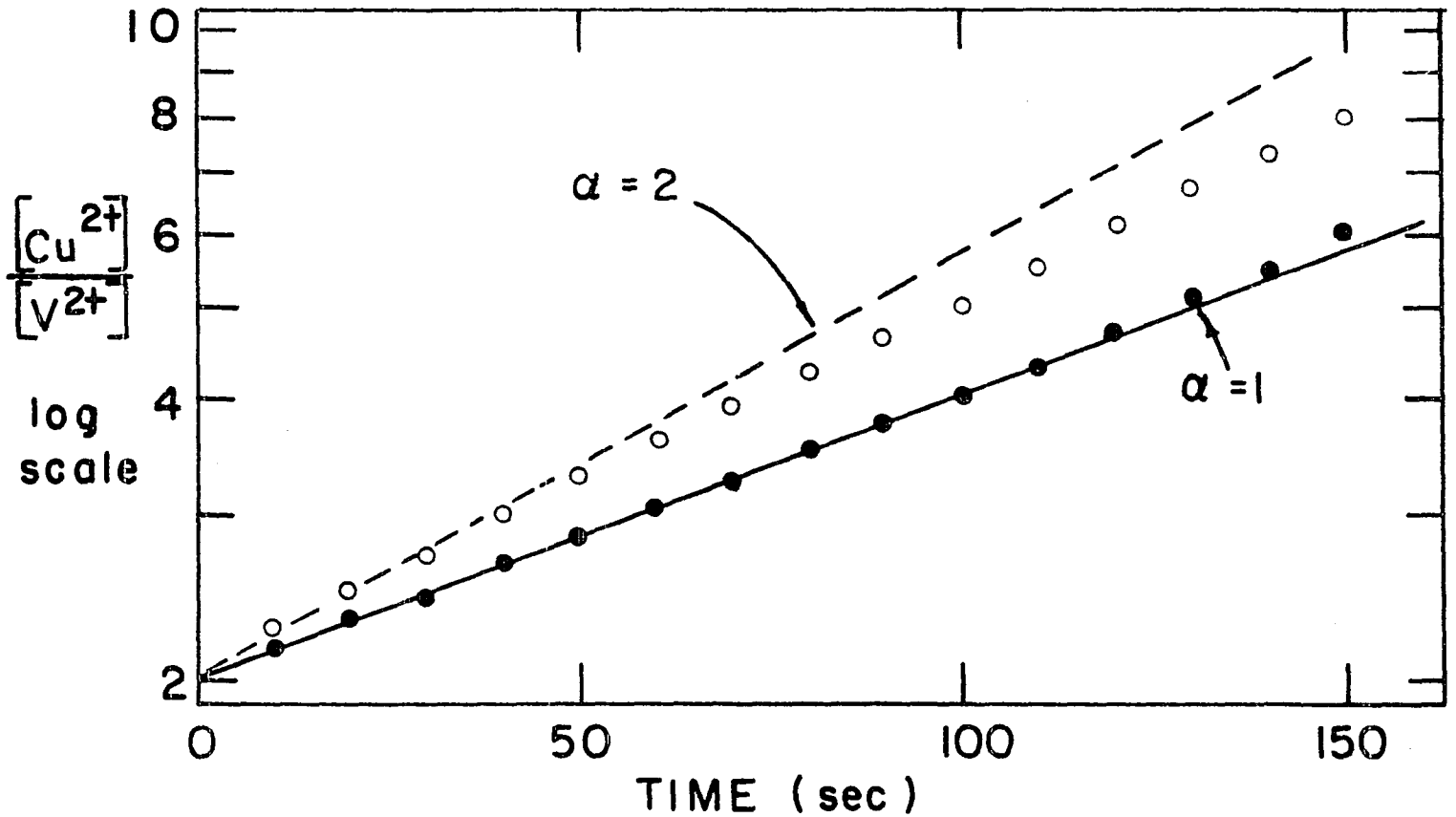
$$Cu^{2+} + 2V^{2+} = Cu^0_{aq} + 2V^{3+} \qquad (19)$$

rate plots at low $[Cu^{2+}]_0/[V^{2+}]_0$ ratios were most noticeably nonlinear, as shown in Figure 3. The stoichiometry of the reaction affects the kinetic calculations in the following manner. The concentrations of vanadium(II) were computed from the fractional charge in absorbance as given in Equation 16. Concentrations of copper(II) were then computed from the initial concentration assuming $\alpha = 1$ or 2 (2 is the present

$$[Cu^{2+}] = [Cu^{2+}]_0 - [V^{2+}]_0/\alpha + [V^{2+}]/\alpha \qquad (20)$$

case). The appropriate rate plots were then made according to Equation 21. The rate constant k is defined by Equation 22.

Figure 3. Second-order plot of $\ln([Cu^{2+}]/[V^{2+}])$ versus time for the reaction of V(II) and Cu(II), $[Cu^{2+}]_0/[V^{2+}]_0 = 2$, experiment 28


10
8
6
4
2
$\frac{[Cu^{2+}]}{[V^{2+}]}$
log scale
α = 2
α = 1
0
50
100
150
TIME (sec)

$$\ln[Cu^{2+}]/[V^{2+}] = \ln[Cu^{2+}]_0/[V^{2+}]_0 + k([Cu^{2+}]_0 - [V^{2+}]_0/\alpha)t \quad (21)$$

$$-d[V^{2+}]/dt = -\alpha\, d[Cu^{2+}]/dt = k[Cu^{2+}][V^{2+}] \quad (22)$$

The most decisive discrepancy in this procedure was the inconsistency of the rate constants compared with those having a high ratio of $[Cu^{2+}]_0/[V^{2+}]_0$. The value of k calculated in this manner for experiment 28 was 34.2 $\underline{M}^{-1}$ sec^{-1} which is definitely inconsistent with 26.6 $\underline{M}^{-1}$ sec^{-1}. The functional dependence on α is very sensitive for a ratio $\leqq$ 2 (5 experiments) and much less sensitive for a ratio $\leqq$ 4 (7 experiments) as shown in Figure 4.

In the case where α = 1 the appropriate rate plots according to Equation 21 were excellently linear to at least 85% completion. Two typical runs are shown in Figures 3 and 4. The observation cited here established that Equation 13 correctly represents the net reaction occurring whenever Cu^{2+} is in excess. The extent to which the production of minor amounts of Cu^0(aq) or Cu^0(s) would have been evident is not apparent, but it has been clearly established that they are not major products.

Further evidence concerning the stoichiometry came from the runs performed at a wavelength of 750 nm, where copper(II) made the main contribution to the absorbance (Cu(II), ε = 11.0; Cu(I), $\varepsilon \sim 0$; V(II), ε = 1.20; V(III), ε = 1.65). In a set of triplicate runs at 750 nm cited in Table 5, the observed

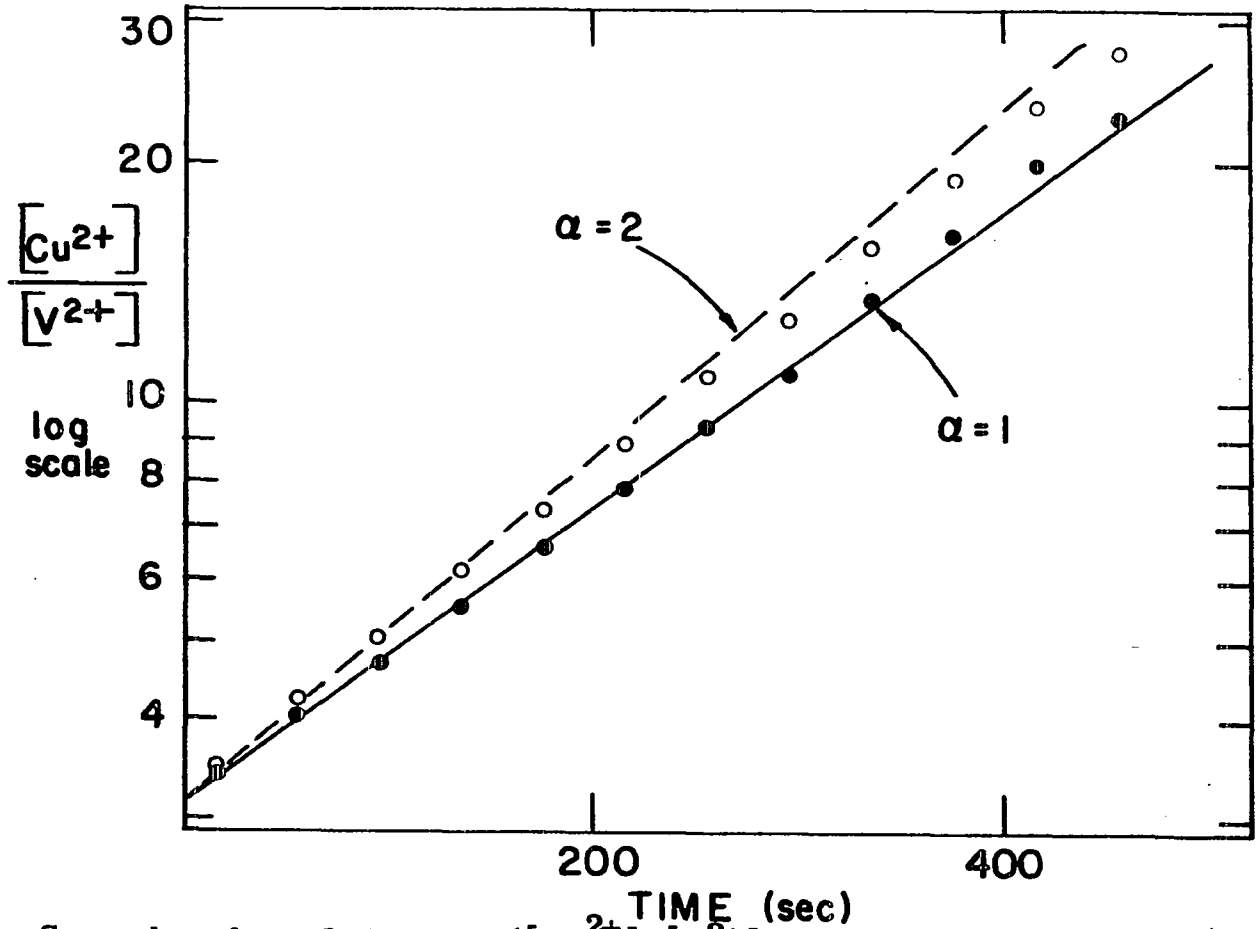


Figure 4. Second-order plot of $\ln([Cu^{2+}]/[V^{2+}])$ versus time for the reaction of V(II) and Cu(II), $[Cu^{2+}]_0/[V^{2+}]_0 = 3.2$, experiment 2

absorbance change was 0.039 ± .001 absorbance units (measured on an expanded scale 0-0.1 slide wire), compared with an expected value of 0.041 for the reaction producing Cu^+ in quantitative yield. The close agreement of calculated and observed absorbance changes substantiates the stoichiometry given in Equation 13. The expected change were Cu^0 produced, 0.021 absorbance units, is clearly not consistent with the observed value. The observed change was reproducible, but it was 5% smaller than the calculated change; the discrepancy probably reflects the uncertainties associated with the molar absorptivity rather than a 10% contribution of a side reaction producing metallic copper. In particular, were metal formed, the disproportionation of copper(I) would have occurred in the time of observation, and that was shown not to have occurred on three accounts, (1) the observed absorbance change was not consistent with the presence of the additional Cu(II), (2) no metal was observed coating the surface of the cell, the process always being quite noticeable in those instances where it did occur, and (3) the solution so produced exhibited the reducing properties of Cu^+. The latter observation was the result of measuring the rate of reduction of $Co(NH_3)_5Br^{2+}$ and $Co(NH_3)_5Cl^{2+}$ with Cu^+ which was produced by both V^{2+} and Cr^{2+}. The agreement of the measured rates is very good.

Disproportionation of Cu^+ in perchlorate solution, not stabilized by complexing anions, is a favorable reaction;

the equilibrium quotient for reaction 23 is 1.3×10^6 $\underline{M}^{-1}$, with $\mu = 0.0196$, at 25° (20). Provided a metallic surface is not present, this reaction occurs quite slowly, however, and over a period of several hours 10^{-3} $\underline{M}$ solutions of Cu^+ remained virtually unchanged provided they are protected from oxygen.

$$2Cu^+ = Cu^0(s) + Cu^{2+} \qquad (23)$$

The beginning of disproportionation generally brings about complete decomposition within a short time. Some runs having an excess of Cu(II) that was barely sufficient produced metallic copper, especially if the concentrations were high (~ 0.01 $\underline{M}$). In this case, the production of metal presumably arose from a second stage of reduction, Equation 24, that was able to compete with the first stage, owing to the low rate of the latter as Cu(II) was depleted.

$$V^{2+} + Cu^+ = Cu^0 + V^{3+} \qquad (24)$$

Hydrogen ion and temperature dependences The greatest number of runs was carried out at high $[H^+]$, ~ 1 $\underline{M}$. Variation of $[H^+]$ down to 0.040 $\underline{M}$ was made in several experiments. This variation was, in all instances, without discernable effect on the value of the second-order rate constant.

Experiments were also carried out at 15.0° and 35.0°. At each of these temperatures the same second-order rate expression was found to hold, and the precision of k at

each temperature was quite high. These experiments are summarized in Tables 7 and 8. A summary of the kinetic parameters for the Cu(II), V(II) system is listed in Table 6.

Table 6. Kinetic parameters[a] for Cu(II) and V(II) μ = 1.00 M ($LiClO_4$)

$k = 13.1 \pm .16\ \underline{M}^{-1}\ sec^{-1}$ at 15.0°
$k = 26.4 \pm .15\ \underline{M}^{-1}\ sec^{-1}$ at 25.0°
$k = 50.7 \pm .4\ \underline{M}^{-1}\ sec^{-1}$ at 35.0°
$\Delta H^{\ddagger} = 11.3 \pm .1$ kcal/mole
$\Delta S^{\ddagger} = -14.1 \pm .5$ cal/mole-deg

[a]Parameters calculated from the Eyring absolute rate theory expression using a nonlinear least-squares computer program (Reference 64).

Table 7. Kinetic data for the reaction of Cu(II) and V(II)

Conditions: 15.0°, $[H^+] = 0.993 \pm 0.005$ M, except as noted; μ = 1.00 M ($LiClO_4$)

Exp.	$10^4[V^{2+}]_0$	$10^4[Cu^{2+}]_0$	λ (nm)	$k(\underline{M}^{-1}\ sec^{-1})^a$
37	0.507	5.04	222	12.8
38	0.760	5.04	222	12.7
39	0.902	20.1	230	13.0
40	0.902	20.1	228	13.5
41	1.725	5.04	222	13.0

[a]$k_{calc} = 13.1 \pm .16$, calculated from the activation parameters given in Table 6.

Table 7. (Continued)

Exp.	$10^4[V^{2+}]_0$	$10^4[Cu^{2+}]_0$	λ (nm)	$k(\underline{M}^{-1}\ sec^{-1})^a$
42	1.725	20.1	231	12.3[b]
43	1.725	20.1	230	12.6
44	1.725	20.1	230	13.0
45	2.00	30.1	235	12.6
46	2.00	30.1	233	12.9
47	2.00	30.1	235	13.0
48	2.51	50.1	235	12.7
49	3.92	20.1	232	(14.2)[c]
50	9.95	50.1	248	13.7
51	9.95	90.3	248	13.6
				Av. k 13.0 ± 0.45[d]

[b] $[H^+]$ = 0.100 $\underline{M}$.

[c] Omitted from average; value exceeded 3 standard deviations.

[d] Uncertainty represents standard deviation.

Table 8. Kinetic data for the reaction of Cu(II) and V(II)

Conditions: 35.0°, $[H^+]$ = 0.993 ± 0.005 $\underline{M}$, except as noted; μ = 1.00 $\underline{M}$ ($LiClO_4$)

Exp.	$10^4[V^{2+}]_0$	$10^4[Cu^{2+}]_0$	λ(nm)	$k(\underline{M}^{-1}\ sec^{-1})^a$
52	0.143	2.51	218	53.7
53	0.253	2.51	211	51.3
54	0.253	5.04	218	49.6
55	0.507	5.04	227	51.4
56	0.507	5.04	221	52.7

[a] k_{calc} = 50.7 ± .4, calculated from the activation parameters given in Table 6.

Table 8. (Continued)

Exp.	$10^4[V^{2+}]_0$	$10^4[Cu^{2+}]_0$	λ(nm)	$k(\underline{M}^{-1}\ sec^{-1})^a$
57	0.760	5.04	222	50.9
58	0.862	10.0	218	(46.2)[b,c]
59	0.862	10.0	227	48.4
60	0.862	10.0	224	48.7[d]
61	0.862	10.0	227	48.9
62	0.862	10.0	224	49.1[c]
63	0.862	10.0	224	51.1
64	0.862	10.0	225	51.2[c]
65	0.862	10.0	225	51.3[c]
66	1.255	25.1	232	47.3
67	1.725	5.04	222	52.2
			Av. k	50.5 ± 1.8[e]

[b]Omitted from average; value exceeded 3 standard deviations.

[c]$[H^+]$ = 0.100 M.

[d]$[H^+]$ = 0.040 M.

[e]Uncertainty represents standard deviation.

Reduction of Cu^{2+} with V^{3+}

Copper(II) catalysis of reactions involving vanadium(III) and an oxidizing substance Higginson and Sykes (32) have studied the reaction of iron(III) and vanadium(III) in aqueous perchloric acid. The reaction is catalyzed by copper(II). They reported the following rate expression under the conditions of their study.

$$-d[V^{3+}]/dt = k_d[Fe^{3+}][V^{3+}] + k_c[Cu^{2+}]_0[V^{3+}] \qquad (25)$$

A mechanism which involves the formation of a steady-state intermediate, copper(I), followed by a rapid reaction between the intermediate and iron(III) was proposed.

$$V^{3+} + Cu^{2+} \underset{2}{\overset{1}{\rightleftharpoons}} V(IV) + Cu^{+} \qquad (26)$$

$$Cu^{+} + Fe^{3+} \overset{\text{rapid}}{\rightarrow} Cu^{2+} + Fe^{2+} \qquad (27)$$

If the proposed mechanism was correct and copper(I) was formed as an intermediate, copper(II) would be a general catalyst for reactions involving vanadium(III) and not just specific for the iron(III)-vanadium(III) reaction. The only restrictions imposed on the relative rates is that k_{Fe} be rapid compared to k_2 in order to obtain the rate expression given in Equation 25. A more general expression is obtained if $k_{Fe}[Fe^{3+}] > k_2[V(IV)]$.

With this in mind a study of the reaction of V^{3+} and $Co(NH_3)_5Br^{2+}$ with copper(II) added was undertaken. The present work provided the following results: (1) additional evidence supporting the proposed formation of an intermediate, copper(I), (2) the form of the rate law after corrections for medium effects, (3) more precise data than were obtainable from the V^{3+}-Fe^{3+} system by avoiding the necessity of correcting for the uncatalyzed path, (4) calculation of the equilibrium constant for the reaction of Cu^{2+} and V^{3+}.

Stoichiometry and catalytic effect of Cu(II) The reaction of V^{3+} and $Co(NH_3)_5Br^{2+}$ at 25.0°, μ = 3.00 ($LiClO_4$)

is very slow. In an experiment with $[V^{3+}]_0 = 1.30 \times 10^{-3}$ M, $[RBr^{2+}]_0 = 2.05 \times 10^{-3}$ M and $[H^+] = 0.210$ M the change in absorbance as a function of time was observed at 360 nm. The rate of reaction between V^{3+} and RBr^{2+} is so low that ~ 90% of the observable absorbance change was a result of the aquation of RBr^{2+}. The aquation rate of RBr^{2+} is 6.5×10^{-6} sec^{-1}. An identical experiment with a trace of copper(II) ($[Cu^{2+}]_0 = 1.0 \times 10^{-4}$ M) showed a marked increase in rate, with $k_{obs} = 1.70 \times 10^{-4}$ sec^{-1}. The experiment was followed for 7 half-lives or about 500 min. A standard analysis for cobalt(II) at the end (7 half-lives) demonstrated that reduction of the cobalt(III) complex had occurred. The concentration of Co^{2+} predicted from the limiting reagent, V^{3+}, was 1.30×10^{-3} M; the analysis yielded 1.23×10^{-3} M. Under the same conditions without added Cu^{2+} the Co^{2+} analysis yielded 1.5×10^{-4} M. Both $[V^{3+}]_0$ and $[RBr^{2+}]_0$ were 15 times the concentration used in most experiments. The observation time in this case was about 16 times that of a typical run.

The observations cited here clearly establish: (1) that Equation 28 represents the net reaction, (2) that

$$Co(NH_3)_5Br^{2+} + V^{3+} + 3H^+ + H_2O = Co^{2+} + VO^{2+} + Br^- + 5NH_4^+ \quad (28)$$

Co(III) is reduced to Co^{2+}, (3) that the stoichiometry is 1:1, (4) that under the conditions of a typical experiment ($[Cu^{2+}]_0 \geq 1.0 \times 10^{-3}$ M) no correction for either RBr^{2+} aquation or the

reaction of RBr^{2+} and V^{3+} is necessary.

Reaction complexities During the course of this study several complexities were uncovered which provided useful information. In order to clarify the presentation of these results the following comments seem pertinent. The rate law was established by variation of the initial concentrations of $[Cu^{2+}]_0$, $[V^{3+}]_0$ and $[RBr^{2+}]_0$ in the usual manner. Next, the form of the rate expression was observed to be independent of the oxidizing agent used (RBr^{2+}, RCl^{2+} and trans-$Co(en)_2Cl_2^+$). Three additional types of experiments were useful: (1) with $[RBr^{2+}]_0 < [V^{3+}]_0$ which resulted in two distinct stages of absorbance changes, (2) experiments involving a direct measurement of the reaction rate of the Cu^{2+} - V^{3+} system, and (3) experiments with a high initial concentration of V(IV) and RCl^{2+} used as the oxidizing agent. In addition to these experiments, two types of experimental checks were done. The results of the Br^- generated during an experiment and the influence of the V(IV) generated during the runs were examined.

Rate law An extensive series of rate experiments was performed in a medium of ionic strength equal to 3.00 M maintained by the addition of lithium perchlorate. The first-order dependence of rate upon $[V^{3+}]$ was indicated by the linearity of plots of $\ln(D_t - D_\infty)$ as a function of time over at least 90% reaction in each run. A typical plot showing the first-order dependence is given in Figure 5; experiment number 18, $[H^+]$ = 1.01 M, $[Cu^{2+}]_0 = 1.53 \times 10^{-2}$ M. The apparent

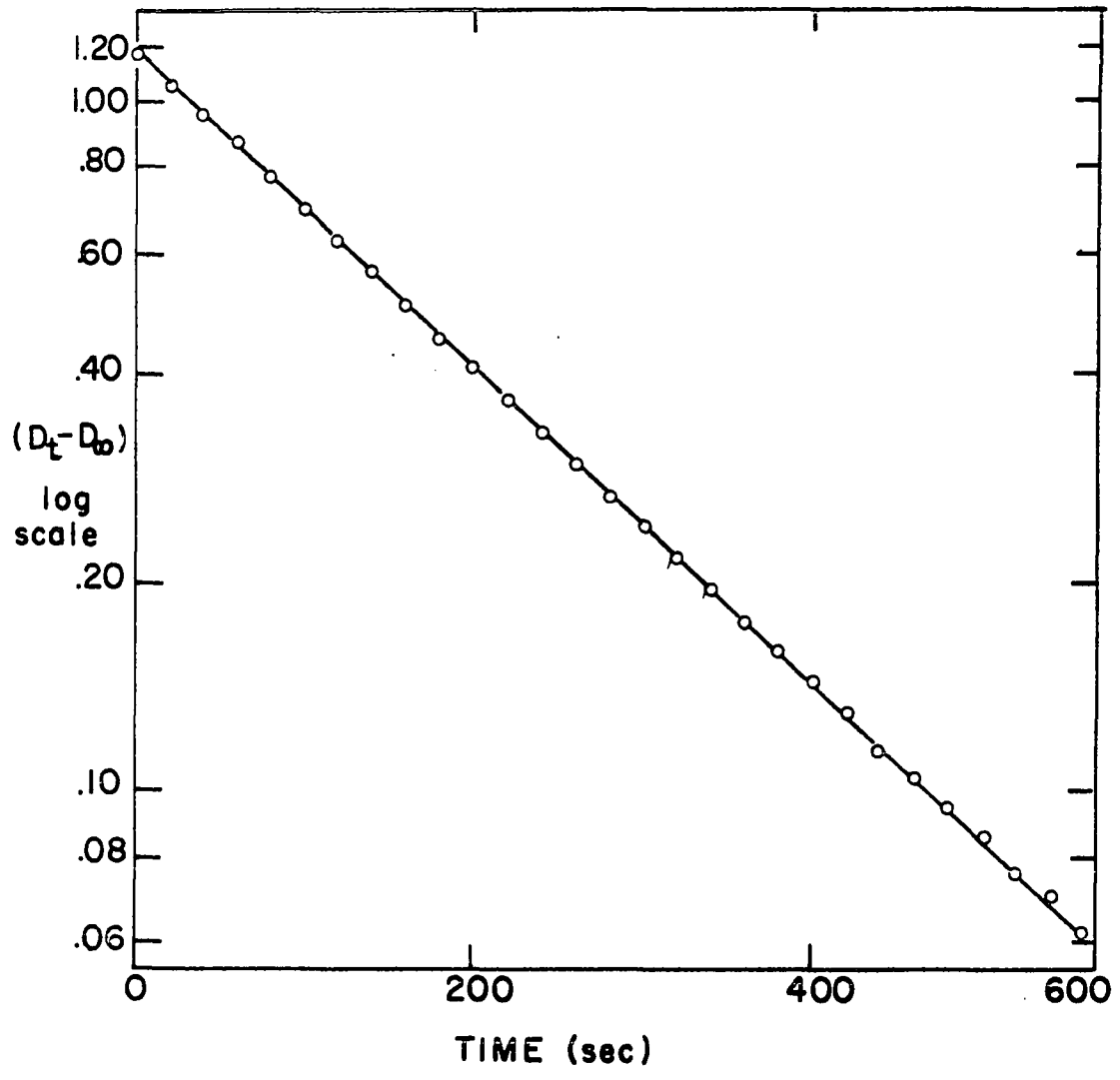


Figure 5. Typical pseudo-first-order plot, experiment 18, $[H^+]_0$ = 1.01 M, $[Cu^{2+}]_0$ = 1.53 x 10^{-2} M, $[V^{3+}]_0$ = 7.50 x 10^{-5} M, $[RBr^{2+}]_0$ = 1.5 x 10^{-4} M, 25.0°, μ = 3.00 M ($LiClO_4$)

Table 9. Kinetic data for the reaction of Cu(II) and V(III)

Conditions: 25.0°, μ = 3.00 M ($LiClO_4$), λ = 280 nm except as noted

Exp.	$[H^+]_0$	$10^2[Cu^{2+}]_0$[a]	$10^4[V^{3+}]_0$	$10^4[RBr^{2+}]_0$[b,c]	k_{app} (M^{-1} sec^{-1})	k_{calc}[d]
1	2.85	0.998	0.75	1.5[c]	0.136[e]	0.136
2	2.85	4.59	3.6	5.5[c]	0.138[e]	
3	2.85	4.67	10.0	12.0[b]	0.138[f]	
4	2.85	4.67	10.0	12.0[b]	0.142[f]	
5	2.85	4.92	1.1	3.4	0.130[g]	
6	2.85	4.92	0.75	2.3	0.134[h]	
7	2.85	4.92	0.75	2.3	0.136[i]	
8	2.85	4.92	0.75	2.3	0.137[j]	
9	2.85	4.92	0.75	2.3	0.138[k]	
10	2.85	4.99	0.75	1.5	0.133	
11	2.85	4.99	0.75	1.5	0.137	
12	2.00	0.998	0.75	1.5	0.184	0.186
13	2.00	4.99	0.75	1.5	0.185	
14	2.00	10.1	0.75	1.5	0.186	
15	2.00	20.1[a]	0.75	1.5	0.180	

[a] Cu^{2+} from $Cu(ClO_4)_2$ preparation.
[b] $[RCl^{2+}]_0$.
[c] $[Co(en)_2Cl_2^+]_0$.
[d] Calculated from the activation parameters given on page 78.
[e] 290 nm.
[f] 533 nm.
[g] $[VO^{2+}]_0 = 50.0 \times 10^{-4}$ M.
[h] $[VO^{2+}]_0 = 10.0 \times 10^{-4}$ M.

Table 9. (Continued)

Exp.	$[H^+]_0$	$10^2[Cu^{2+}]_0$	$10^4[V^{3+}]_0$	$10^4[RBr^{2+}]_0$	k_{app} (M^{-1} sec^{-1})	k_{calc}
16	1.01	0.299	0.75	1.5	0.356	0.350
17	1.01	0.499	0.75	1.5	0.355	
18	1.01	1.53	0.75	1.5	0.347	
19	1.01	1.60	3.6	5.5[c]	0.348[e]	
20	1.01	1.60	3.0	5.5[c]	0.350[e]	
21	1.01	1.60	3.6	11.1[c]	0.353[l]	
22	1.01	3.19	0.75	2.3	0.348[i]	
23	1.01	3.19	0.75	2.3	0.349[h]	
24	1.01	3.19	0.75	2.3	0.351[j]	
25	1.01	3.19	1.1	3.4	0.355[e,g]	
26	1.01	3.19	0.75	2.3	0.359[k]	
27	1.01	4.99	0.75	1.5	0.347[m]	
28	1.01	4.99	0.75	1.5	0.349	
29	1.01	4.99	0.75	1.5	0.352[e]	
30	1.01	4.99	0.75	1.5[b]	0.352[n]	
31	1.01	4.99	0.75	1.5[b]	0.361[n]	
32	1.01	10.0[a]	0.75	1.5	0.345	
33	0.506	0.299	0.75	1.5	0.670	0.677
34	0.506	1.53	0.75	1.5	0.686	
35	0.506	2.99	0.75	1.5	0.680	

[i] $[VO^{2+}]_0 = 1.0 \times 10^{-4}$ M.
[j] $[Br^-]_0 = 2.5 \times 10^{-4}$ M.
[k] $[Br^-]_0 = 7.5 \times 10^{-4}$ M.
[l] 325 nm.
[m] 275 nm.
[n] 255 nm.

Table 9. (Continued)

Exp.	$[H^+]_0$	$10^2[Cu^{2+}]_0$	$10^4[V^{3+}]_0$	$10^4[RBr^{2+}]_0$	k_{app} (M^{-1} sec^{-1})	k_{calc}
36	0.506	5.07 [a]	0.75	1.5	0.662	
37	0.210	0.0100	13.0	21.0	1.70 [o]	1.60
38	0.210	0.0765[a]	12.0	21.0	1.65 [o]	
39	0.210	0.0989	10.0	15.0	1.67 [o]	
40	0.210	0.206	10.0	15.0	1.64 [o]	
41	0.210	0.319	3.6	5.5 [c]	1.62 [e]	
42	0.210	0.752	0.75	1.5	1.58	
43	0.210	0.752	0.75	1.5	1.62	
44	0.210	0.752	2.0	3.0	1.62 [p]	
45	0.210	0.752	3.0	2.0	1.69 [p]	
46	0.210	1.17	1.1	3.4	1.59 [e,g]	
47	0.210	1.17	0.75	2.3	1.62 [q]	
48	0.210	1.53	0.75	1.5	1.59	
49	0.210	1.64[a]	0.75	1.5	1.56	
50	0.210	1.64[a]	0.75	1.5	1.66	
51	0.210	2.99	0.75	1.5	1.56	

[o] 360 nm.

[p] 300 nm.

[q] $[Br^-]_0 = 10.0 \times 10^{-4}$ M.

rate constants, computed on the assumption that rate Equation 29 applied,

$$-d[V^{3+}]/dt = k_{app}[Cu^{2+}]_0[V^{3+}] \qquad (29)$$

are tabulated in Table 9. In a series of experiments at constant $[H^+]$ (compare runs 1 thru 11, 16 thru 32, for example), the constancy of k_{app} on this basis is very good. An extensive variation in $[Cu^{2+}]_0$ at constant $[H^+]$ for all of the hydrogen ion concentrations studied in this sytem (i.e. a 33 fold variation at $[H^+] = 1.01$ M and a 300 fold variation at $[H^+] = 0.210$ M) demonstrated the first-order dependence of the rate on the initial concentration of copper(II). The kinetic behavior illustrates that copper(II) is a true catalyst. The total variation of $[Cu^{2+}]_0$ considering all experiments was 1.0×10^{-4} M to 2.0×10^{-1} M. In all cases the hydrogen ion concentration was in great excess over $[V^{3+}]_0$ so that $[H^+]$ remained effectively constant during the course of an experiment.

To ensure that the rate law was correctly represented in Equation 29 with no contribution from an additional functional dependence upon vanadium(III), runs were done with $[V^{3+}]_0$ varied from 7.5×10^{-5} M to 1.3×10^{-3} M. The variation in $[V^{3+}]_0$ showed that the product, vanadium(IV) at concentration levels of $\leq 1.3 \times 10^{-3}$ M, was not exerting an influence upon the rate. Because small concentrations of VO^{2+} did not alter the kinetics and the presence of V^{2+} in V^{3+} stock solutions

was considered undesirable, all V^{3+} solutions had ~ 5% excess VO^{2+}. A more detailed consideration of this point is discussed later. In most experiments $[Cu^{2+}]_0 > [V^{3+}]_0$, which was necessary to achieve convenient reaction times. Three experiments with $[V^{3+}]_0 > [Cu^{2+}]_0$ were performed to demonstrate that Cu^{2+} was a catalyst capable of accelerating the reaction under conditions where the reactants were present initially at a higher concentration than the catalyst. The three experiments; 37, 38 and 39, exhibited the normal pseudo-first-order absorbance traces. These data suggest that copper(II) is replenished rapidly and that the Cu^{2+} concentration does not change to any appreciable extent even in runs where its concentration is lower than that of V^{3+} or RBr^{2+}.

Considerable variation of $[RBr^{2+}]_0$ established that the rate is not a function of its concentration, which was varied in the range 1.5×10^{-4} M to 2.1×10^{-3} M. Further studies involving the use of RCl^{2+} and trans-$Co(en)_2Cl_2^+$ in place of RBr^{2+} supported this observation. Experiments with $[RBr^{2+}]_0 > [Cu^{2+}]_0$ gave kinetic evidence that the reaction between V^{3+} and RBr^{2+} is insignificant under typical conditions employed.

A possible effect from the bromide ion released during the course of an experiment was eliminated by the variation of $[RBr^{2+}]_0$. Further evidence on this point is discussed later. A majority of the experiments was done with

$[RBr^{2+}]_0 > [V^{3+}]_0$. The data also establish that the rate constant is independent of the wavelength used.

The form of the rate expression suggests that the nature of the oxidizing agent (cobalt(III) complex in this case) is unimportant except that it must be capable of replenishing the Cu^{2+} rapidly. A study of the rates of oxidation of Cu^+ by several cobalt(III) complexes was undertaken in order to select such oxidizing agents. Three systems that were potentially useful are (1) $Cu^+ + Co(NH_3)_5Br^{2+}$, (2) $Cu^+ + Co(NH_3)_5Cl^{2+}$ and (3) $Cu^+ +$ trans-$Co(en)_2Cl_2^+$. The rates of all are very rapid relative to the $V^{3+} - Cu^{2+}$ reaction; the Cu^+ - Co(III) rate constants are $k = 4.46 \times 10^5$ $\underline{M}^{-1}$ sec^{-1} (RBr^{2+}), $k = 4.88 \times 10^4$ $\underline{M}^{-1}$ sec^{-1} (RCl^{2+}) and $k > 1 \times 10^7$ $\underline{M}^{-1}$ sec^{-1} ($Co(en)_2Cl_2^+$). A more detailed discussion of these Co(III) reactions is presented in the appropriate sections. The rate expression for V^{3+}-Cu^{2+}, Equation 29, was shown to be valid at various hydrogen ion concentrations with either RCl^{2+} or trans-$Co(en)_2Cl_2^+$ substituted for the RBr^{2+}. All experiments of this type had $[Co(III)]_0 > [V^{3+}]_0$. The agreement of the rate constant determined with the various cobalt(III) complexes is excellent. The quality of this agreement is shown in Table 10. Similar experiments using $Co(NH_3)_5NCS^{2+}$ in place of RBr^{2+} failed because of the formation of a precipitate of CuSCN.

Table 10. Determination of k_{app} ($\underline{M}^{-1}$ sec^{-1}) using three different Co(III) complexes[a,b]

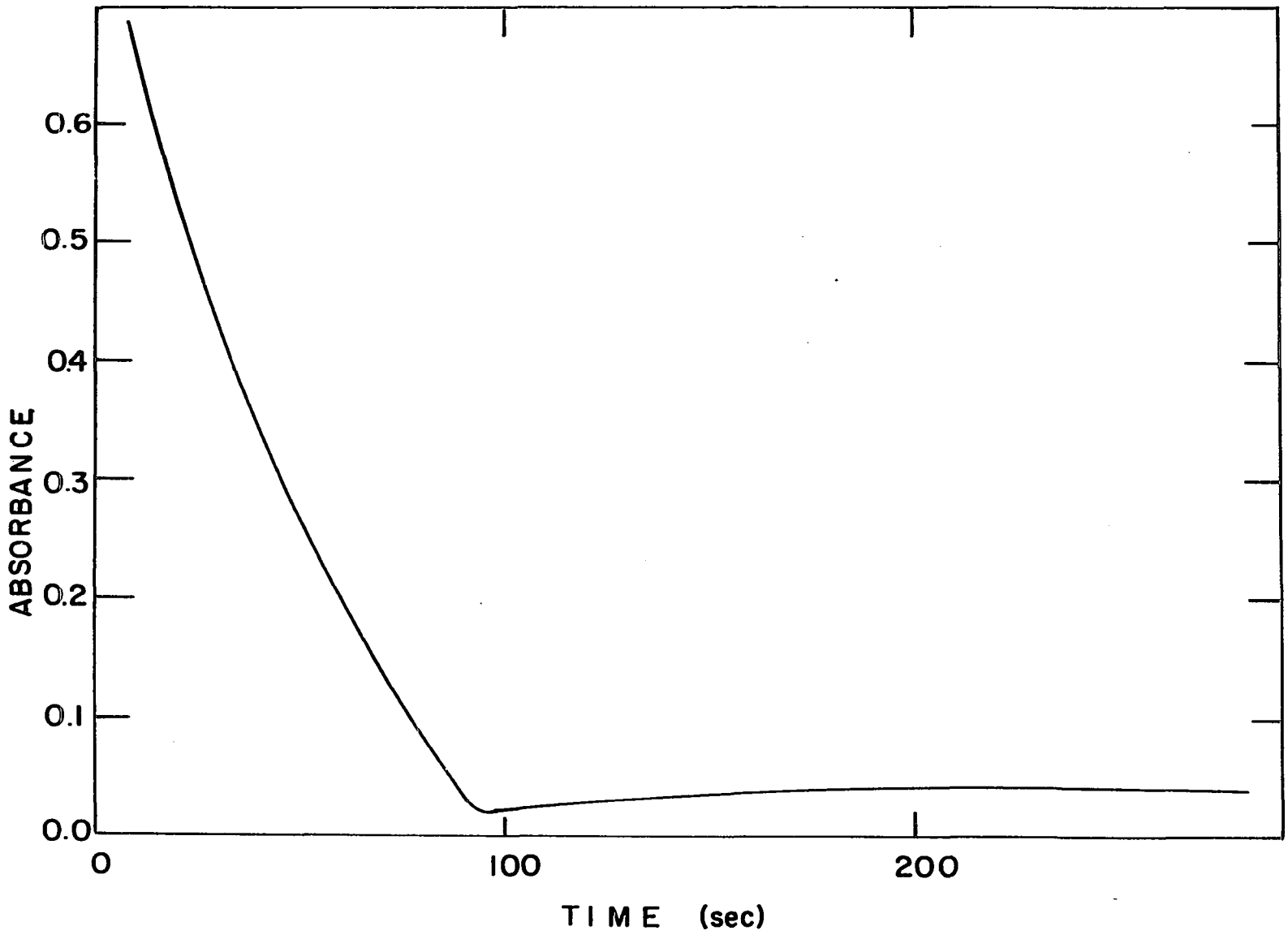
Conditions: 25.0°, μ = 3.00 $\underline{M}$ ($LiClO_4$)					
$[H^+]$	RBr^{2+}		RCl^{2+}	trans-$Co(en)_2Cl_2^+$	
2.85	0.135±.002	(8)	0.140±.002 (2)	0.138	(1)
1.01	0.352±.004	(12)	0.356±.005 (2)	0.350±.002	(3)
0.210	1.62 ±.04	(14)		1.62	(1)

[a]Average values are given at each hydrogen ion concentration.

[b]The number of experiments is given in parenthesis

A rather unique behavior was observed in experiments where $[RBr^{2+}]_0 < [V^{3+}]_0$. In Figure 6, a plot of absorbance as a function of time for experiment 45, page 57, demonstrates this unusual sequence of absorbance changes for a typical experiment. These data were interpreted in the following manner. The large initial absorbance decrease is due to the disappearance of RBr^{2+} since this species has a large molar absorptivity in comparison with other species undergoing concentration changes (λ = 280 nm; ε = 3430, RBr^{2+}; $\varepsilon \sim 6$, V^{3+}; $\varepsilon \sim 80$, V(IV); $\varepsilon < 0.5$, Co^{2+}). This reaction is the copper(II) catalyzed reaction of RBr^{2+} and V^{3+} that was given in Equation 28, a brief form of which is indicated by Equation 32.

Figure 6. Absorbance versus time plot of experiment 45; $[H^+] = 0.210$ M, $[Cu^{2+}]_0 = 7.52 \times 10^{-3}$ M, $[V^{3+}]_0 = 3.0 \times 10^{-4}$ M, $[RBr^{2+}]_0 = 2.0 \times 10^{-4}$ M, 25.0°, $\mu = 3.00$ M ($LiClO_4$)


ABSORBANCE
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
100
200
TIME (sec)

$$V^{3+} + Cu^{2+} \underset{2}{\overset{1}{\rightleftharpoons}} V(IV) + Cu^{+} \qquad (30)$$

$$Cu^{+} + RBr^{2+} \xrightarrow{\text{rapid}} Cu^{2+} + Co^{2+} + \text{Products} \qquad (31)$$

$$\text{net reaction: } V^{3+} + RBr^{2+} = V(IV) + Co^{2+} + \text{Products} \qquad (32)$$

The reaction of Cu^{+} and RBr^{2+} is very rapid so that the depletion of RBr^{2+} is very abrupt. At this point the absorbance begins to increase due to reaction 30 achieving equilibrium (λ = 280 nm; $\varepsilon \sim 6$, V^{3+}; ε = 10.2, Cu^{2+}; $\varepsilon \sim 80$, V(IV); $\varepsilon \sim 340$, Cu^{+}). In most experiments of this type the second stage produced very small absorbance changes due to the unfavorable equilibrium constant. This type of data could not be treated quantitatively. The first stage was easily put to a quantitative test by using the Guggenheim (65) method or by using a computer program to find absorbance at infinite time when ca. $[RBr^{2+}]_0$ was equal to 0.65 or 0.90 $[V^{3+}]_0$. Rate constants determined in this manner gave excellent agreement with those where $[RBr^{2+}]_0 > [V^{3+}]_0$. Table 11 lists these results.

The equilibrium constant for reaction 30 is given by Equation 33. An experiment with a low initial concentration of hydrogen ion and very high concentration of copper(II)

$$K = 8.5 \times 10^{-4} \ (\mu = 3.00, LiClO_4) = [Cu^{+}][VO^{2+}][H^{+}]^2/[Cu^{2+}][V^{3+}] \qquad (33)$$

Table 11. Rate constants determined with $[V^{3+}]_0 > [RBr^{2+}]_0$

Conditions: 25.0° μ = 3.00 M			
Exp.	$k(\underline{M}^{-1}\ sec^{-1})$	$k_{av}(\underline{M}^{-1}\ sec^{-1})^a$	medium
45	1.69	1.62 ±.03	Li^+
18	0.0419	0.0423±.0000	Na^{+b}
41	0.973	0.971 ±.015	Na^{+b}

[a]Average of all other experiments at the same hydrogen ion concentration.

[b]Results presented later.

($[Cu^{2+}]_0/[V^{3+}]_0 \sim 170$) allows sufficient Cu(I) and V(III) to be formed so that quantitative measurements of the second stage are possible. Both products have a higher absorbance at 251 nm that Cu(II) and V(III) so that the reaction may be conveniently monitored. The anticipated rate expression involves the five species Cu^{2+}, V^{3+}, H^+, VO^{2+} and Cu^+ approaching equilibrium as shown by Equation 34. The form of the reverse rate expression

$$-d[Cu^{2+}]/dt = k_{app}[Cu^{2+}][V^{3+}] - k_r[H^+][VO^{2+}][Cu^+] \qquad (34)$$

was established by K. Shaw and J. H. Espenson[6]. The forward rate constant, k_{app}, must have a hydrogen ion dependence but

[6]K. Shaw and J. H. Espenson, Ames, Iowa. Kinetics and Mechanism of the Oxidation-Reduction between Vanadium(IV) and Copper(I). Private communication.

because of the high hydrogen ion concentration, relative to the species changing concentrations, the rate constant, k_{app}, is valid. In order to simplify the kinetic rate expression the concentration of RBr^{2+} was adjusted so that at its depletion enough V(IV) was present to ensure that the V(IV) concentration remained essentially constant during the second stage of the experiment. Thus the data for the second stage approached equilibrium according to the pseudo-first-order expression given in Equations 35 and 36.

$$-d[Cu^{2+}]/dt = \{k_{app}[Cu^{2+}]_0\}[V^{3+}] - \{k_r[H^+]_0[VO^{2+}]_{av}\}[Cu^+] \quad (35)$$

thus

$$\ln(D_t - D_\infty)/(D_0 - D_\infty) = -(k_I + k_{II})t \quad (36)$$

where $k_I = k_{app}[Cu^{2+}]_0$ and $k_{II} = k_r[H^+]_0[VO^{2+}]$. The initial concentrations were: $[H^+]_0 = 0.210$ M, $[Cu^{2+}]_0 = 4.99 \times 10^{-2}$ M, $[V^{3+}]_0 = 3.10 \times 10^{-4}$ M, $[RBr^{2+}]_0 = 2.70 \times 10^{-4}$ M, $\mu = 3.00$ M ($LiClO_4$) at 25.0°. A first-order plot of this experiment yielded $k_{obs} = (k_I + k_{II}) = 0.100\ sec^{-1}$. If the reverse reaction is assumed negligible and k_{II} is deleted the resulting k_{app} is 2.00 M^{-1} sec^{-1}. This result is inconsistent with previous values of k_{app}. Considering the reverse reaction[6] ($k_2 = k_r[H^+] = 80.6\ sec^{-1}$), the calculated result is k_{app} = 1.56 M^{-1} sec^{-1}. This is in excellent agreement with the value of 1.62 M^{-1} from experiments where $[Co(III)]_0 > [V^{3+}]_0$.

Direct measurement of the V(III) and Cu(II) reaction

It is possible to measure the rate of reaction of Cu(II) and V(III) without any added cobalt(III) complex under rather limited conditions. Although the equilibrium constant for the reaction is very unfavorable for such a study, conditions of low hydrogen ion concentration and high copper(II) allow measurements to be made. The conditions are essentially the same as those in the previous experiment on the second stage of the absorbance changes. Copper(II) and hydrogen ion concentrations are large enough with respect to V(III), V(IV) and Cu(I) so that the kinetics can be represented by the following scheme

$$A \underset{k_2}{\overset{k_1}{\rightleftarrows}} B + C \qquad (37)$$

where $k_1 = k_{app}[Cu^{2+}]_0$ and $k_2 = k_r[H^+]_0$. The rate equation becomes

$$dx/dt = k_1(A_0 - X) - k_2(B_0 + X)(C_0 + X) \qquad (38)$$

or

$$-d[Cu^{2+}]/dt = \{k_{app}[Cu^{2+}]_0\}[V^{3+}] - \{k_r[H^+]_0\}[Cu^+][VO^{2+}] \qquad (39)$$

Using the value of $k_r = 384\ \underline{M}^{-2}\ sec^{-1}$, from K. Shaw and J. H. Espenson[6], allows the determination of k_{app}. With initial concentrations $[V^{3+}]_0 = 3.1 \times 10^{-4}\ \underline{M}$, $[Cu^{2+}]_0 = 4.99 \times 10^{-2}\ \underline{M}$ and $[H^+]_0 = 0.210\ \underline{M}$, the rate constant k_{app} was evaluated in two experiments using a mixed first and second

order computer program (64). The values determined were k_{app} = 1.53 and 1.71 $\underline{M}^{-1}$ sec^{-1}, which again is in good agreement with 1.62 $\underline{M}^{-1}$ sec^{-1}.

Effect of high concentrations of Vanadium(IV) Experiments with a very high initial concentration of V(IV) showed a marked decrease in rate when RCl^{2+} was present as the oxidizing agent. Two experiments with $[V(IV)]_0$ = 0.0421 $\underline{M}$ and 0.0840 $\underline{M}$ were done at 533 nm. The experiment with the higher initial concentration of V(IV) showed the greatest decrease in rate and these data were consistent with a rate expression involving a denominator term. Again in order to treat all data adequately it was necessary to assume the mechanism given in Equations 30, 31 and 32 was valid. This mechanism demands the following general rate law

$$- \frac{d[V^{3+}]}{dt} = \frac{k_1 k_{RCl}[Cu^{2+}]_0[V^{3+}][RCl^{2+}]}{k_2[V(IV)] + k_{RCl}[RCl^{2+}]} \qquad (40)$$

It was necessary to use the integrated form of the rate expression and to calculate absorbance values as a function of time. For integration purposes Equation 40 may be simplified to

$$\frac{dx}{dt} = \frac{a(V - x)(R - x)}{b + c\ (R - x)} \qquad (41)$$

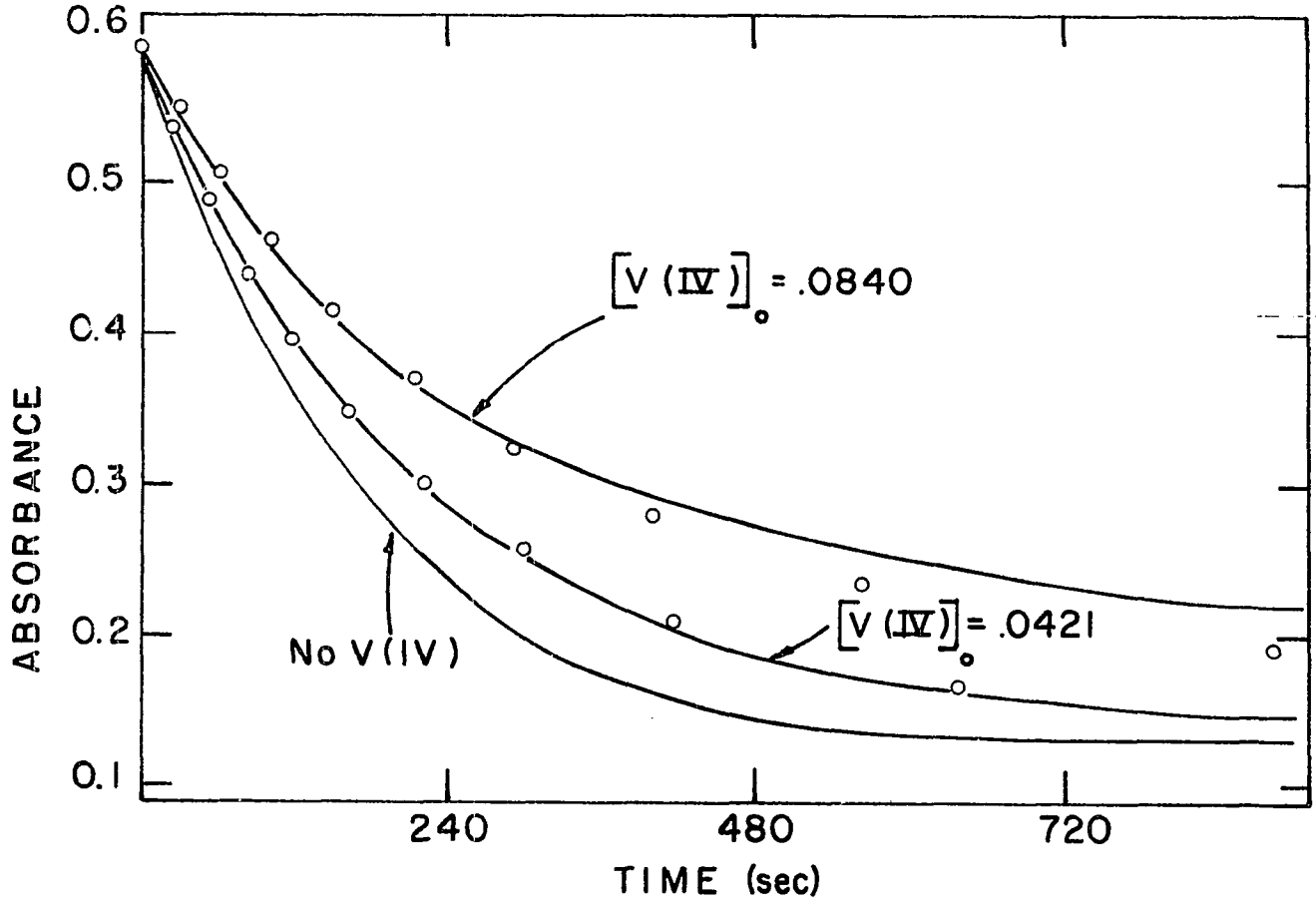
where $a = k_1 k_{RCl}\ [Cu^{2+}]_0$, $b = k_2[V(IV)]$ and $c = k_{RCl}$.
Integration of this differential equation yields

$$- \frac{c(V - R) - b}{a(V - R)} \ln \left[\frac{V - x}{V}\right] - \frac{b}{a} \cdot \frac{1}{V - R} \ln \left[\frac{R - x}{R}\right] = t \qquad (42)$$

Use of this equation and the known molar absorptivities allows the calculation of absorbance versus time data. Initial concentrations used in these experiments were; $[H^+]_0$ = 2.66 M, $[Cu^{2+}]_0 = 4.01 \times 10^{-2}$ M, $[V^{3+}]_0 = 9.00 \times 10^{-4}$ M, $[RCl^{2+}]_0 = 1.20 \times 10^{-3}$ M, μ = 3.00 ($LiClO_4$) at 25.0°. The absorbance values were calculated by using the following values for the molar absorptivities at 533 nm; Cu^{2+}, $\varepsilon < 0.25$; V^{3+}, $\varepsilon = 3.5$; V(IV), $\varepsilon = 1.4$; Cu^+, $\varepsilon \sim 0$; RCl^{2+}, $\varepsilon = 49.0$ The rate constants used for this sytem were; $k_1 = 0.147\ M^{-1}\ sec^{-1}$, $k_2 = 1020\ M^{-1}\ sec^{-1}$ and $k_{RCl} = 1.13 \times 10^5\ M^{-1}\ sec^{-1}$. The latter rate constant was determined independently at μ = 3.00 ($LiClO_4$) and is discussed later. In all experiments a stop watch was used to measure the time of mixing so that the absorbance values start at time equal zero. Figure 7 shows the results of the calculated values (points) and the experimentally observed values (solid lines). Three experiments are represented with initial concentrations as given above and $[V(IV)]_0$ = 0.0, 0.0421 and 0.0840 M respectively. The agreement between calculated and observed values is considered good.

Effect of Br^- generated during an experiment The possibility of a rate effect due to the bromide ion released during the course of an experiment was carefully checked. Free bromide ion was added initially to experiments at $[H^+]$ = 0.210, 1.01 and 2.85 M. The added bromide ion concentration was comparable or greater than the highest concentration

Figure 7. Experiments with a high concentration of V(IV) initially present, $[H^+]_0 = 2.66$ M, $[Cu^{2+}]_0 = 4.01 \times 10^{-2}$ M, $[V^{3+}]_0 = 9.00 \times 10^{-4}$ M, $[RCl^{2+}]_0 = 1.20 \times 10^{-3}$ M, $\mu = 3.00$ ($LiClO_4$) at 25.0°


0.6
0.5
0.4
0.3
0.2
0.1
ABSORBANCE
240
480
720
TIME (sec)
[V (IV)]o = .0840
[V (IV)]o = .0421
No V(IV)

generated at a given hydrogen ion concentration. Table 12 presents these data and in the case of $[H^+]$ = 0.210 M, the majority of experiments was conducted with $[Br^-]_\infty < 1.2 \times 10^{-3}$ M . No significant changes were noted.

Table 12. Determination of k_{app} with $[Br^-]$ added

$[H^+]$	$10^4[Br^-]_0$	$k_{app}(M^{-1}\ sec^{-1})$	highest $[Br^-]$ produced x 10^4	$k_{av}(M^{-1}\ sec^{-1})^a$
0.210	10.0	1.62	12.0	1.62 ±.03
1.01	2.5	0.351	1.1	0.351±.004
1.01	7.5	0.359		
2.85	2.5	0.137	1.1	0.136±.002
2.85	7.5	0.138		

[a]Average with Br^- added experiments omitted.

A study of the effect of higher concentrations of the anions Cl^- and Br^- upon the rate is documented later and supports this conclusion.

Effect of V(IV) generated during an experiment The possibility of the product, V(IV) influencing the rate law and rate constants when present at concentration levels comparable to that generated during an experiment was also carefully checked. No significant changes were observed and these results are listed in Table 13.

Table 13. Determination of k_{app} with V(IV) added

$[H^+]$	$10^3[V(IV)]_0$	$k(\underline{M}^{-1}\ sec^{-1})$	high [V(IV)] produced x 10^3	$k_{av}(\underline{M}^{-1}sec^{-1})^a$
0.210	5.00	1.59	1.26	1.62 ±.04
1.01	0.10	0.348	0.08	0.352±.004
1.01	1.00	0.349		
1.01	5.00	0.355		
2.85	0.10	0.136	0.08	0.135±.002
2.85	1.00	0.134		
2.85	5.00	0.130		

[a]Average value of all rate constants with the added V(IV) experiments omitted.

All V^{3+} preparations (from approximately equimolar VO^{2+} and V^{2+} solutions) used in all of the experiments had ~ 5% excess VO^{2+} present to ensure that no V^{2+} remained.

Hydrogen ion dependence and medium effects A sizeable and regular increase in k_{app} was noted as the hydrogen ion concentration was decreased in a series of runs. The simplest interpretation consistent with these data is

$$k_{app} = g + h/[H^+] \qquad (43)$$

Although the contribution of the first term to the apparent rate constant is very small in comparison with the second, both are necessary to describe the variation of k_{app} with $[H^+]$ within the precision of these data. Typical plots of k_{app} as a function of $1/[H^+]$ are present in Figure 8 and

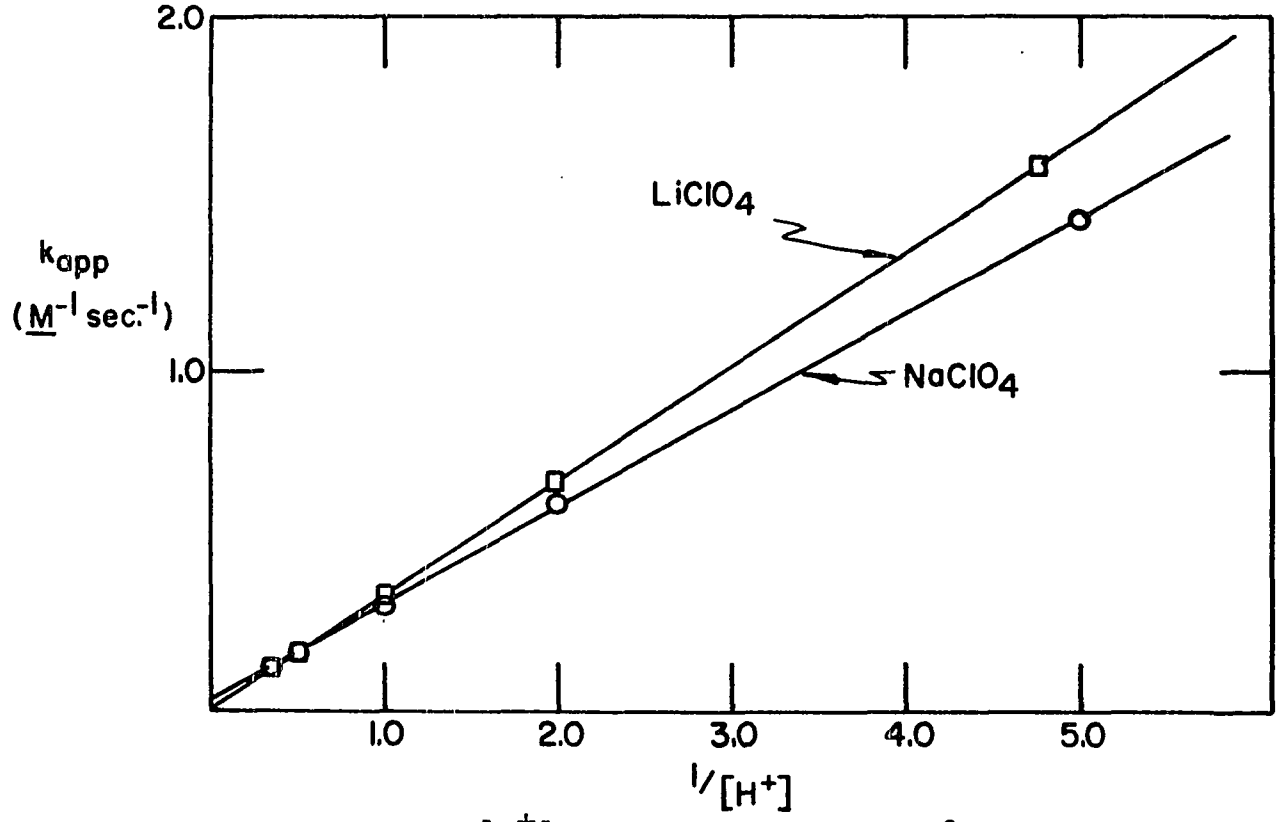


Figure 8. Plot of k_{app} versus $1/[H^+]$, conditions: 25.0°, μ = 3.00 $\underline{M}$ maintained with $LiClO_4$ or $NaClO_4$

show the excellent linearity achieved by this function. In order to compare the data of Higginson and Sykes (32) with this system, a rather extensive study was conducted in a medium of ionic strength 3.00 M adjusted with $NaClO_4$. These data are tabulated in Table 14. The rate expression, Equation 29, is valid under all of the conditions studied in this medium. Values of k_{app} at a given $[H^+]$ are slightly smaller than those observed in the $LiClO_4$ medium. The hydrogen ion dependence is adequately described by Equation 43. In the $NaClO_4$ medium, however, the contribution of the first term to the apparent rate constant is quite substantial at $[H^+] = 1.0$ M. Table 15 represents the best values of g and h in the different media as computed using a non-linear least squares computer program (64).

These values reproduce the experiment data quite well as is shown in Table 16.

A limited study of the rate constant at $\mu = 1.00$ M was conducted. These values are listed in Table 17. The average value is; $k_{app} = 0.258 \pm .003$ M^{-1} sec^{-1}, which implies that $h_f = 0.220$ sec^{-1}.

Temperature dependence The reaction was studied at two different temperatures in both sodium perchlorate and lithium perchlorate media. The temperature effect is quite large with a 10 fold increase in rate for a corresponding 20° change in temperature. These data are presented in Tables 18, 19, 20 and 21. The activation parameters were calculated using the

Table 14. Kinetic data for the reaction of Cu(II) and V(III)

Conditions: 25.0°, μ = 3.00 M ($NaClO_4$), λ = 280 nm except as noted.

Exp.	$[H^+]_0$	$10^2[Cu^{2+}]_0$	$10^4[V^{3+}]_0$	$10^4[RBr^{2+}]_0$	k_{app} (M^{-1} sec^{-1})	k_{calc} [a]
1	2.85	1.66	0.75	1.4	0.137	0.136
2	2.85	1.66	0.75	1.4	0.140	
3	2.85	4.92	0.75	1.4	0.141	
4	2.00	1.33	0.75	1.4	0.176	0.178
5	2.00	13.3	0.75	1.4	0.179	
6	1.00	0.319	0.75	1.4	0.316	0.318
7	1.00	0.652	0.75	1.4	0.314	
8	1.00	3.19	1.5	2.8	0.333[b]	
9	1.00	3.19	0.75	1.4	0.335	
10	1.00	6.52	0.75	1.4	0.314	
11	0.498	0.319	0.75	1.4	0.633	0.602
12	0.498	3.19	0.75	1.4	0.605	
13	0.201	0.133	0.75	1.4	1.49	1.43
14	0.201	0.286	0.75	1.4	1.42	
15	0.201	0.586	0.75	1.4	1.44	
16	0.201	0.586	0.75	1.4	1.45	

[a] Calculated from the activation parameters given on page 78.

[b] 290 nm.

Table 15. Rate constants for the reaction of V^{3+} + Cu^{2+}

Medium	Temp.	g($\underline{M}^{-1}$ sec^{-1})	h(sec^{-1})
$LiClO_4$	15.0	0.0076±0.0008	0.0999±0.0006
$LiClO_4$	25.0	0.018 ±0.002	0.336±±0.001
$LiClO_4$	35.1	0.083 ±0.010	0.981 ±0.008
$NaClO_4$	15.0	0.0117±0.0006	0.0837±0.0005
$NaClO_4$	25.0	0.038 ±0.003	0.285 ±0.002
$NaClO_4$	35.0	0.111 ±0.005	0.852 ±0.004

Eyring absolute rate expression and are listed below: $LiClO_4$, $\Delta H^{\ddagger}$ = 19.1 ± .1 kcal/mole, $\Delta S^{\ddagger}$ = 3.3 ± .4 cal/mole-deg; $NaClO_4$, $\Delta H^{\ddagger}$ = 19.7 ± .1 kcal/mole, $\Delta S^{\ddagger}$ = 5.1 ± .3 cal/mole-deg.

Effect of the anions Cl^- and Br^- The rate of reaction of V^{3+} and Cu^{2+} was noticeably increased when either Br^- or Cl^- were initially present at concentrations equal to or greater than ca. 0.01 M. A limited study of this anion effect has been made. Bromide ion was varied from 2.5 x 10^{-3} M to 4.04 x 10^{-2} M and chloride ion was varied from 2.0 x 10^{-2} M to 6.0 x 10^{-2} M. Under these conditions plots of $\ln(D_t - D_\infty)$ as a function of time, Equation 44, were linear indicating the first order dependence on $[V^{3+}]$. No variation of $[Cu^{2+}]_0$

$$\ln[(D_t - D_\infty)/(D_o - D_\infty)] = -k'_{app}t \qquad (44)$$

Table 16. Observed and calculated values of k_{app} at μ = 3.00 M ($LiClO_4$ or $NaClO_4$) and various temperatures, using $g + h/[H^+] = k_{app}$

		k_{app} (M^{-1} sec^{-1})									
		$[H^+]$=0.210		$[H^+]$=0.506		$[H^+]$=1.0		$[H^+]$=2.00		$[H^+]$=2.85	
		obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.
Li^+	15.0°	0.480	0.484	0.209	0.205	0.109	0.107	0.0561	0.0575	0.0428[a]	0.0440[a]
Li^+	25.0°	1.62	1.62	0.675	0.682	0.352	0.351	0.184	0.185	0.136	0.135
Li^+	35.1°	4.74	4.76	2.04	2.02	1.08	1.06	0.569	0.574	0.419	0.427
		$[H^+]$=2.01		$[H^+]$=0.498		$[H^+]$=1.00		$[H^+]$=2.00		$[H^+]$=2.85	
		obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.
Na^+	15.0°	0.429	0.428	0.176	0.180	0.0958	0.0954	0.0537	0.0536	0.0422[a]	0.0422[a]
Na^+	25.0°	1.45	1.45	0.619	0.610	0.322	0.323	0.178	0.181	0.139	0.138
Na^+	35.0°	4.35	4.35	1.82	1.82	0.972	0.964	0.533	0.537	0.408	0.410

[a] $[H^+]$ = 2.75 M.

Table 17. Values of k_{app} at μ = 1.00 M, 25.0°, $[H^+]$ = 0.852 M

Exp.	$10^2[Cu^{2+}]_0$	$10^4[V^{3+}]_0$	$10^4[RBr^{2+}]_0$	k_{app} (M^{-1} sec^{-1})
1	0.499	0.75	1.4	0.261
2	0.499	0.75	1.4	0.263
3	2.00	0.75	1.4	0.258
4	2.00	0.75	1.4	0.259
5	4.79	0.75	1.4	0.253
6	4.79	0.75	1.4	0.256

Table 18. Kinetic data for the reaction of Cu(II) and V(III)

Conditions: 15.0°, μ = 3.00 M ($LiClO_4$), λ = 280 nm except as noted

Exp.	$[H^+]_0$	$10^2[Cu^{2+}]_0$ [a]	$10^4[V^{3+}]_0$	$10^4[RBr^{2+}]_0$	k_{app} (M^{-1} sec^{-1})	k_{calc} [b]
52	2.75	2.06	0.75	1.5	0.0426	0.0428
53	2.75	8.32	0.75	1.5	0.0427	
54	2.75	8.32	0.75	1.5	0.0431	
55	2.00	3.99	0.75	1.5	0.0570	0.0571
56	2.00	33.4[a]	0.75	1.5	0.0552	
57	1.01	2.00	0.75	1.5	0.109	0.109
58	1.01	9.98	0.35	0.75	0.108[c]	
59	1.01	9.98	0.75	1.5	0.110	
60	1.01	9.98	0.75	1.5	0.110	
61	1.01	9.98	3.0	6.0	0.112[d]	

[a] Cu^{2+} from $Cu(ClO_4)_2$.

[b] Calculated from the activation parameters given on page 78 .

[c] 270 nm.

[d] 300 nm.

Table 18. (Continued)

Exp.	$[H^+]_0$	$10^2[Cu^{2+}]_0$	$10^4[V^{3+}]_0$	$10^4[RBr^{2+}]_0$	k_{app} ($\underline{M}^{-1}$ sec^{-1})	k_{calc}[b]
62	1.01	20.1[a]	0.75	1.5	0.107	
63	0.506	1.01	0.75	1.5	0.209	0.212
64	0.506	10.1	0.75	1.5	0.209	
65	0.209	0.406	0.75	1.5	0.482	0.504
66	0.209	1.60	0.75	1.5	0.475	
67	0.209	1.60	0.75	1.5	0.479	
68	0.209	4.06	0.75	1.5	0.485	

Table 19. Kinetic data for the reaction of Cu(II) and V(III)

Conditions: 35.1°, μ = 3.00 $\underline{M}$ ($LiClO_4$), λ = 280 nm except as noted

Exp.	$[H^+]_0$	$10^2[Cu^{2+}]_0$	$10^4[V^{3+}]_0$	$10^4[RBr^{2+}]_0$	k_{app} ($\underline{M}^{-1}$ sec^{-1})	k_{calc}[a]
69	2.85	0.605	0.75	1.5	0.439	0.425
70	2.85	5.06	0.75	1.5	0.408	
71	2.85	5.06	0.75	1.5	0.409	
72	2.00	0.406	0.75	1.5	0.575	0.572
73	2.00	4.06	0.75	1.5	0.562	
74	1.01	0.206	0.75	1.5	1.10	1.06
75	1.01	1.00	0.44	0.75	1.05[b]	
76	1.01	1.01	0.75	1.5	1.07	
77	1.01	1.01	0.75	1.5	1.08	
78	1.01	1.01	3.0	6.0	1.09[c]	
79	1.01	2.06	0.75	1.5	1.06	
80	0.506	0.101	0.75	1.5	2.02	2.03
81	0.506	1.01	0.75	1.5	2.05	
82	0.210	0.0416	0.75	1.5	4.70	4.78
83	0.210	0.181	0.75	1.5	4.60	

[a] Calculated from the activation parameters given on page 78.

[b] 274 nm.

[c] 300 nm.

Table 19. (Continued)

Exp.	$[H^+]_0$	$10^2[Cu^{2+}]_0$	$10^4[V^{3+}]_0$	$10^4[RBr^{2+}]_0$	k_{app} ($\underline{M}^{-1}$ sec^{-1})	k_{calc}[a]
84	0.210	0.181	0.75	1.5	4.90	
85	0.210	0.406	0.75	1.5	4.77	

Table 20. Kinetic data for the reaction of Cu(II) and V(III)

Conditions: 15.0°, μ = 3.00 $\underline{M}$ ($NaClO_4$), λ = 280 nm except as noted

Exp.	$[H^+]_0$	$10^2[Cu^{2+}]_0$	$10^4[V^{3+}]_0$	$10^4[RBr^{2+}]_0$	k_{app} ($\underline{M}^{-1}$ sec^{-1})	k_{calc}[a]
17	2.75	2.06	0.75	1.4	0.0423	0.0429
18	2.75	8.32	0.90	0.80	0.0419	
19	2.75	8.32	0.75	1.4	0.0423	
20	2.00	3.99	0.75	1.4	0.0526	0.0546
21	2.00	33.3	0.75	1.4	0.0547	
22	1.00	2.00	0.75	1.4	0.0948	0.0973
23	1.00	14.6	0.45	0.69	0.0931[b]	
24	1.00	14.6	1.5	2.8	0.0959[c]	
25	1.00	14.6	0.75	1.4	0.0969	
26	1.00	14.6	0.75	1.4	0.0972	
27	1.00	20.0	0.75	1.4	0.0971	
28	0.498	1.01	0.75	1.4	0.178	0.184
29	0.498	10.1	0.75	1.4	0.175	
30	0.201	0.406	0.75	1.4	0.438	0.437
31	0.201	1.60	0.75	1.4	0.424	
32	0.201	1.60	0.75	1.4	0.427	
33	0.201	4.06	0.75	1.4	0.427	

[a]Calculated from the activation parameters given on page 78.

[b]270 nm.

[c]300 nm.

Table 21. Kinetic data for the reaction of Cu(II) and V(III)

Conditions: 35.0°, μ = 3.00 M ($NaClO_4$), λ = 280 nm except as noted						
Exp.	$[H^+]_0$	$10^2[Cu^{2+}]_0$	$10^4[V^{3+}]_0$	$10^4[RBr^{2+}]_0$	k_{app} (M^{-1} sec^{-1})	k_{calc}[a]
34	2.85	0.605	0.90	1.4	0.418	0.411
35	2.85	5.06	0.90	1.4	0.398	
36	2.85	5.06	0.90	1.4	0.408	
37	2.00	0.406	0.90	1.4	0.537	0.539
38	2.00	4.06	0.90	1.4	0.528	
39	1.00	0.206	0.90	1.4	0.983	0.966
40	1.00	1.01	0.69	0.45	0.960[b]	
41	1.00	1.01	0.90	0.80	0.973	
42	1.00	1.01	0.90	1.4	0.979	
43	1.00	1.01	1.8	2.8	0.989[c]	
44	1.00	2.06	0.90	1.4	0.946	
45	0.498	0.406	0.75	1.4	1.84	1.83
46	0.498	1.01	0.90	1.4	1.79	
47	0.201	0.166	0.75	1.4	4.34	4.36
48	0.201	0.406	0.75	1.4	4.35	
49	0.201	0.725	0.75	1.4	4.32	
50.	0.201	0.725	0.75	1.4	4.38	

[a]Calculated from the activation parameters given on page 78.

[b]270 nm.

[c]300 nm.

was carried out in these experiments. These data are presented in Tables 22 and 24.

The rate constant, k'_{app}, was shown to be a linear function of $[Br^-]$ by plotting k'_{app} at constant acid concentration versus $[Br^-]_0$, Figures 9 and 10. At constant acid the following rate equation was assumed valid;

$$-d[V^{3+}]/dt = \{k_{app} + k_{Br}[Br^-]\}[Cu^{2+}]_0[V^{3+}] \qquad (45)$$

where k_{app} represents the non-anion path previously discussed.

Experiments were conducted at two different initial hydrogen ion concentrations and a slight hydrogen ion dependence was observed. The functional dependence was assumed to be

$$k_{Br} = k'_{Br} + k''_{Br}/[H^+] \qquad (46)$$

The resulting rate constants at $\mu = 3.00$ ($LiClO_4$) and 25.0° are $k'_{Br} = 2.83\ \underline{M}^{-2}\ sec^{-1}$ and $k''_{Br} = 3.59\ \underline{M}^{-1}\ sec^{-1}$. Table 23 shows added evidence that these paths did not interfere with the previous study of k_{app}, in which small amounts of Br^- were generated.

A small study of the effect of Cl^- was done at $\mu = 3.00$ ($LiClO_4$) and is presented in Table 24. The results are similar to the Br^- study and a plot of k'_{app} as a function of chloride ion, Figure 11, suggested the following rate expression

$$-d[V^{3+}]/dt = \{k_{app} + k_{Cl}[Cl^-]\}[Cu^{2+}]_0[V^{2+}] \qquad (47)$$

Table 22. Rate constants for the reaction of V^{3+} + Cu^{2+} with Br^- added

Conditions: 25.0°, μ = 3.00 M ($LiClO_4$), λ = 280 nm

Exp.	$[H^+]_0$	$10^2[Cu^{2+}]_0$	$10^2[Br^-]_0$	k'_{app} (M^{-1} sec^{-1})[a]	k_{calc}[b]
1	2.85	4.99	0.25	0.144	0.145
2	2.85	4.99	1.00	0.174	0.176
3	2.85	4.99	1.01	0.166	0.176
4	2.85	4.99	2.02	0.217	0.218
5	2.85	4.99	3.03	0.260	0.259
6	2.85	4.99	4.04	0.300	0.301
7	1.00	4.99	0.25	0.375	0.368
8	1.00	4.99	1.00	0.439	0.416
9	1.00	4.99	1.01	0.427	0.416
10	1.00	4.99	2.02	0.472	0.480
11	1.00	4.99	3.03	0.539	0.545
12	1.00	4.99	4.04	0.605	0.612

[a] $[RBr^{2+}]_0$ = 1.5 x 10^{-4} M, $[V^{3+}]_0$ = 7.5 x 10^{-5} M in all experiments.

[b] Calculated on the basis that $k'_{obs} = k_{app} + k_{Br}[Br^-]$.

Table 23. Comparison of k_{app} and $k_{Br}[Br^-]$

$[H^+]$	k_{app} (M^{-1} sec^{-1})	highest $10^4[Br^-]$ produced	$k_{Br}[Br^-]$
0.210	1.62	12.0	.02
1.01	0.352	1.1	.001
2.85	0.136	1.1	.0004

Table 24. Rate constants for the reaction of V^{3+} + Cu^{2+} with Cl^- added

Conditions: 25.0°, μ = 3.00 M ($LiClO_4$) λ = 280 nm, $[H^+]$ = 1.00 M

Exp.	$[H^+]_0$	$10^2[Cu^{2+}]_0$	$10^2[Cl^-]_0$	$10^4[V^{3+}]$	$10^4[RBr^{2+}]$	k'_{app} (M^{-1} sec^{-1})
1	1.00	3.06	2.0	4.5	6.0	0.593
2	1.00	3.06	2.0	3.0	4.5	0.631
3	1.00	3.06	4.0	3.0	4.5	0.831
4	1.00	3.06	4.0	4.5	6.0	0.848
5	1.00	3.06	6.0	3.0	4.5	1.24

The rate constant, k_{Cl}, was evaluated to be 13.6 M^{-2} sec^{-1} at $[H^+]$ = 1.00 M. Thus the Cl^- path did not interfere with evaluation of k_{app}; k_{app} = 0.352 ± 0.004 M^{-1} sec^{-1}, $k_{Cl}[Cl^-]$ = 0.0010 M^{-1} sec^{-1}. The hydrogen ion dependence was not investigated for the anion system with Cl^-.

Reduction of Cu^{2+} with Cr^{2+}

Preparation of Cu^+ using Cu^{2+} and Cr^{2+} Shaw and Espenson (24) have shown that Equation 48 describes the reaction

$$Cu^{2+} + Cr^{2+} = Cu^+ + Cr^{3+} \qquad (48)$$

between Cu^{2+} and Cr^{2+} when $[Cu^{2+}]_0 > [Cr^{2+}]_0$ and if the final concentration of Cu^+ is less than ca. 0.01 M. This is a convenient method of preparing Cu+ for subsequent studies. Considerable use of this reaction was made in order to study the reducing properties of Cu^+ where the presence of Cr^{3+} was considered more desirable than V^{3+}. Oxidation of Cr^{3+} to

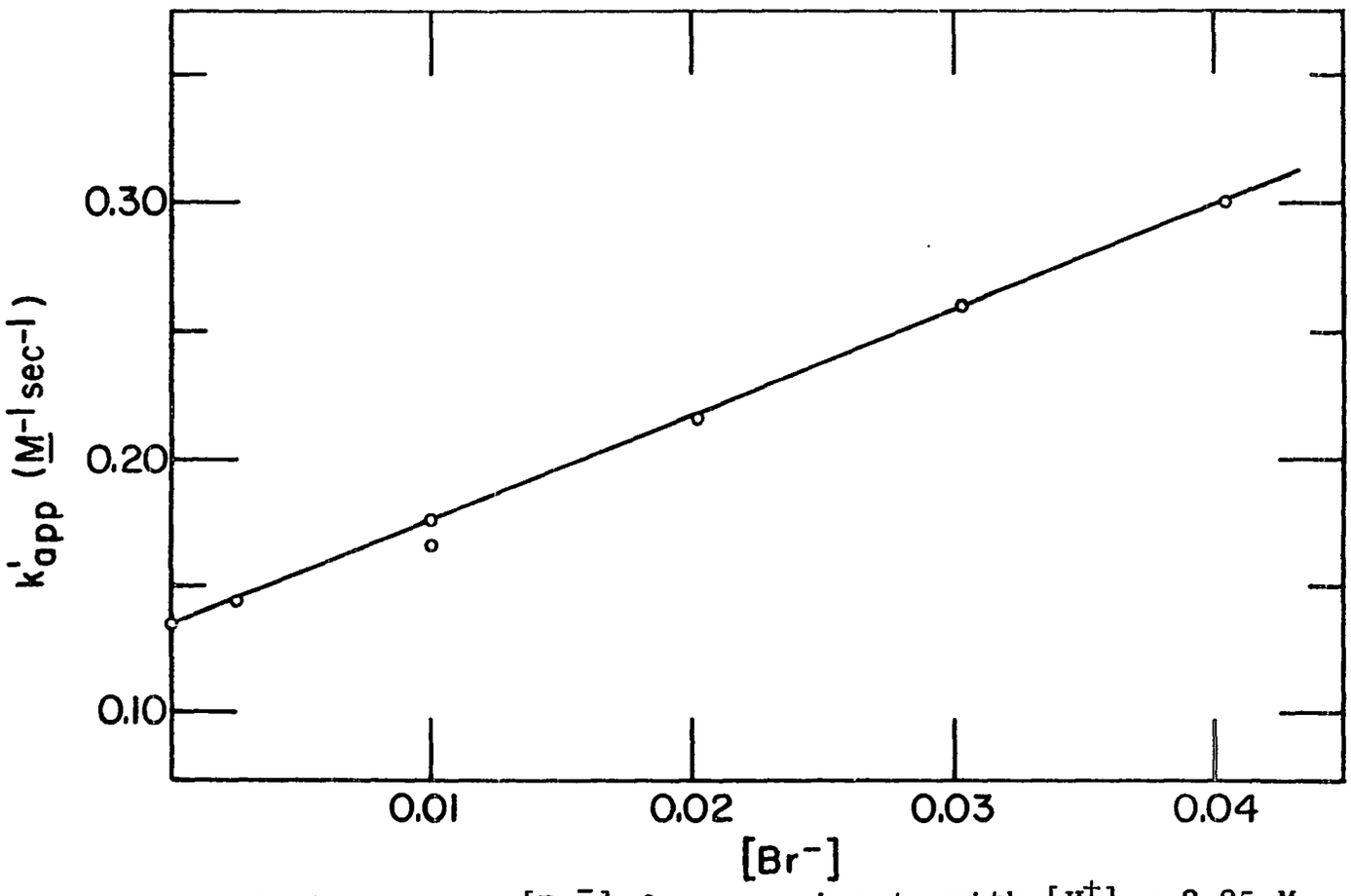


Figure 9. Plot of k'_{app} versus [Br^-] for experiments with [H^+] = 2.85 $\underline{M}$, μ = 3.00 $\underline{M}$, 25°

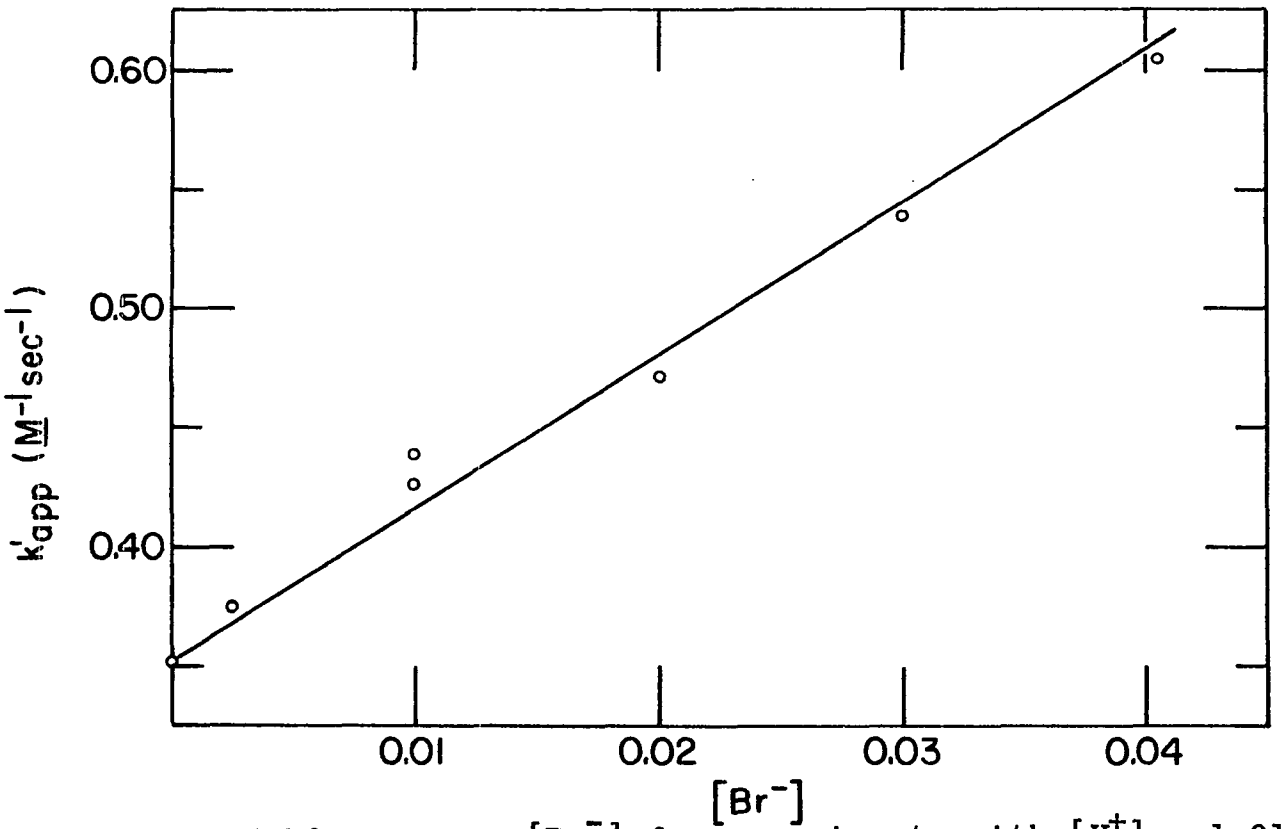


Figure 10. Plot of k'_{app} versus [Br^-] for experiments with [H^+] = 1.01 $\underline{M}$, μ = 3.00 $\underline{M}$, 25°

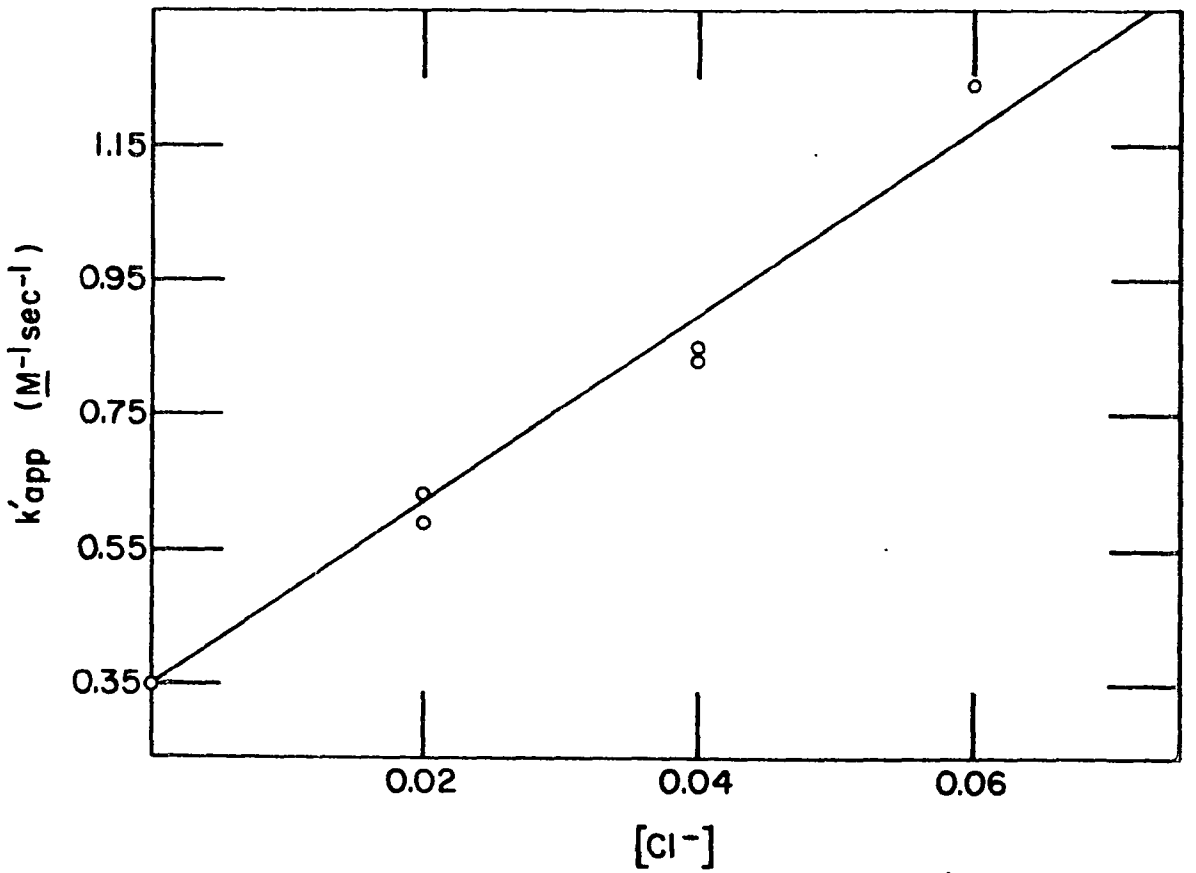


Figure 11. Plot of k'_{app} versus $[Cl^-]$ for experiments with $[H^+] = 1.01$, $\mu = 3.00$ M, 25°

higher oxidation states is very difficult whereas the possibility of oxidizing V^{3+} is not as unlikely. The reported (24) rate law is

$$-d[Cu^{2+}]/dt = (a+b/[H^+])[Cu^{2+}][Cr^{2+}] \qquad (49)$$

The acid dependent path carries the bulk of the reaction (78% at $[H^+]$ = 1.0 M) especially at low acid concentrations. This acid dependence allows the preparation of a wide range of Cu^+ concentrations in a reasonable length of time ($t \leq 30$ min). For all the rapid reactions it was necessary to calculate the appropriate time for the preparation of Cu^+. Because most of the studies using copper(I) were at different ionic strengths than the reported values ($a = 0.17\ M^{-1}\ sec^{-1}$, $b = 0.587\ sec^{-1}$ at $\mu = 1.00$ M), it was necessary to evaluate b at different ionic strength. These studies were at low $[H^+]$ and b was assumed to be the only term. Table 25 lists these results and a plot of log b vs. $\sqrt{\mu}$ is presented in Figure 12. The theoretical line predicted by the Debye-Hückel equation is shown in Figure 12.

Oxidation-Reduction Reactions of Copper(I)

Oxidation of Cu^+ with Fe(III)

Stoichiometry Iron(III) is rapidly reduced by copper(I), Equation 50, in aqueous perchloric acid solutions. The stoichiometry indicated by Equation 50 was confirmed by

$$Fe^{3+} + Cu^+ = Fe^{2+} + Cu^{2+} \qquad (50)$$

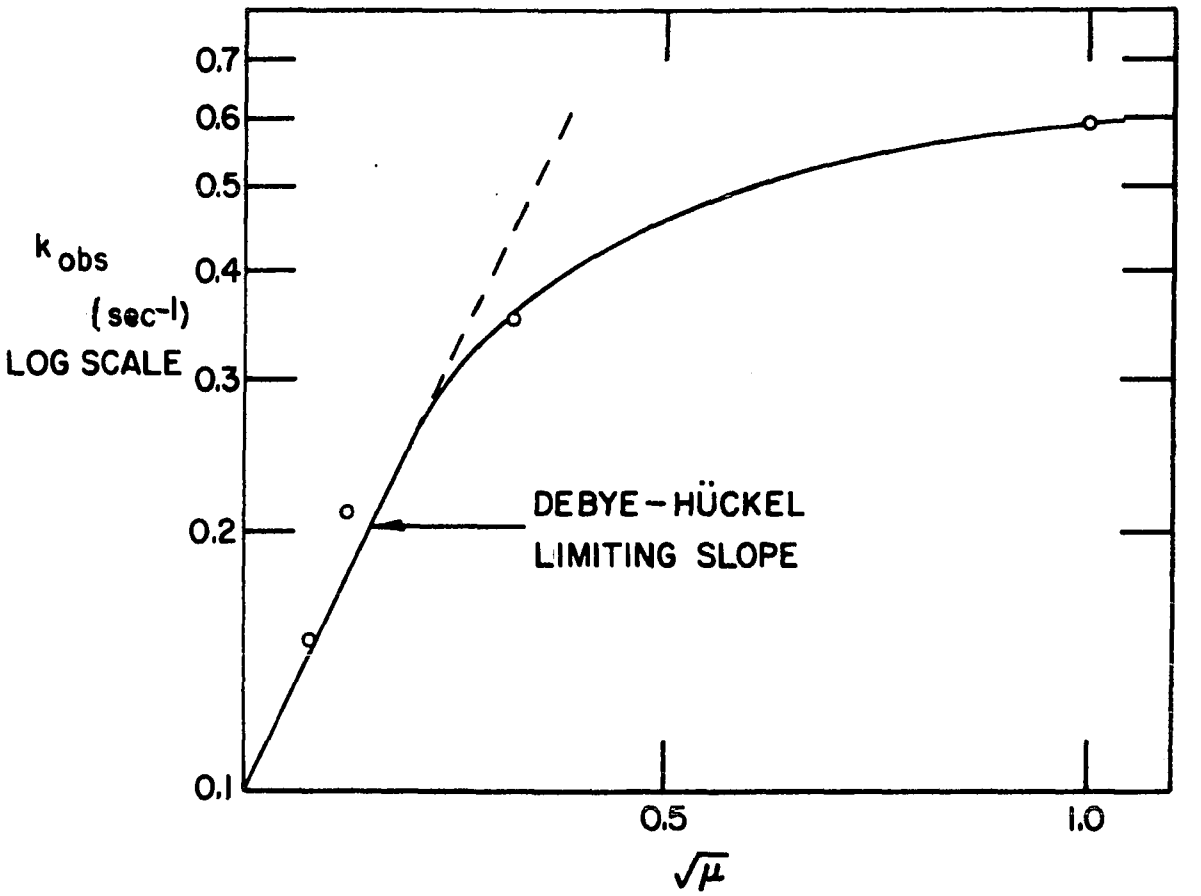


Figure 12. Plot of k_{obs} versus $\sqrt{\mu}$ for the reaction of Cu^{2+} and Cr^{2+}, 25°, the dashed line represents $2AZ_aZ_b$, the solid line represents the rate constant defined by $-d[Cu^{2+}]/dt = k_{obs}[Cr^{2+}][Cu^{2+}]/[H^+]$

Table 25. Rate constant k_{obs} as a function of μ

Conditions: 25.0°

μ	$[H^+]$	$10^3[Cu^{2+}]_0$	$10^4[Cr^{2+}]_0$	k_{obs} ($\underline{M}^{-1}$ sec^{-1})
0.1037	0.0503	2.51	4.72	8.01
0.1037	0.0223	2.51	4.72	16.8
0.0137	0.00489	2.01	4.72	43.5
0.00678	0.00328	0.694	2.36	45.7

two different methods. First, the reduction in the concentration of Fe^{3+} when insufficient Cu^+ was added was observed at 240 nm. At this wavelength iron(III) is the principal absorbing species although a slight correction was necessary for the copper(II) formed (Fe^{3+}, ε = 4230 $\underline{M}^{-1}$ cm^{-1}; Cu^{2+}, ε = 76; Cr^{3+}, ε = 5). The results are shown in Table 26. Second, the rate constant, k_{app}, under pseudo-first-order conditions, (concentration ratio 13:3) was substantially the same as under normal second-order conditions (ratio 2:1). All copper(I) solutions were prepared with chromium(II) perchlorate as described in the experimental section.

Rate law The simplest rate expression that adequately describes these data is given by Equation 51.

$$-d[Fe^{3+}]/dt = k_{app}[Cu^+][Fe^{3+}] = \{k'/[H^+]\}[Cu^+][Fe^{3+}] \quad (51)$$

This rate law was verified by an extensive variation of $[H^+]$, $[Cu^+]_0$ and $[Fe^{3+}]_0$. The major variation of $[H^+]$ was done at 1.6° because of the necessity for the slowest reaction

Table 26. Determination of stoichiometry of Fe(III) and Cu(I)

Exp.	$10^4[Fe^{3+}]_0$	$10^4[Cu^{2+}]_0$	$10^4[Cu^+]_0$[a]	ΔD[b]	$\Delta[Fe^{3+}]/[Cu^+]_0$
1	2.34	3.33	0.986	0.800	0.96
2	2.34	3.33	0.986	0.808	0.97
3	2.40	3.34	0.976	0.764	0.93
4	2.40	3.34	0.976	0.786	0.95

[a] $[Cu^+]_0$ was determined by analysis with RBr^{2+} at 253 nm.

[b] 2.0 cm cell.

conditions possible. The acid dissociation constant for Fe^{3+} is 3.81×10^{-4} M at 1.6° (66) so that $[Fe^{3+}] \gg [FeOH^{2+}]$ under all the conditions of this study. Copper(I) was varied from 0.66×10^{-4} to 6.05×10^{-4} M and the formal concentration of iron(III) from 0.275×10^{-4} to 11.3×10^{-4} F at 1.6°. At this temperature, hydrogen ion was varied from 0.075 M to 0.995 M.

The results of these experiments are tabulated in Table 27. The column of $[H^+]k_{app}$ is constant to within ±4.5% . The deviations appear random so that any term involving a direct path between the aquo species is $\leq$ 5% of the reaction at $[H^+]$ = 1.0 M. Figure 13 shows a plot of k_{app} versus $1/[H^+]$.

The rate constant, k', was independent of which reagent was in excess. Most of the experiments had $[Cu^+]_0 > [Fe^{3+}]_0$, however, experiments 3 and 10 had $[Fe^{3+}]_0 > [Cu^+]_0$. The rate constant was not dependent upon the wavelength used to monitor the reaction.

Table 27. Rate constants for the reaction of Cu(I) and Fe(III)

Conditions: 1.6°, μ = 1.00 M ($LiClO_4$)

Exp.	$[H^+]$	$10^4[Cu^+]_0$	$10^4[Fe^{3+}]_0$	$10^4[Cu^{2+}]_0$	λ(nm)	$10^{-4}k_{app}$ (M^{-1} sec^{-1})	$10^{-4}[H^+]$ k_{app} (sec^{-1})[a]
1	0.995	2.50	0.275	0.775	240	2.85	2.84
2	0.985	6.05	0.455	2.64	255	2.46	2.42
3	0.980	2.36	11.3	0.790	300	2.56	2.51
4	0.980	2.36	0.550	0.790	275	2.67	2.62
5	0.980	2.36	0.275	0.790	240	2.57	2.52
6	0.750	6.05	0.455	2.64	255	2.89	2.17
7	0.750	2.50	0.275	0.775	240	3.70	2.78
8	0.500	3.51	0.455	2.88	255	4.81	2.41
9	0.500	2.50	0.275	0.775	240	4.88	2.44
10	0.400	1.17	5.00	0.388	280	5.79	2.32
11	0.350	1.16	0.319	0.403	240	6.91	2.42
12	0.350	1.13	0.275	0.405	240	7.20	2.52
13	0.260	1.13	0.319	0.405	240	9.30	2.42
14	0.200	1.11	0.319	0.408	240	12.0	2.40
15	0.200	0.97	0.275	0.421	240	12.3	2.46
16	0.100	0.82	0.275	0.436	240	24.9	2.49
17	0.0750	0.66	0.275	0.453	240	32.1	2.41

[a]Average, $k' = (2.48 \pm .11) \times 10^4$ sec^{-1} at 1.6°

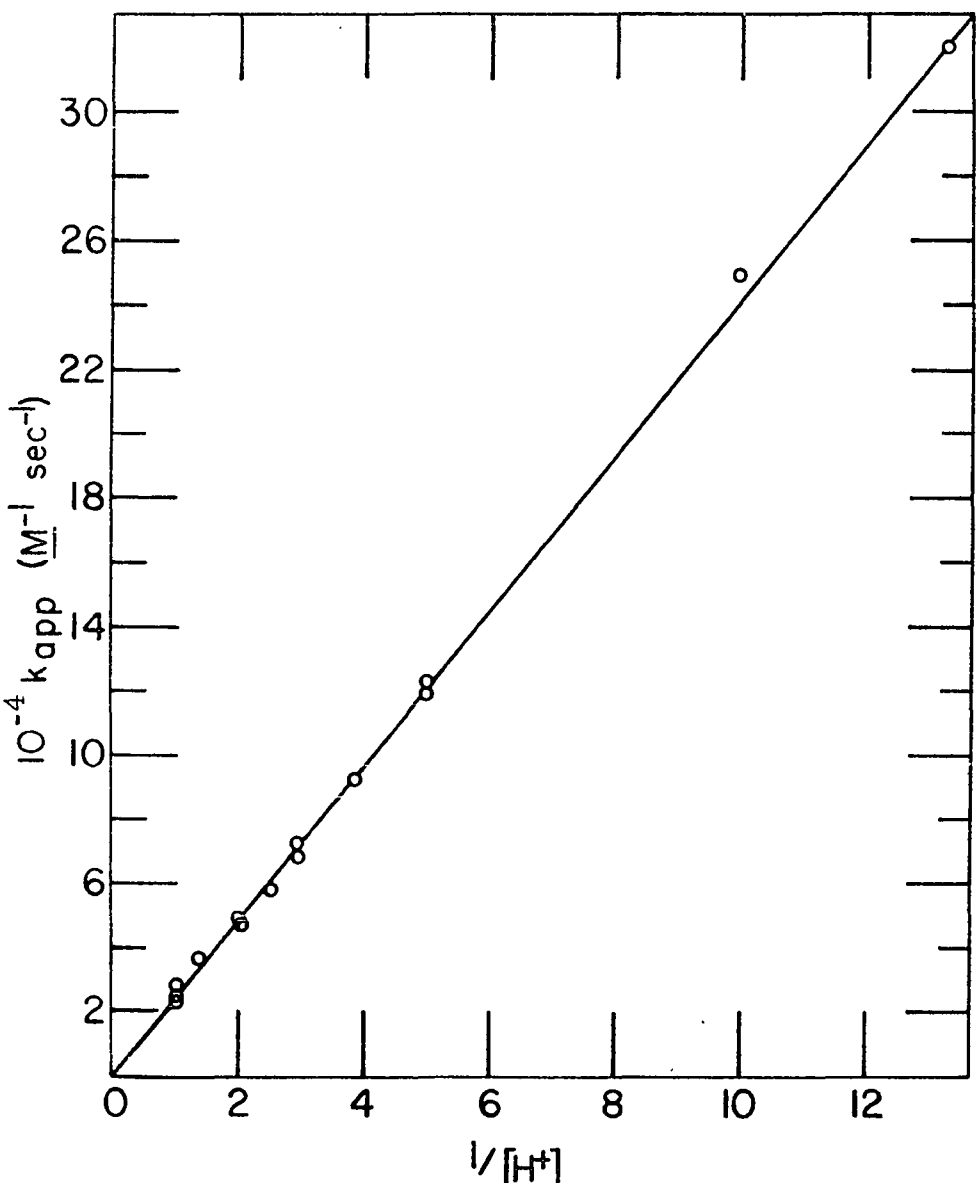


Figure 13. Plot of 10^{-4} k_{app} versus $1/[H^+]$ at 1.6°, μ = 1.00 $\underline{M}$ ($LiClO_4$) for the reaction of Cu^+ and Fe^{3+}

Temperature dependence The reaction was studied at 15.8° and 25.0° in order to obtain the activation parameters. The results are listed in Tables 28 and 29.

Effect of anions N_3^- and F^- The reaction between FeN_3^{2+} and Cu^+ is very rapid. Experiments attempting to measure this rate at 460 nm (FeN_3^{2+}, ε = 4400 $\underline{M}^{-1}$ cm^{-1}) were unsuccessful. From these experiments a lower limit of $k_{FeN_3} \geq 1 \times 10^8$ $\underline{M}^{-1}$ sec^{-1} can be calculated. The conditions for calculating this limit were as follows: $[Cu^+]_0 = 1.42 \times 10^{-5}$ $\underline{M}$, $[Cu^{2+}]_0 = 4.92 \times 10^{-4}$ $\underline{M}$ and $[FeN_3^{2+}]_0 = .44 \times 10^{-5}$ $\underline{M}$ [7] at μ = 1.00 $\underline{M}$ ($LiClO_4$). With a sweep speed of 2 msec/cm, the reaction was observed to be complete before the initial reading. The total time elapsed was approximated as 3.5 msec allowing for the time required for the mixed solution to flow from the mixing chamber to the observation point. It was established that a reaction had taken place by observing the absorbance of the individual solutions separately and then mixed.

The reaction between FeF^{2+} and Cu^+ was also observed to be very rapid. A lower limit of $k_{FeF} \geq 5 \times 10^6$ $\underline{M}^{-1}$ sec^{-1} was

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[7] The FeN_3^{2+} was formed in one flask of the stopped-flow apparatus under the following conditions: $[Fe^{3+}]_0 = 2.08 \times 10^{-5}$ $\underline{M}$, $[H^+]_0 = .147$ $\underline{M}$, $[NaN_3]_0 = .0986$ $\underline{M}$. The equilibrium constant for the formation of FeN_3^{2+} is given by $([FeN_3^{2+}][H^+])/([HN_3][Fe^{3+}]) = Q = .364$ at 1.6°, from Reference 38.

Table 28. Rate constants for the reaction of Cu(I) and Fe(III)

Conditions: 15.8°, μ = 1.00 M ($LiClO_4$), λ = 240 nm

Exp.	$[H^+]$	$10^4[Cu^+]_0$	$10^4[Fe^{3+}]_0$	$10^4[Cu^{2+}]_0$	$10^{-4}\ k_{app}$	$10^{-4}[H^+]k_{app}$ [a]
18	0.995	2.50	0.275	7.76	7.25	7.51
19	0.750	2.43	0.275	7.84	10.2	7.65
20	0.500	2.43	0.275	7.84	14.7	7.35
21	0.350	1.12	0.275	8.14	20.9	7.32
22	0.260	1.09	0.275	8.21	32.0	8.32
23	0.200	1.09	0.275	8.21	40.8	8.16

[a]Average, k' = (7.72 ± .35) x 10^4 sec^{-1} at 15.8°.

Table 29. Rate constants for the reaction of Cu(I) and Fe(III)

Conditions: 25.0°, μ = 1.00 M ($LiClO_4$), λ = 240 nm

Exp.	$[H^+]$	$10^4[Cu^+]_0$	$10^4[Fe^{3+}]_0$	$10^4[Cu^{2+}]_0$	$10^{-5}\ k_{app}$	$10^{-5}[H^+]k_{app}$ [a]
24	0.995	2.36	0.319	7.91	1.64	1.63
25	0.750	2.36	0.319	7.91	2.09	1.57
26	0.500	2.36	0.319	7.91	3.30	1.65
27	0.350	1.06	0.319	4.12	4.50	1.58
28	0.200	1.06	0.319	4.12	8.12	1.62

[a]Average, k' = (1.61 ± .03) x 10^5 sec^{-1} at 25.0°.

calculated. The initial concentrations were: $[Cu^+]_0 = 1.17 \times 10^{-4}$ M, $[Cu^{2+}]_0 = 8.90 \times 10^{-4}$ M and $[FeF^{2+}]_0 = 5.00 \times 10^{-5}$ M [8] at $\mu = 1.00$ M ($LiClO_4$). It was established that a reaction had taken place by observing the absorbance of the individual solutions separately and mixed.

Reactions of Cu^+ and Co(III) complexes

Stoichiometry The stoichiometry of the reaction of various cobalt(III) complexes and copper(I) has been determined. The stoichiometry was shown to be

$$Co(NH_3)_5X^{2+} + Cu^+ + 5H^+ = Co^{2+} + Cu^{2+} + 5NH_4^+ + X^- \quad (52)$$

where $X = Br^-$, Cl^-, N_3^-.

The stoichiometry was determined by analyzing the decrease in concentration of the oxidizing agent when it was brought into reaction with an insufficient quantity of Cu^+. No correction for the absorbance of the Cu^{2+} formed was necessary except for a minor one in the case of RCl^{2+} as shown in Table 30.

The $[Cu^+]_0$ was calculated from the amount of Cr^{2+} added in preparation of Cu^+ only in the case of RBr^{2+}. The Cr^{2+} concentration and total chromium concentration of stock solutions were determined as described in the experimental

[8] The FeF^{2+} was formed in one flask of the stopped-flow apparatus under the following conditions: $[Fe^{3+}]_0 = 1.11 \times 10^{-4}$ M, $[H^+]_0 = 5.01 \times 10^{-2}$ M, $[HF]_0 = 3.10 \times 10^{-3}$ M. The equilibrium constant for the formation of FeF^{2+} is given by $([FeF^{2+}][H^+])/([Fe^{3+}][HF]) = 166$ at 1.6° from Reference 67.

Table 30. Wavelengths and molar absorptivities used for determination of the stoichiometry of the reaction of $Co(NH_3)_5X^{2+}$ and Cu^+

λ(nm)	RX^{2+} (ε, $\underline{M}^{-1}$ cm^{-1})	Cu^{2+} (ε)	Cr^{3+} (ε)
253	RBr^{2+} (16700)	(18)	(4)
260	RCl^{2+} (1750)	(12)	(5)
302	RN_3^{2+} (7874)	(9)	(11)

section on chromium(II) and chromium(III) perchlorate. The deviation of these two methods was less than 1%. The results of the determination with RBr^{2+} verified that this method of analysis was valid as had been assumed.

In the stoichiometry determinations with RCl^{2+} and RN_3^{2+}, the $[Cu^+]_0$ concentration was determined by analysis with RBr^{2+} at 253 nm. Table 31 lists the results of these experiments.

Rate law Rate constants for the oxidation of copper(I) with eleven different cobalt(III) complexes have been determined. For each complex the reactant concentrations were varied over sizeable limits. These concentration variations and experimental conditions for the studies are tabulated in Table 32.

All of the experiments (~80) conducted on the oxidation of Cu^+ by cobalt(III) complexes suggested the following rate expression, Equation 53.

$$-d[Cu^+]/dt = k_{app}[Cu^+][Co(III)] \qquad (53)$$

Table 31. Determination of stoichiometry of RX^{2+} and Cu(I)

Exp.	$10^4[RX^{2+}]_0$	$10^4[Cu^{2+}]_0$	$10^4[Cu^+]_0$	ΔD[a]	$\Delta[RX^{2+}]/[Cu^+]_0$
RBr^{2+}					
1	0.472	1.71	0.408[b]	1.349	0.99
2	0.445	1.71	0.408	1.307	0.96
3	0.461	0.779	0.184	0.618	0.99
4	0.423	0.779	0.184	0.620	0.99
5	0.457	0.779	0.184	0.612	1.00
RCl^{2+}					
1	3.29	7.50	1.71[c]	0.584	1.01
2	3.28	7.50	1.71	0.586	1.01
RN_3^{2+}					
1	0.678	1.15	0.276[c]	0.438	1.01
2	0.788	1.48	0.341	0.546	1.02
3	0.783	1.48	0.341	0.557	1.04

[a] 2 cm cell

[b] $[Cu^+]_0$ was calculated from the amount of Cr^{2+} added in preparation of Cu^+.

[c] $[Cu^+]_0$ was determined by analysis with RBr^{2+} at 253 nm.

Hydrogen ion variations were done in all cases except for the reactions involving trans-$Co(en)_2Cl_2^+$, $RNCS^{2+}$ and $Co(en)_3^{3+}$. The only reaction dependent upon hydrogen ion concentrations was the reaction of Cu^+ and ROH_2^{3+}, all the others were notably insensitive to the hydrogen ion concentration.

Temperature dependence was investigated for the three halogen systems and the azido.

The rate constant, k_{app}, showed considerable variation in different reactions. The identity of the ligands bonded to the cobalt(III) ion markedly influenced the rate of reaction.

Table 32. Concentration variations and experimental conditions for the reactions of Cu^+ and Co(III) complexes, μ = 0.200 M ($LiClO_4$)

Complex	Temp.	$[H^+]$ (M)	$10^4[Cu^+]_0$ (M)	$10^4[Co(III)]_0$ (M)
trans-$Co(en)_2Cl_2^+$	25.0°	0.025	0.910	0.0935
$Co(NH_3)_5Br^{2+}$	1.6 -25.0°	0.025-0.199	0.0625- 1.98	0.105 - 0.930
$Co(NH_3)_5Cl^{2+}$	1.6 -25.0°	0.025-0.198	0.134 -12.0	0.107 - 2.53
cis-$Co(en)_2Cl_2^+$	25.0°	0.021-0.195	2.19 -12.8	0.210 - 1.99
$Co(NH_3)_5N_3^{2+}$	15.8-34.2°	0.021-0.195	2.11 -12.8	0.050 - 2.35
$Co(NH_3)_5F^{2+}$	15.0-35.0°	0.019-0.184	0.940 -10.0	12.0 -128.
trans-$Co(NH_3)_4(OH_2)CN^{2+}$	25.0°	0.039-0.181	5.04	37.7
$Co(NH_3)_5NCS^{2+}$	25.0°	0.192	5.04	0.700
$Co(NH_3)_5CN^{2+}$	25.0°	0.039-0.149	5.04	144.
$Co(NH_3)_5OH_2^{3+}$	25.0°	0.018-0.075	5.04	193.
$Co(en)_3^{3+}$	25.0°	0.016	10.1	274.

The rate varied from the rapid reaction of Cu^+ and trans-$Co(en)_2Cl_2^+$ ($k_{app} \geq 1 \times 10^7$ $\underline{M}^{-1}$ sec^{-1}) to the slow reaction of Cu^+ and $Co(en)_3^{3+}$ ($k_{app} \leq 1 \times 10^{-4}$ $\underline{M}^{-1}$ sec^{-1}). The rate constants are listed in the following tables with appropriate comments on each complex. The complexes are discussed in the arbitrary orders of most rapid to slowest reaction rate.

The reaction of trans-$Co(en)_2Cl_2^+$ is too rapid to be studied in a precise manner. However, under the conditions used for this experiment it was possible to establish a lower limit. Initial concentrations were: $[Cu^+]_0 = 9.10 \times 10^{-5}$ $\underline{M}$, $[Cu^{2+}]_0 = 3.09 \times 10^{-4}$ $\underline{M}$, $[Co(III)]_0 = 9.35 \times 10^{-6}$ $\underline{M}$. The calculated limit is $k_{app} \geq 1 \times 10^7$ $\underline{M}^{-1}$ sec^{-1}.

The reaction of $Co(NH_3)_5Br^{2+}$ and Cu^+ is very rapid but reasonable concentration variations were possible. The results are presented in Table 33. In these experiments Cu^+ was prepared from three independent sources. Copper(II) was reduced by either Cr^{2+} or V^{2+} as previously discussed. As a third source, Cu^+ was prepared from $Cu(ClO_4)_2$ by reduction with clean copper metal as described by Endicott and Taube (6,20). The temperature variation yielded the following activation parameters, $\Delta H^{\ddagger} = 3.82 \pm .48$ kcal/mole, $\Delta S^{\ddagger} = -19.9 \pm 1.7$eu.

The reaction of $Co(NH_3)_5Cl^{2+}$ and Cu^+ is rapid but extensive concentration variations were possible. The results are listed in Table 34. Copper(I) used in these runs was prepared by reducing Cu^{2+} with either Cr^{2+} or V^{2+}, or by equilibrating

Table 33. Rate constants for the reaction of Cu^{+} and RBr^{2+}

Conditions: μ = 0.200 M ($LiClO_4$), λ = 253 nm

Exp.	Temp.	$[H^+]$	$10^5[Cu^+]_0$	$10^5[Cu^{2+}]_0$	$10^5[RBr^{2+}]_0$	$10^{-5}k_{RBr}$ (M^{-1} sec^{-1})
1	1.6°	0.197	12.5	50.0	6.00	2.28[a]
2	1.6°	0.197	12.5	50.0	2.97	2.58
3	1.6°	0.199	2.23	30.8	1.33	2.25
4	15.8°	0.196	10.9	24.1	1.05	3.44
5	15.8°	0.199	2.32	30.8	1.34	3.65
6	25.0°	0.197	19.8	128.	3.42	4.18[b]
7	25.0°	0.025	9.10	30.9	3.27	4.43
8	25.0°	0.198	9.10	30.9	3.27	4.54
9	25.0°	0.192	4.18	127.	9.30	4.28[c]
10	25.0°	0.199	2.51	30.5	1.37	4.44
11	25.0°	0.198	1.34	51.7	2.28	4.55[d]
12	25.0°	0.199	0.625	16.4	2.45	4.82[d]

[a] 270 nm.

[b] Cu^+ prepared by V^{2+} reduction of Cu^{2+}.

[c] Cu^+ prepared using Cu^0 + Cu^{2+}, 274 nm.

[d] Cu^+ prepared using Cu^0 + Cu^{2+}.

Table 34. Rate constants for the reaction of Cu^{+} and RCl^{2+}

Conditions: μ = 0.200 M ($LiClO_4$), λ = 245 nm

Exp.	Temp.	$[H^+]$	$10^5[Cu^+]_0$	$10^5[Cu^{2+}]_0$	$10^5[RCl^{2+}]_0$	$10^{-4}k_{RCl}$ (M^{-1} sec^{-1})
1	1.6°	0.194	24.8	200.	4.74	2.25[a]
2	1.6°	0.194	24.8	200.	4.60	2.01[a,b]
3	1.6°	0.197	13.3	98.4	1.32	2.18
4	15.8°	0.194	48.5	153.	4.90	3.14[a]
5	15.8°	0.194	47.0	156.	3.37	3.16[a]
6	15.8°	0.194	45.8	158.	9.80	3.10[a,b]
7	25.0°	0.171	128.	640.	25.3	4.75[a,c]
8	25.0°	0.188	56.5	243.	4.74	4.84[a]
9	25.0°	0.190	47.0	153.	2.10	4.75
10	25.0°	0.195	23.2	79.5	2.10	4.68
11	25.0°	0.197	19.8	127.	1.30	5.16[d,e]
12	25.0°	0.025	9.10	31.0	1.07	4.85[e]
13	25.0°	0.198	9.10	31.0	1.07	5.11[e]
14	25.0°	0.192	4.18	427.	8.25	4.69[f]
15	25.0°	0.198	1.34	51.5	2.32	5.07[f]

[a] Cr^{2+} prepared electrolytically.

[b] 260 nm.

[c] 280 nm.

[d] Cu^{+} prepared by reduction of Cu^{2+} with V^{2+}.

[e] 230 nm.

[f] Cu^{+} prepared using Cu^{0} + Cu^{2+}.

Cu^{2+} solutions over clean copper shavings. The activation parameters are $\Delta H^{\ddagger}$ = 5.52 ± 0.37 kcal/mole and $\Delta S^{\ddagger}$ = - 18.6 ± 1.3 eu. The reaction of Cu^{+} and RCl^{2+} was also studied in media of 1.00 M and 3.00 M maintained with lithium perchlorate. These results are listed in Table 35.

The results for cis-$Co(en)_2Cl_2^{+}$ and Cu^{+} are presented in Table 36.

The reaction of $Co(NH_3)_5N_3^{2+}$ and Cu^{+} is moderately rapid. The rate and conditions were ideal for collecting very precise data. Extensive concentration variations were carried out. The data are presented in Table 37. The possibility of Cu^{+} reacting with free HN_3 during the course of an experiment was investigated. Experiment number 12 had hydrazoic acid present initially, $[NH_3]_0 = 5.0 \times 10^{-4}$ M, $[Cu^{+}]_0 = 2.11 \times 10^{-4}$ M, $[RN_3^{2+}]_0 = 1.48 \times 10^{-5}$ M. Under these initial conditions, if Cu^{+} reacted with free N_3^{-} or HN_3 at a rate comparable to the oxidation-reduction reaction, the observed rate constant would be altered considerably. This definitely was not observed. The transmittance trace after the completion of a reaction (~5 sec) was extremely stable up to 4 times (~ 20 sec) the time necessary for completion of the reaction. The activation parameters are $\Delta H^{\ddagger}$ = 5.32 ± 0.26 kcal/mole, $\Delta S^{\ddagger}$ = -26.2 ± 0.9 eu.

Table 35. Rate constants for the reaction of Cu^+ and RCl^{2+}

Conditions: 25°, μ = 1.00 M and 3.00 M ($LiClO_4$)

Exp.	μ	$[H^+]$	$10^5[Cu^+]_0$	$10^5[RCl^{2+}]_0$	$10^{-4}k$ (M^{-1} sec^{-1})
1	1.00	1.00	9.05	1.00	7.87
2	1.00	0.500	9.05	1.00	7.37
3	1.00	0.250	9.05	1.00	7.37
4	1.00	0.250	9.60	1.00	7.77
5	1.00	0.100	9.60	1.00	7.62
6	3.00	2.58	11.7	1.07	11.5
7	3.00	2.58	11.7	1.07	11.0

Complications arose in the attempt to study the reaction of $Co(NH_3)_5NCS^{2+}$ and Cu^+ because of the precipitation of CuSCN ($Cu^+ + NCS^- = CuSCN(s)$)[9]. The precipitate began to form immediately upon mixing (mixing time ~8 sec) and continued to form during the time of reaction. Under the conditions of the experiment the solution was observed to form a finely divided precipitate that did not coalesce. The initial concentrations were $[Cu^+]_0 = 5.04 \times 10^{-4}$ M and $[RNCS^{2+}]_0 = 7.00 \times 10^{-5}$ M. The absorbance trace began to increase immediately after mixing and continued to increase for ~ 5000 sec. The expected behavior was a decrease in absorbance due to the disappearance of Cu^+. No claim of accurate rate measurements can be made; however, it seems reasonable that

[9]The solubility product is $K = 4.8 \times 10^{-15}$ M at 25° according to Reference 68.

Table 36. Rate constants for the reaction of Cu^+ and cis-$Co(en)_2Cl_2^+$

Conditions: μ = 0.200 M ($LiClO_4$), 25.0°

Exp.	λ(nm)	$[H^+]$	$10^4[Cu^+]_0$	$10^4[Cu^{2+}]_0$	$10^4[Co(III)]_0$	10^{-4} k_{cis} (M^{-1} sec^{-1})[a]
1	275	0.171	12.8	64.1	1.99	2.17
2	265	0.171	12.8	64.1	1.00	2.22
3	250	0.188	5.65	24.3	0.477	2.10
4	245	0.190	4.81	15.2	0.477	1.98
5	255	0.021	4.51	8.00	0.502	2.05
6	240	0.195	2.19	8.05	0.210	2.27

[a] Cr^{2+} was prepared electrolytically

Table 37. Rate constants for the reaction of Cu^+ and RN_3^{2+}

Conditions: μ = 0.200 M ($LiClO_4$), λ = 330

Exp.	Temp.	$[H^+]$	$10^4[Cu^+]_0$	$10^4[Cu^{2+}]_0$	$10^4[RN_3^{2+}]_0$	10 $k_{RN_3}^{-3}$ (M^{-1} sec^{-1})[a]
1	15.8°	0.189	8.00	27.8	0.250	1.05
2	15.8°	0.194	4.87	15.2	0.250	1.12
3	15.8°	0.194	4.69	15.6	0.0500	1.02[b]
4	25.0°	0.171	12.8	54.2	1.00	1.51[c]
5	25.0°	0.179	10.7	43.3	2.35	1.52[d]

[a] Cr^{2+} prepared electrolytically.

[b] 302 mn.

[c] 355 nm.

[d] 370 nm.

Table 37. (Continued)

Exp.	Temp.	$[H^+]$	$10^4[Cu^+]_0$	$10^4[Cu^{2+}]_0$	$10^4[RN_3^{2+}]_0$	$10\ k^{-3}_{RN_3}$ ($\underline{M}^{-1}$ sec^{-1})[a]
6	25.0°	0.179	10.7	43.3	0.500	1.52[e]
7	25.0°	0.179	10.7	43.3	0.250	1.51
8	25.0°	0.179	10.0	55.0	0.500	1.49[e]
9	25.0°	0.021	4.51	20.5	0.500	1.50[e]
10	25.0°	0.195	2.25	20.9	0.500	1.46[e]
11	25.0°	0.195	2.21	20.9	0.104	1.57[f]
12	25.0°	0.195	2.11	21.0	0.148	1.46[f,g]
13	34.2°	0.193	4.96	7.55	0.250	1.93
14	34.2°	0.193	2.78	12.5	0.200	2.08
15	34.2°	0.193	2.78	12.5	0.0500	1.95[b]

[e] 340 nm.

[f] 310 nm.

[g] $[HN_3]_0 = 5.0 \times 10^{-4}$ $\underline{M}$.

an estimate of the order of magnitude can be made. The observed rate constant is thus 1-3 $\underline{M}^{-1}$ sec^{-1}.

The results for $Co(NH_3)_5F^{2+}$ + Cu^+ are presented in Table 38. Extensive concentration variations were done with $[Cu^+]_0$, $[RF^{2+}]_0$ and $[H^+]$. The rate constant was observed to be independent of the hydrogen ion concentration. This result establishes two independent conclusions. First, the oxidation-reduction reaction is not affected by the acid concentration. Second, under the conditions of these experiments, the aquation rate of RF^{2+} is of no importance. The rate of water substitution (Equation 54) is given by Equation 55

$$Co(NH_3)_5F^{2+} + H_2O + H^+ = Co(NH_3)_5H_2O^{3+} + HF \quad (54)$$

$$-d[RF^{2+}]/dt = k_{app}[RF^{2+}] \quad (55)$$

where $k_{app} = 8.7 \times 10^{-8} + 1.07 \times 10^{-4}\ [H^+]$. Experiment number 8 has conditions that would favor competition by aquation if it is ever important. This experiment was complete in approximately 20 min which at $[H^+] = 0.180$ $\underline{M}$ means that 2.3% of the complex would be lost to aquation if aquation were the only path operating. With the oxidation-reduction reaction competing, the amount of complex lost to the aquation path would be even smaller. Another point of evidence is experiment number 5. The hydrogen ion concentration is reduced ~10 fold and the reaction is complete in ~7 min. For this experiment aquation could not possibly compete. The observed rate constant is

Table 38. Rate constants for the reaction of Cu^{+} and RF^{2+}

Conditions: μ = 0.200 M ($LiClO_4$), λ = 265 nm

Exp.	Temp.	$[H^+]$	$10^3[Cu^+]_0$	$10^3[Cu^{2+}]_0$	$10^3[RF^{2+}]_0$	k_{RF} (M^{-1} sec^{-1})
1	15.0°	0.159	0.504	1.56	9.67	0.504
2	15.0°	0.171	0.330	1.73	6.10	0.529
3	15.0°	0.184	0.237	1.18	3.05	0.480[a]
4	25.0°	0.141	1.00	3.12	12.8	1.06[b]
5	25.0°	0.0187	0.50	1.56	12.8	1.09
6	25.0°	0.171	0.494	1.57	6.10	1.11
7	25.0°	0.180	0.380	1.68	3.05	1.12
8	25.0°	0.180	0.360	1.70	3.05	1.11
9	25.0°	0.0374	0.220	1.44	3.84	1.10[c]
10	25.0°	0.0187	0.200	1.46	3.84	1.14[c]
11	25.0°	0.0187	0.094	0.322	1.20	1.13[c]
12	35.0°	0.159	0.504	1.56	9.94	2.33
13	35.0°	0.171	0.504	1.56	6.10	2.10
14	35.0°	0.184	0.237	1.82	3.05	2.30[d]

[a] 260 nm.

[b] 285 nm.

[c] 255 nm.

[d] 250 nm.

substantially the same in both experiments showing that aquation was unimportant in experiment number 8. The activation parameters are $\Delta H^{\ddagger} = 12.3 \pm 0.3$ kcal/mole, $\Delta S^{\ddagger} = -17.2 \pm 0.9$ eu.

A limited study of the reaction of <u>trans</u>-$Co(NH_3)_4(OH_2)CN^{2+}$ and Cu^+ was conducted. No hydrogen ion dependence was observed. The results are shown in Table 39.

Table 39. Rate constants for the reaction of Cu^+ and <u>trans</u>-$CoA_4(OH_2)CN^{2+}$

Conditions: $\mu = 0.200$ <u>M</u> ($LiClO_4$), 25.0°, $\lambda = 265$ nm

Exp.	$[H^+]$	$10^3[Cu^+]_0$	$10^3[Cu^{2+}]_0$	$10^3[Co(III)]_0$	$k(\underline{M}^{-1}\ sec^{-1})$
1	0.0389	0.504	1.56	3.77	0.460
2	0.181	0.504	1.56	3.77	0.449
3	0.181	0.504	1.56	3.77	0.487

The reaction of $Co(NH_3)_5CN^{2+}$ and Cu^+ is very slow, thus only a limited study was conducted. The results are listed in Table 40.

The reaction of $Co(NH_3)_5OH_2^{3+}$ and Cu^+ is very slow, and it was thus difficult to obtain precise data. The results are tabulated in Table 41. Because of the low rate, a limited study of the hydrogen ion dependence was conducted. It was established that the rate was definitely affected by hydrogen ion. The simplest interpretation for the hydrogen ion dependence is

$$k_{app} = a + b/[H^+] \qquad (56)$$

Table 40. Rate constants for the reaction of Cu^+ and RCN^{2+}

Conditions: μ = 0.200 M ($LiClO_4$), 25.0°, λ = 265 nm

Exp.	$[H^+]$	$10^3[Cu^+]_0$	$10^3[Cu^{2+}]_0$	$10^3[RCN^{2+}]_0$	$10^3 k_{RCN}$ ($M^{-1}sec^{-1}$)
1	0.149	0.504	1.56	14.4	3.5
2	0.039	0.504	1.56	14.4	3.1
3	0.039	0.504	1.56	14.4	3.2

Table 41. Rate constants for the reaction of Cu^+ and ROH_2^{3+}

Conditions: μ = 0.200 M ($LiClO_4$), 25.0°, λ = 265

Exp.	$[H^+]_{av}$	$10^3[Cu^+]_0$	$10^3[Cu^{2+}]_0$	$10^3[ROH_2^{3+}]_0$	$10^3 k_{ROH_2}$ ($M^{-1}sec^{-1}$)[a]
1	0.0747	0.504	1.56	19.3	3.73
2	0.0747	0.504	1.56	19.3	4.18
3	0.0378	0.504	1.56	19.3	6.80
4	0.0378	0.504	1.56	19.3	7.80
5	0.0183	0.504	1.56	19.3	13.2
6	0.0183	0.504	1.56	19.3	13.4

[a]Assuming $k_{ROH_2} = a+b/[H^+]$; k_{calc} = 4.0 x 10^{-3} M^{-1} sec^{-1}, at $[H^+]$ = 0.0747 M; k_{calc} = 7.0 x 10^{-3} M^{-1} sec^{-1} at $[H^+]$ = 0.0378 M; k_{calc} = 13.6 x 10^{-3} M^{-1} sec^{-1} at $[H^+]$ = 0.0183 M.

The data fit this expression reasonably well with a = 9.8 x 10^{-4} M^{-1} sec^{-1}, b = 2.3 x 10^{-4} sec^{-1} at 25°.

The reaction of $Co(en)_3^{2+}$ and Cu^+ is slow and only a limited study was possible. One experiment with the following conditions was done, $[Cu^+]_0$ = 1.01 x 10^{-4} M, $[Co(III)]_0$ = 2.74 x 10^{-2} M at 25°, μ = 0.200 M. On the basis of this

experiment the rate constant, $k \leq 4 \times 10^{-4}$ $\underline{M}^{-1}$ sec^{-1} was evaluated. This rate constant is best regarded as an upper limit because of the unknown rate of disproportionation and rate of oxidation of Cu^+ by ClO_4^-.

A summary of the rate constants found in these studies is presented in Table 42. The activation parameters are summarized in Table 43.

Ionic strength dependence The kinetics of the reaction of Cu^+ and RBr^{2+} or RCl^{2+} (Equation 57) were examined

$$Cu^+ + RBr^{2+} \xrightarrow{k} Cu(II) + Co(II) \qquad (57)$$

as a function of ionic strength. The second-order rate constant, k, should depend upon ionic strength as indicated by Equation 58,

$$\log k/k^0 = 2AZ_aZ_b \sqrt{\mu} \qquad (58)$$

where A = 0.509 at 25°, Z_a = charge on A, $\mu = 1/2 \sum_i m_i Z_i^2$, k^0 = the rate constant at $\mu = 0$. A plot of log k_{obs} versus $\sqrt{\mu}$ has a slope of $2AZ_aZ_b$, 2.04. Such behavior is only to be expected at concentrations where $\mu \leq 0.04$. The only anion present in the reaction mixture was ClO_4^-.

Copper(I) was produced by reacting copper(II) with chromium(II) and allowing sufficient time for the formation of Cu(I). For the ionic strength dependence, Cu(I) was always the reactant in excess and its concentration was determined (four to six times) by reaction with RBr^{2+}. A fresh stock solution

Table 42. Summary of the rates of reduction of Co(III) complexes by Cu^+

Conditions: μ = 0.200 M ($LiClO_4$), units M, sec.

Complex	1.6°	15.0°	25.0°	35.0°
trans-$Co(en)_2Cl_2^+$			$\geq 1\times10^{7}$	
$Co(NH_3)_5Br^{2+}$	$(2.37\pm.14)\times10^{5}$	$(3.55\pm .10)\times10^{5}$[a]	$(4.46\pm.15)\times10^{5}$	
$Co(NH_3)_5Cl^{2+}$	$(2.15\pm.09)\times10^{4}$	$(3.13\pm .02)\times10^{4}$[a]	$(4.88\pm.17)\times10^{4}$	
cis - $Co(en)_2Cl_2^+$			$(2.13\pm.09)\times10^{4}$	
$Co(NH_3)_5N_3^{2+}$		$(1.06\pm0.04)\times10^{3}$[a]	$(1.50\pm.02)\times10^{3}$	$(1.99\pm.06)\times10^{3}$[b]
$Co(NH_3)_5NCS^{2+}$			1-3	
$Co(NH)_5F^{2+}$		(0.506 ± 0.017)	$(1.11\pm.02)$	$(2.24\pm.10)$
trans-$Co(NH_3)_4(OH_2)CN^{2+}$			$(4.65\pm.11)\times10^{-1}$	
$Co(NH_3)_5CN^{2+}$			$(3.3\ \pm0.2)\times10^{-3}$	
$Co(NH_3)_5OH_2^{3+}$			$(9.8\ \pm4.0)\times10^{-4}$	
$Co(NH_3)_5OH^{2+}$			$(2.3\ \pm0.2)\times10^{-4}$[c]	
$Co(en)_3^{3+}$			$\leq 4\times10^{-4}$	

[a] 15.8°.

[b] 34.2°.

[c] Value is for b, where $b = k_{OH}K_a$

Table 43. Summary of the activation parameters for the reduction of Co(III) complexes by Cu^{+}

Conditions: μ = 0.200 M ($LiClO_4$)		
Complex	$\Delta H^{\ddagger}$ (kcal/mole)	$\Delta S^{\ddagger}$ (cal/mole-deg)
$Co(NH_3)_5Br^{2+}$	3.82±0.48	-19.9±1.7
$Co(NH_3)_5Cl^{2+}$	5.52±0.37	-18.6±1.3
$Co(NH_3)_5N_3^{2+}$	5.32±0.26	-26.2±0.9
$Co(NH_3)_5F^{2+}$	12.3 ±0.3	-17.2±0.9

of RBr^{2+} and RCl^{2+} was prepared for each experiment and analyzed. If the ratio of reactants was $\geq$ 10, the molar absorptivity at 253 nm, ε = 16700 M^{-1} cm^{-1} for RBr^{2+} or at 229 nm, ε = 17800 M^{-1} cm^{-1} for RCl^{2+} was used. If the ratio of reactants was < 10 then the cobalt(III) complex was analyzed also, using reduction with an excess of Cr^{2+} and a standard Co(II) analysis. The second-order rate constants as a function of ionic strength are tabulated in Table 44 (RBr^{2+}) and Table 45 (RCl^{2+}). Figures 14 and 15 illustrate the function dependence of the rate constant upon ionic strength in a plot of log k_{obs} versus $\sqrt{\mu}$. The solid line represents the values predicted by the Debye-Hückel equation, Equation 58, using the value of 2.04 for $2AZ_aZ_b$.

Table 44. The dependence of k_{RBr} on μ

Conditions: 25.0°, $LiClO_4$

Exp.	$10^3\ \mu$	$10^4[Cu^+]_0$	$10^4[Cu^{2+}]_0$	$10^5[RBr^{2+}]_0$	$10^{-5}k_{RBr}$ ($\underline{M}^{-1}sec^{-1}$)
1	0.934	0.322	0.870	0.800	1.74
2	0.935	0.319	0.870	0.725	1.50
3	4.23	0.975	3.02	0.970	2.03
4	9.57	0.890	3.11	1.02	1.95
5	10.0	0.985	3.01	1.00	1.95
6	22.5	0.925	3.06	0.890	2.74
7	39.6	0.890	3.11	1.02	2.70
8	40.0	0.955	3.04	1.25	3.00
9	62.5	0.925	3.07	1.39	3.22
10	100.0	0.970	3.02	1.23	4.13
11	200.0	0.910	3.09	3.27	4.43[a]
12	200.0	0.910	3.09	3.27	4.54[b]

[a] $[H^+]$ = 0.0989 $\underline{M}$.

[b] $[H^+]$ = 0.0125 $\underline{M}$.

Table 45. The dependence of k_{RCl} on μ

Conditions: 25.0°, $LiClO_4$

Exp.	$10^3\ \mu$	$10^4[Cu^+]_0$	$10^4[Cu^{2+}]_0$	$10^5[RCl^{2+}]_0$	$10^{-4}k_{RCl}$ ($\underline{M}^{-1}\ sec^{-1}$)
1	0.936	0.319	0.870	0.765	1.49
2	0.936	0.322	0.870	0.735	1.52
3	4.23	0.975	3.02	1.11	1.84
4	9.57	0.950	3.05	1.12	2.09
5	10.0	0.985	3.01	1.07	2.33
6	22.5	0.925	3.07	1.09	2.86
7	39.6	0.950	3.05	1.12	2.80
8	40.0	0.955	3.04	1.10	2.82
9	62.5	0.925	3.07	1.09	4.08
10	100.0	0.970	3.02	1.07	3.79

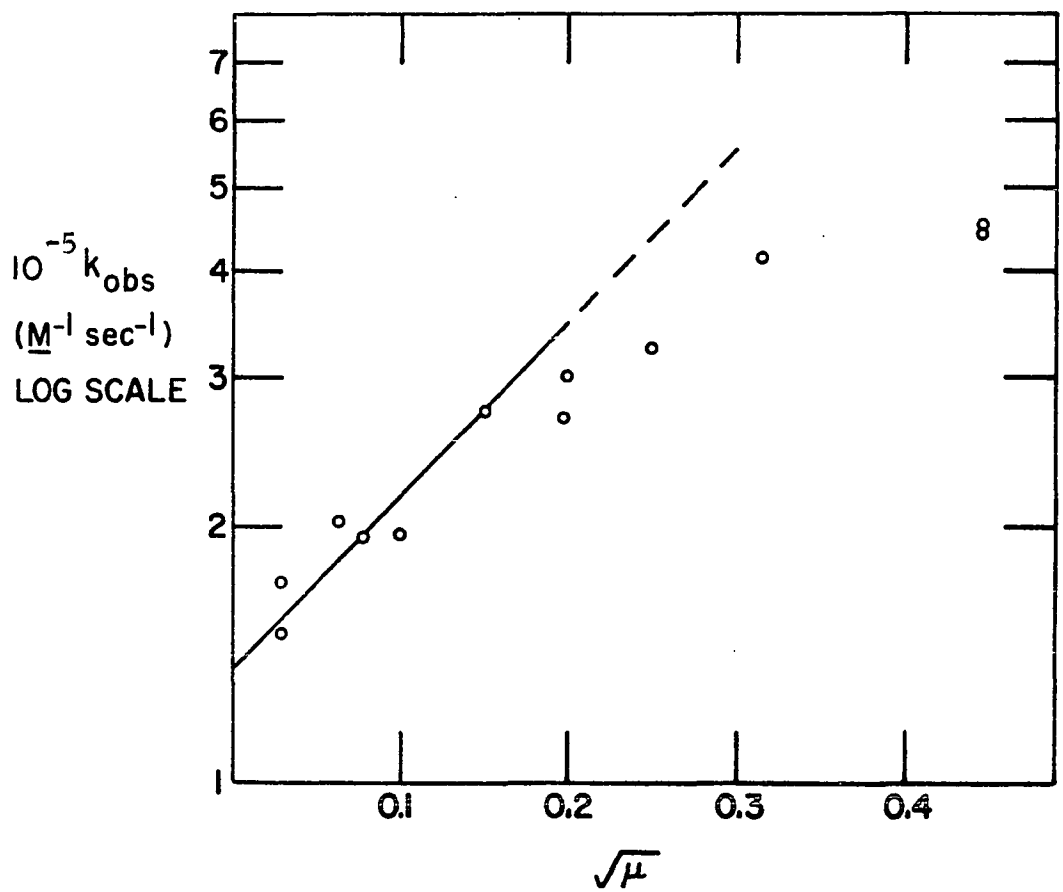


Figure 14. Plot of $10^{-5} k_{obs}$ versus $\sqrt{\mu}$ for the reaction of RBr^{2+} and Cu^{+}, 25°, line represents $2AZ_aZ_b$

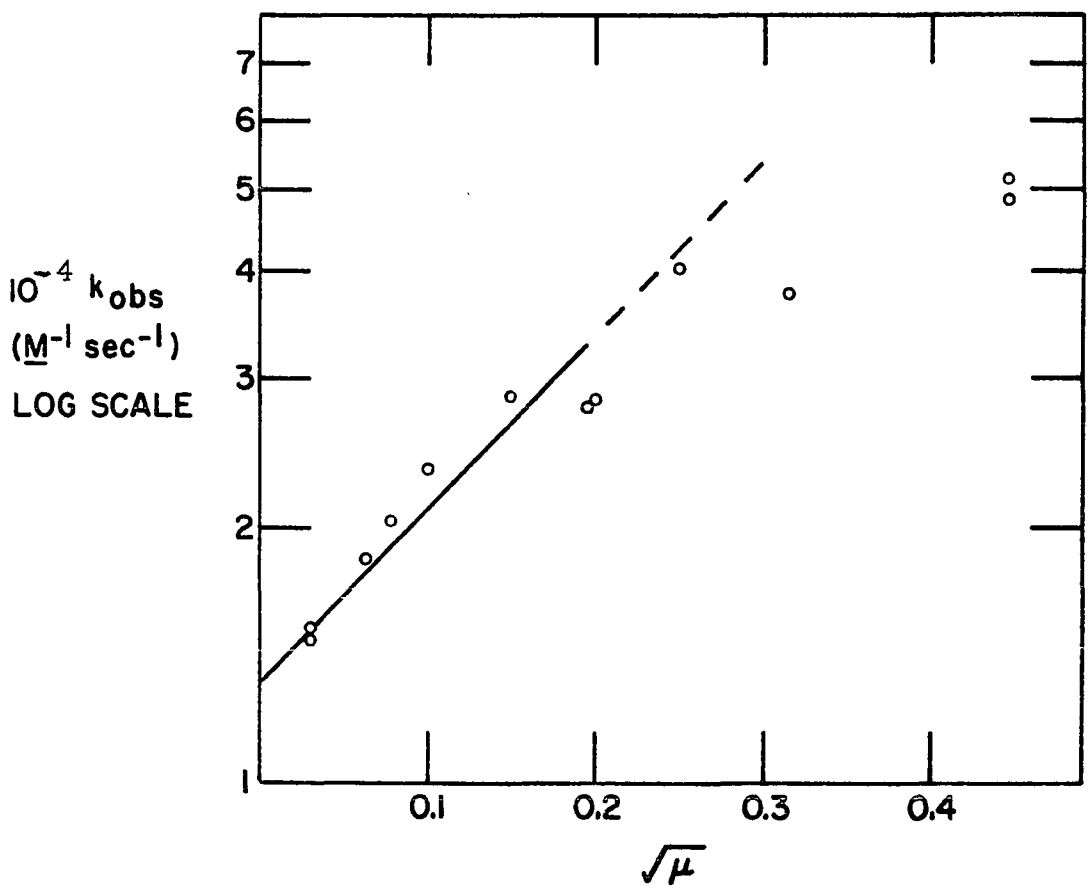


Figure 15. Plot of $10^{-4}k_{obs}$ versus $\sqrt{\mu}$ for the reaction of RCl^{2+} and Cu^{+}, 25°, line represents $2AZ_aZ_b$

Table 45. (Continued)

Exp.	$10^3\ \mu$	$10^4[Cu^+]_0$	$10^4[Cu^{2+}]_0$	$10^5[RCl^{2+}]_0$	$10^{-4}k_{RCl}$ ($\underline{M}^{-1}$ sec^{-1})
11	200.0	0.910	3.09	1.07	4.85[a]
12	200.0	0.910	3.09	1.07	5.11[b]

[a] $[H^+] = 0.0989$ $\underline{M}$.

[b] $[H^+] = 0.0125$ $\underline{M}$.

Vanadium(II) and Chlorochromium(III) Reaction

Reaction scheme The processes under consideration represent a reasonably complicated set of reactions. The rate measurements made on the various reactions are related to one another. To clarify the presentation of results, a skeleton mechanism will first be set forth, and the data presented within this general framework. Consider the two step sequence shown as follows:

$$CrCl^{2+} + V^{2+} \underset{2}{\overset{1}{\rightleftharpoons}} Cr^{2+} + Cl^- + V^{3+} \qquad (59)$$

$$Cr^{2+} + V^{3+} \underset{4}{\overset{3}{\rightleftharpoons}} Cr^{3+} + V^{2+} \qquad (60)$$

$$\text{Net:}\quad CrCl^{2+} = Cr^{3+} + Cl^- \qquad (61)$$

The rate constants shown are pseudo constants referring to constant $[H^+]$, and each of them shows a further dependence upon $[H^+]$.

Several independent measurements of these processes have been made: (1) a study of the reaction of Cr(II) and V(III) in perchlorate solution, evaluating k_3; (2) a study of the reaction of Cr(II) and V(III) in solutions containing various concentrations of chloride and perchlorate ions from which k_2 can be computed; (3) a study of the reaction of $CrCl^{2+}$ and V^{2+} under conditions where the first step is rate-determining, thereby evaluating k_1; (4) a study of the reaction of $CrCl^{2+}$ and V^{2+} under conditions where the rate constants k_2 and k_3, in addition to k_1, are important; (5) an evaluation of the equilibrium quotient for the over-all formation of $CrCl^{2+}$, and thereby an independent value for k_3/k_4.

Reaction of chromium(II) and vanadium(III) The electron-transfer reaction between the aquo ions was studied previously in perchlorate solution (34) although in a rather different medium (μ = 0.65 M previously, 2.50 M here). The rate law at constant $[H^+]$ was the expected mixed-second-order equation (Equation 62) in which the apparent rate constant k_3 is a function of $[H^+]$. These results are listed in Table 46. The same expression was also found to hold at constant $[H^+]$,

$$-d[Cr^{2+}]/dt = k_3[V^{3+}][Cr^{2+}] \qquad (62)$$

at ionic strength 2.50 M.

It was noted in the original study (34) of the reaction in perchlorate solution that there was a slight increase in

Table 46. Rate constants for the reaction of Cr^{2+} and V^{3+}

Conditions: 25.0°, μ = 2.50 M perchlorate solution

Exp.	$[H^+]$	$10^2[Cr^{2+}]_0$	$10^2[V^{3+}]_0$	λ(nm)	k_{obs}(M^{-1} sec^{-1})
1	1.00	7.12	0.719	574	0.970
2	1.00	3.51	0.722	574	0.930
3	1.00	3.51	0.722	574	0.930
4	1.00	2.00	0.952	574	0.886
5	1.00	1.53	0.942	574	0.860
6	1.00	0.526	5.41	574	1.04
7	1.00	0.526	5.41	574	1.06
8	1.00	0.531	5.41	574	1.04
9	1.00	0.900	2.03	574	1.03
10	0.500	2.10	0.988	574	1.82
11	0.500	1.00	2.10	574	1.81
12	0.200	0.330	0.0976	250	3.18
13	0.200	0.330	0.0976	250	2.49
14	0.133	0.330	0.0976	250	3.89
15	0.133	0.330	0.0976	250	3.74
16	0.100	2.10	1.00	574	6.02
17	0.100	0.988	2.10	574	5.83
18	0.100	0.331	0.0976	250	5.10
19	0.100	0.296	0.0912	250	5.32
20	0.100	0.296	0.0912	250	5.47
21	0.100	0.296	0.0912	250	5.48
22	0.100	0.228	0.0600	250	5.24

second order rate constant in runs with excess V(III). The same effect was noted in this study. A systematic error in concentrations could cause this effect; all of the Cr(II) and V(III) solutions were reanalyzed by independent methods, and a number of rate runs were analyzed for the reagent in excess after completion of the run. In every case, agreement was quite

good ($\leq$2%), whereas the discrepancy in rate constants was often as large as 10%, being higher in runs with excess V(III). This effect may be due to an undetected systematic error in analysis or it may represent a small but genuine kinetic effect. The effect is barely beyond experimental error, however, it will not be considered further. The rate constants reported refer to runs with excess Cr(II) or a small excess of V(III).

A series of experiments was also carried out in which varying concentrations of perchlorate ion were replaced by equal concentrations of chloride ion, up to 1.0 M Cl^-. Results of these studies are tabulated in Table 47. Second-order kinetics continued to be obeyed, but the rate constant at a given $[H^+]$ increased linearly with $[Cl^-]$. Typical series of experiments are presented in Figure 16, which is a plot of k_{obs} vs. $[Cl^-]$. Lack of appreciable curvature in such plots suggested that an appreciable fraction of vanadium(III) was not converted to the chloro complex (Equation 63), at the chloride concentrations involved

$$V^{3+} + Cl^- \rightleftarrows VCl^{2+} \qquad (63)$$

The formation of VCl^{2+} has been examined by Furman and Garner (69), who concluded that VCl^{2+} was not a very stable species[10].

[10]The generally similarity of V^{3+} with Fe^{3+} and Cr^{3+} with respect to stability constants implies that Q_V is probably not near zero. The spectral data (69) do not appear to be inconsistent with 6% VCl^{2+} at $[Cl^-]$ = 1.0 M (Q_{CrCl} = 0.06 M^{-1} under these conditions.

Table 47. Rate constants for the reaction of Cr^{2+} and V^{3+}

Conditions: 25.0°, μ = 2.50 M perchlorate and chloride solution, λ = 574

Exp.	$[H^+]$	$[Cl^-]$	$10^2[Cr^{2+}]_0$	$10^2[V^{3+}]_0$	k_{obs} (M^{-1} sec^{-1})
1	1.00	0.100	2.00	0.952	1.41
2	1.00	0.100	1.06	1.76	1.54
3	1.00	0.200	3.51	0.719	1.87
4	1.00	0.200	3.51	0.719	1.91
5	1.00	0.200	1.53	0.942	1.87
6	1.00	0.250	2.00	0.952	1.83
7	1.00	0.250	1.06	1.76	2.29
8	1.00	0.250	0.331	0.0976	2.71[a]
9	1.00	0.400	3.51	0.719	2.78
10	1.00	0.400	3.51	0.719	2.92
11	1.00	0.400	1.53	0.942	2.96
12	1.00	0.400	1.53	0.942	2.98
13	1.00	0.500	0.331	0.0976	4.02[a]
14	1.00	0.500	2.11	0.952	2.79
15	1.00	0.500	1.53	0.942	3.86
16	1.00	0.500	1.06	1.76	3.61
17	1.00	0.750	0.331	0.0976	5.21[a]
18	1.00	0.800	1.53	0.942	4.92
19	1.00	0.900	2.13	0.527	4.65
20	1.00	0.900	1.10	2.00	5.89
21	1.00	0.900	0.533	1.00	5.63
22	1.00	0.900	0.533	2.00	5.69
23	1.00	0.977	1.06	1.76	6.06
24	1.00	0.982	0.331	0.0976	6.19[a]
25	0.500	0.150	2.10	1.00	2.44
26	0.500	0.150	0.988	2.10	2.58
27	0.500	0.250	2.10	1.00	2.98
28	0.500	0.250	0.988	2.10	3.07
29	0.500	0.351	2.10	1.00	3.39
30	0.500	0.351	0.988	2.10	3.97
31	0.500	0.470	0.988	2.10	4.27
32	0.500	0.470	0.988	2.10	4.32
33	0.200	0.250	0.330	0.0976	3.88[a]
34	0.200	0.250	0.330	0.0976	4.92[a]
35	0.200	0.500	0.330	0.0976	5.94[a]

[a] 250 nm.

Table 47. (Continued)

Exp.	$[H^+]$	$[Cl^-]$	$10^2[Cr^{2+}]_0$	$10^2[V^{3+}]_0$	k_{obs} (M^{-1} sec^{-1})
36	0.200	0.500	0.330	0.0976	6.10[a]
37	0.200	0.500	0.330	0.0976	6.38[a]
38	0.200	0.500	0.330	0.0976	6.40[a]
39	0.200	0.750	0.330	0.0976	7.70[a]
40	0.200	0.750	0.330	0.0976	8.02[a]
41	0.200	0.750	0.330	0.0976	8.13[a]
42	0.200	0.980	0.330	0.0976	8.10[a]
43	0.200	0.980	0.330	0.0976	8.33[a]
44	0.200	0.980	0.330	0.0976	8.87[a]
45	0.133	0.250	0.330	0.0976	5.84[a]
46	0.133	0.500	0.330	0.0976	7.50[a]
47	0.133	0.750	0.330	0.0976	8.58[a]
48	0.133	0.980	0.330	0.0976	9.69[a]
49	0.100	0.100	0.331	0.0976	5.43[a]
50	0.100	0.150	2.10	1.00	6.78
51	0.100	0.200	0.331	0.0976	6.43[a]
52	0.100	0.200	0.331	0.0976	5.97[a]
53	0.100	0.300	2.10	1.00	7.85
54	0.100	0.300	0.331	0.0976	6.48[a]
55	0.100	0.300	0.331	0.0976	7.29[a]
56	0.100	0.400	0.331	0.0976	7.48[a]
57	0.100	0.450	2.10	1.00	8.69
58	0.100	0.500	0.331	0.0976	7.56[a]
59	0.100	0.500	0.331	0.0976	8.16[a]
60	0.100	0.500	0.331	0.0976	8.59[a]
61	0.100	0.500	0.331	0.0976	8.81[a]
62	0.100	0.750	0.331	0.0976	9.69[a]
63	0.100	0.750	0.331	0.0976	9.54[a]

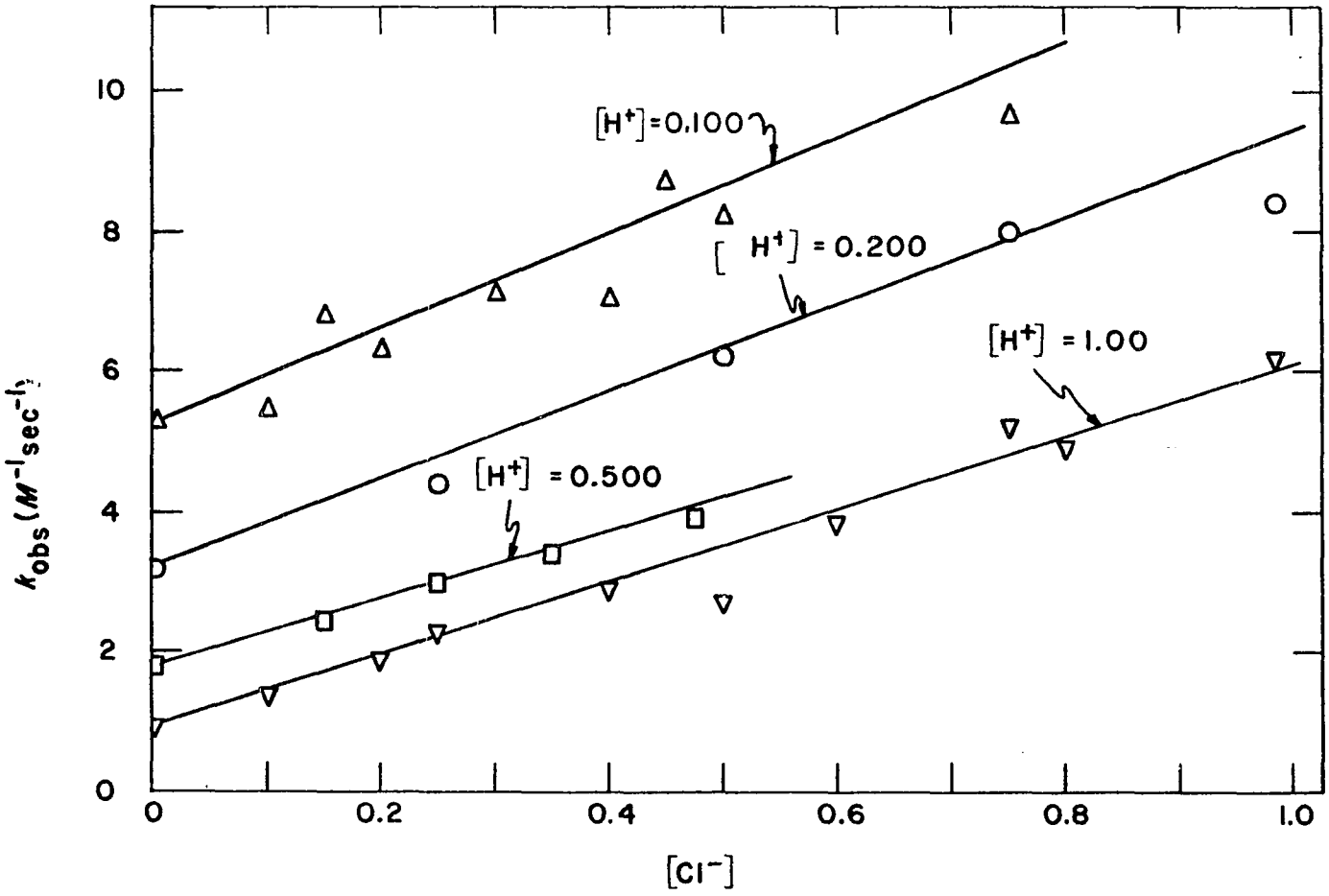


Figure 16. Illustrating the chloride dependence of the observed second-order rate constants for the reaction of V^{3+} and Cr^{2+}

The kinetic data are consistent with this result, but are not sufficiently precise to reveal minor contributions of VCl^{2+} formation

A linear relation of k_{obs} and $[Cl^-]$ leads to the following rate equation.

$$-d[Cr^{2+}]/dt=k_{obs}[V^{3+}][Cr^{2+}]=(k_3+k_2[Cl^-])[V^{3+}][Cr^{2+}] \quad (64)$$

Values of k_2 were obtained from plots of k_{obs} vs. $[Cl^-]$ at each particular $[H^+]$, as shown in Figure 16. A small but regular trend was noted in the value of k_2 as a function of $[H^+]$. The values of $[H^+]$, $k_2(\underline{M}^{-2}sec^{-1})$ are as follows at 25.0°: 1.00, 4.87±0.28; 0.50, 4.3±0.3; 0.200, 5.7±0.3; 0.133, 6.2±0.4; 0.100, 6.8±0.5. Except for the unexplained deviation at $[H^+]$ = 0.5, there is a steady increase of k_2 with decreasing $[H^+]$. As expected from the earlier work (34), k_3 increases with decreasing $[H^+]$. The values of k_3, the second-order rate constant in the absence of chloride, at these five values of $[H^+]$ are 0.93, 1.82, 3.18, 3.83, and 5.25 $\underline{M}^{-1}$ sec^{-1}.

The monochlorochromium(III) complex $(H_2O)_5CrCl^{2+}$ was the product of the k_2 reaction path. This complex was identified on the basis of its known absorption spectrum (70,71), measured both in the reaction solution and also after its separation by ion exchange chromatography from all other components of the solution. Quantitative experiments were carried out on the reaction stoichiometry in chloride solution. The

concentration of $CrCl^{2+}$ in the product solution was estimated by the extent of the decrease in absorbance at 609 nm comparing the value at the end of the run with that after a period of 10-20 hr. In the presence of the V^{2+} formed in the reactions, this was ample time for the chromium(III) substitution reaction (Equation 61) to come to equilibrium. The results of several such experiments are presented in Table 48. The observed values for $[CrCl^{2+}]/([CrCl^{2+}]+[Cr^{3+}])$ can be compared with those computed from the ratio $k_2[Cl^-]/(k_2[Cl^-]+k_3)$. The latter expression assumed that the k_2 pathway formed exclusively $CrCl^{2+}$ and that k_3 formed Cr^{3+}. The observed and calculated values agree within the estimated experimental error, except for one unaccountably discrepant result. In particular, this analysis served to demonostrate that the chloride-dependent path does not have a component leading to $Cr(H_2O)_6^{3+}$.

Chlorochromium(III) and vanadium(II)-steady-state data

In terms of the two-step mechanism presented above (Equations 59 and 60) equations can be derived for the net rate of aquation of $CrCl^{2+}$ and the formation of Cr^{3+}, without assuming that the steady-state approximation holds. The resulting rate equations (in the absence of added Cr^{2+} or V^{3+}) are

$$\frac{-d[CrCl^{2+}]}{dt} = \frac{k_1k_3[CrCl^{2+}][V^{2+}] + k_2[Cl^-](d[Cr^{2+}]/dt)}{k_3 + k_2[Cl^-]} \qquad (65)$$

Table 48. Production distribution in the reaction of V^{3+} and Cr^{2+} in chloride solution

Conditions: 25.0°, μ = 2.50 M

$[H^+]$	$[Cl^-]$	fraction $CrCl^{2+}$ obsd (no.)[a,b]	fraction $CrCl^{2+}$ calcd
1.00	0.90	0.86(8)	0.834
0.500	0.25	0.34(1)	0.371
0.500	0.478	0.53(1)	0.531
0.500	0.75	0.90(2)	0.640

[a]Number of independent runs under a given set of conditions in which the analysis for $CrCl^{2+}$ was carried out.

[b]Corrected for the $CrCl^{2+}$ remaining at equilibrium.

$$\frac{d[Cr^{3+}]}{dt} = \frac{k_1 k_3 [CrCl^{2+}][V^{2+}] - k_3 (d[Cr^{2+}]/dt)}{k_3 + k_2[Cl^-]} \qquad (66)$$

When the steady-state approximation for the intermediates Cr^{2+} and V^{3+} becomes valid, one ordinarily would write[11]

$$d[Cr^{2+}]/dt = d[V^{3+}]/dt = 0$$

---

[11] This expression is unduly restrictive, however; as seen from Equations 65 and 66, a sufficient condition for the steady-state is given by the inequalities

$$(k_3 + k_2 [Cl^-]) \mid d[Cr^{2+}]/dt \mid \ll k_1 k_3 [CrCl^{2+}][V^{2+}]$$

or

$$\mid d[Cr^{2+}]/dt \mid \ll \mid d[CrCl^{2+}]/dt \mid$$

which leads to an expression (Equation 67) for the steady-state rate law.

$$\frac{-d[CrCl^{2+}]}{dt} = \frac{d[Cr^{3+}]}{dt} = \frac{k_1 k_3 [CrCl^{2+}][V^{2+}]}{k_3 + k_2[Cl^-]} \qquad (67)$$

This relation was not generally valid in the present work, however, owing to a failure of the steady-state approximation. The problem can be stated in terms of the two-step mechanism shown above: Cr^{2+} and V^{3+} were formed (k_1) at a rate higher than they reacted (k_2 and k_3). As a consequence, the maximum values of the concentrations of these ions were sufficiently high that appreciable fractions of the total chromium and of the total vanadium at any instant were present as Cr^{2+} and V^{3+}. Under such circumstances the nonsteady-state equations could not be solved in closed form. These data will be considered in detail later since their treatment depends in part upon the steady-state data to be presented next.

Consider the alterations in reaction conditions that could be made to force the reaction to conform more closely to the steady-state relation. One may add a high concentration of <u>one</u> of the potential intermediates, say V^{3+}. The concentration of the other intermediate, Cr^{2+}, would be kept at a considerably lower value than in a situation where V^{3+} was not added, since Cr^{2+} is converted to $CrCl^{2+}$ or Cr^{3+} by its reaction with V^{3+}. This is in contrast to the situation in the absence of added V^{3+}, when both intermediate ions would be at equal

concentration. The addition of sufficient V^{3+} lowered Cr^{2+} to the point where $[Cr^{2+}] \ll [CrCl^{2+}]$, and the steady-state inequalities were reasonably well satisfied. What V^{3+} concentration was required? At $[H^+]$ = 0.10 M and 25.0°, the rate constants are k_2 = 6.8 M^{-2} sec^{-1}, k_3 = 5.25 M^{-1} sec^{-1}. In addition an approximate value of 0.06 M^{-1} sec^{-1} for k_1 shall be assumed. For the steady-state approximation to be valid to within 5% accuracy[12], the inequality in Equation 68 must hold. On the basis, at the least favorable point,

$$\frac{[Cr^{2+}]ss}{[CrCl^{2+}]_0} = \frac{k_1[V^{2+}]_0\{\exp(-k_1[V^{2+}]_0 t)\}}{(k_3 + k_2[Cl^-])[V^{3+}]} \leq 0.05 \qquad (68)$$

t near 0, $[V^{3+}]$ must be larger than ~0.23 $[V^{2+}]_0$. In runs with $[V^{2+}]_0$ = 0.066 M, $[V^{3+}]$ must be $\geq$ 0.015 M. Runs 14-20 in Table 49 had $[V^{3+}]$ = 0.020 M, and met this criterion. Since the argument for added Cr^{2+} rather than added V^{3+} ran exactly parallel to this, exp 9-13 with $0.015 < [Cr^{2+}] < 0.074$ M at $[H^+]$ = 0.100 M also met this arbitrary 5% requirement.

The absorbance of the steady-state runs on $CrCl^{2+}$ + V^{2+} was followed with time in an appropriate quartz spectrophotometer cell, at fixed wavelength. Most experiments were performed at 440 nm, but runs were also carried out at 609 and 620 nm. The kinetic data were independent of the wavelength

[12] A measure of the validity of the steady-state approximation is given by the maximum fraction of the concentration of $CrCl^{2+}$ or V^{2+}, whichever is lower, that was converted to intermediate.

Table 49. Apparent second-order rate constant at various concentrations[a]

Conditions: 25.0°C, μ = 2.50 M at 440 nm

Run	$[V^{2+}]_0$	$[Cr^{2+}]_0$	$[V^{3+}]_0$	$[H^+]$	k_1 ($M^{-1}sec^{-1}$)
1	0.100	0.0784		1.00	0.0409
2	0.0760	0.080		1.00	0.0417
3	0.0760	0.080		1.00	0.0403
4	0.0760	0.080		0.500	0.0428
5	0.0608	0.040		0.250	0.0485
6	0.0608	0.040		0.200	0.0514
7	0.0608	0.040		0.200	0.0500
8	0.0608	0.040		0.125	0.0577
9	0.0304	0.015		0.100	0.0641
10	0.0304	0.015		0.100	0.0616
11	0.0760	0.020		0.100	0.0652
12	0.0760	0.040		0.100	0.0681
13	0.0760	0.074		0.100	0.0616
14	0.0657		0.020	0.100	0.0629
15	0.0657		0.020	0.100	0.0619
16	0.0657		0.020	0.100	0.0631
17	0.0657		0.020	0.100	0.0628
18	0.0657		0.020	0.100	0.0621[b]
19	0.0657		0.020	0.100	0.0617[c]
20	0.0657		0.020	0.100	[d]
21	0.0608	0.040		0.062	0.0708

[a] In all these experiments, $[CrCl^{2+}]_0$ was 0.0120 M.

[b] Studied at 609 nm.

[c] Studied at 620 nm.

[d] Studied at 578 nm which is an isosbestic point for $CrCl^{2+}$ and Cr^{3+}; under these conditions there was essentially no change in the observed absorbance.

used to monitor the reaction. Moreover, a run was performed at λ = 578 nm (run 20, Table 49), which is an isosbestic wavelength for Cr^{3+} and $CrCl^{2+}$. Provided conversion of $CrCl^{2+}$ to Cr^{3+} remained the only significant process, as indicated in Equation 61, then no absorbance change whatever should be observed at this wavelength. The absence of an observable absorbance change in this experiment indicated that notable concentrations of other ions, V^{3+} and Cr^{2+} in particular, were not formed in the course of the experiment.

The pseudo-first-order dependence of rate upon $[CrCl^{2+}]$ in the steady-state runs was indicated by the linearity of plots of $\ln(D_t - D_\infty)$ *vs.* time (D = absorbance) over at least 80% reaction in each run. The slopes of such plots were used in the computation of the second-order rate constant k_1 by the relation

$$k_1 = [V^{2+}]^{-1} \cdot \frac{-d \ln (D_t - D_\infty)}{dt} \qquad (69)$$

A value of k_1 for each of the steady-state runs is given in Table 49.

The variation in $[V^{2+}]$ was not large although there was a two-fold variation in the runs at $[H^+]$ = 0.100 (runs 9 and 10). The first-order dependence upon $[V^{2+}]$ is indicated by those experiments. The nonsteady-state data considered later in detail encompassed a much wider range of $[V^{2+}]$, and confirmed this aspect of the rate expression, as assumed in Equation

69. It is especially important to note that the rate constant k_1 was independent of whether Cr^{2+} or V^{3+} is used for this purpose, and independent as well of its concentration, once the steady-state conditions had been established. There was regular variation of k_1 with $[H^+]$ that will be considered in detail in a later section.

According to Equation 67, the steady-state rate constant should be a function of $[Cl^-]$ according to the equation

$$k_{obs} = \frac{k_1 k_3}{k_2[Cl^-] + k_3} \qquad (70)$$

In experiments without added chloride ion, the term k_3 generally was the main denominator term, leading to a value of $k_{obs} \simeq k_1$. A number of steady-state runs (0.080 M added Cr^{2+}) were also performed containing added Cl^-, in the range of up to 0.60 M Cl^- at t_0, with $[H^+]$ = 1.00 M. Table 50 presents these results. Figure 17 shows a plot of $1/k_{obs}$ vs. $[Cl^-]$ and compares the data obtained with the predictions of Equation 70 based on the independently known values of k_1, k_2, and k_3. The agreement is considered to be satisfactory, giving additional support to the rate law and mechanism proposed.

Chlorochromium(III) and vanadium(II)-nonsteady-state data

The reaction of V^{2+} and $CrCl^{2+}$ was also studied without added vanadium(III) or chromium(II). Initial concentrations were varied as follows: $CrCl^{2+}$, 0.005-0.091 M, and V^{2+}, 0.010-0.082 M. Plots of ln $(D - D_\infty)$ vs. time were not linear, indicating

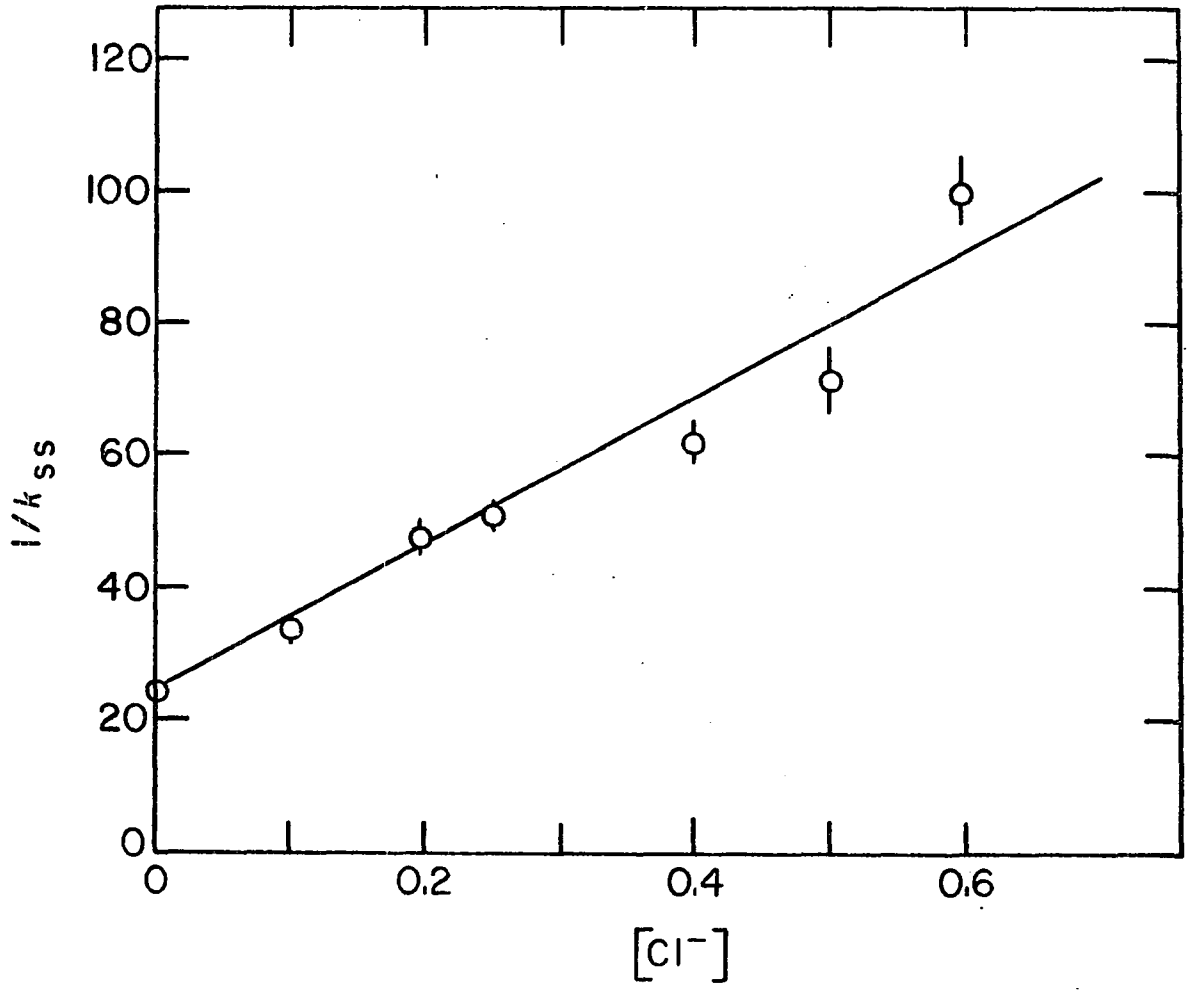
Table 50. Rate constant for the V^{2+} catalyzed aquation of $CrCl^{2+}$ with added Cl^-

Conditions: 25.0°, μ = 2.5 M, λ = 440 nm, $[H^+]$ = 1.00 M

Exp.	$10^2[CrCl^{2+}]_0$	$10^2[Cr^{2+}]_0$	$10^2[V^{2+}]_0$	$[Cl^-]_0$	k_{obs} (M^{-1} sec^{-1})
1	1.24	8.0	7.60	0.100	0.0293
2	1.24	8.0	7.60	0.200	0.0210
3	1.24	8.0	7.60	0.250	0.0196
4	1.24	8.0	7.60	0.400	0.0161
5	1.24	8.0	7.60	0.500	0.0140
6	1.25	8.0	7.60	0.600	0.0100

the reaction did not follow pseudo-first-order kinetics. Plots were curved upward near the start of a run, approximated linearity for much of the run, but became curved downward as the reaction neared completion. Some semi-quantitative observations on the curves were made as follows. The general shape of the anomalous rate curves persisted when $[V^{2+}]$ and $[CrCl^{2+}]$ were varied over sizeable limits. Moderate changes in $[H^+]$ and in $[Cl^-]$ did not appreciably affect the pattern although the pseudo rate constant was altered somewhat. Changes in $[CrCl^{2+}]$ and $[V^{2+}]$ did not produce large changes in the calculated instantaneous second-order rate constants k_1 (Equation 69), indicating the problem probably did not arise from incorrect concentration dependences in the rate law. Chromium(III) was without effect on the pattern and on the rate.

Figure 17. Illustrating the chloride dependence of the observed second-order rate constant for the reaction of V^{2+} and $CrCl^{2+}$ at 25.0° and $[H^+] = 1.00$ M under steady-state conditions. In each run, $[CrCl^{2+}]_0 = 0.012$, $[V^{2+}]_0 = 0.076$, and $[Cr^{2+}]_0 = 0.08$ M. The solid line is that predicted from combination of 3 independently known rate constants, according to Equation 70, and corresponds to the values $k_1 = 0.0409\ M^{-1}\ sec^{-1}$, $k_2 = 4.87\ M^{-1}\ sec^{-1}$, and $k_1 = 0.93\ M^{-1}\ sec^{-1}$


120
100
80
60
40
20
0
0
0.2
0.4
0.6
$1/k_{ss}$
$[Cl^-]$

An attempt was made to learn whether the decrease in the apparent value of k_1 (Equation 69) as the reaction progressed in the early stages could be attributed to a side reaction that consumed V^{2+}, thereby lowering its concentration. Samples from the reaction solution were removed intermittently, and the V^{2+} content of each analyzed by the spectrophotometric method based on $Co(NH_3)_5Br^{2+}$. The amount of cobalt(II) produced by this reaction was the same(±2%), within experimental error, at all points during the run. Such experiments presumably verified the assumed catalytic stoichiometry. In fact, the experiment measured not $[V^{2+}]$, but the sum $[V^{2+}]+[Cr^{2+}]$, and showed only the constancy of total reducing strength.

The experiments that demonstrated most conclusively the complexities encountered and that provided the best clues to interpreting the complex kinetics were rate runs at 578 or 580 nm, an isosbestic point for Cr^{3+} and $CrCl^{2+}$. In such experiments the absorbance first fell with time, passed through a gradual minimum, then rose to very nearly its starting value. Such an observation is clearly inconsistent with occurrence of a single reaction. Consider the two-step reaction scheme shown earlier (Equations 59 and 60) under the circumstances where the intermediates V^{3+} and Cr^{2+} build up to appreciable levels. Since the molar absorptivities of these ions differ from those of the major species, such an occurrence will manifest itself spectrally. At λ = 578 nm,

for example, conversion of V^{2+} (ϵ 3.8) to V^{3+} (ϵ 5.6) and conversion of $CrCl^{2+}$ (ϵ 13.1) to Cr^{2+} (ϵ 2.3) rather than to Cr^{3+} (ϵ 13.1) would lead to the observed minimum in absorbance with time. According to this same scheme, the sum $[V^{2+}]$ + $[Cr^{2+}]$ would be constant, thereby accounting for the observed constancy of reducing strength.

Given that the demonstrated complexities in this system were due to the reactions cited, how does one handle the kinetic situation? The two differential equations associated with the reaction scheme outlined cannot be solved in closed form. In order to treat these nonsteady-state data a computer program was devised that would calculate individual concentrations and total absorbance as a function of time, given values for the rate constants k_1, k_2, and k_3 and given the initial concentrations and molar absorptivities of each species.[13]

The computer program utilized the Runge-Kutta method with Runge's coefficients to solve the differential equations in an iterative technique. It should be noted, however, that the program does not generate any values for rate constants. Rather, it utilizes the known values to compute concentrations and absorbances which can be compared with the observed spectral

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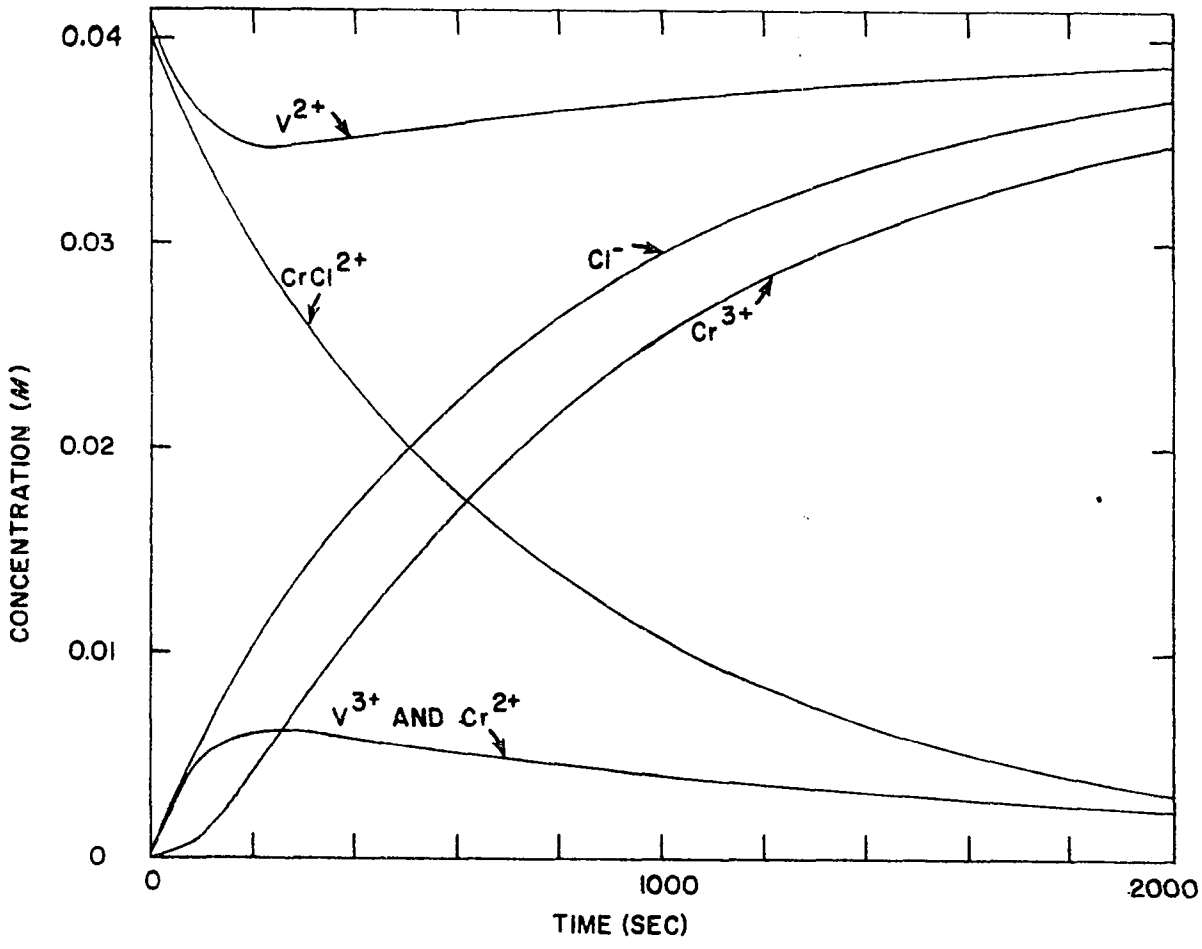
[13]The author is grateful to Dr. T. W. Newton for help in formulating the program, and to Dr. J. P. Birk for adapting it to the problem in question in a form suited to the IBM 360 computer.

data. The value of k_1 used in these computations was that derived from the steady-state experiments at the appropriate $[H^+]$.

A direct comparison of calculated absorbances with experimentally observed absorbances was limited by two factors. An unknown blank absorbance resulted from the thermostating compartment, the cell, and the water surrounding the cell. Since the primary comparison was not D_{obsd} and D_{calcd}, but $(D_t - D_\infty)$, obsd and calcd, the problem proved immaterial. Secondly, the uncertainty in the time elapsed between the initiation of the reaction and the first absorbance reading was variable. Values of 5-12 sec were estimated for cell mixing and placement in the spectrophotometer, but the value chosen did not critically affect the fit.

The utility of the program can be demonstrated best by examining the results it computed for the theoretical behavior of the nonsteady-state situation. Consider a particular run having $[CrCl^{2+}]_0 = 0.0403$ and $[V^{2+}]_0 = 0.0410$ M at 1.00 M H^+. Figure 18 illustrates the computed time dependence of every species. It is instructive to examine the results. The intermediates V^{3+} and Cr^{2+} rose rapidly to a maximum value and then decreased slowly. The maximum so achieved was appreciable; 15.3% of the initial $CrCl^{2+}$ and V^{2+} had been converted to Cr^{2+} and V^{3+} at this point. Since the intermediates decayed relatively slowly once they had reached their

Figure 18. Concentrations of reactants, products, and intermediates as a function of time in a typical nonsteady-state experiment with $[V^{2+}]_0 = 0.0410$, $[CrCl^{2+}]_0 = 0.0403$, at $[H^+] = 1.00$ M and 25.0°. Lines shown here give the theoretical values computed from the assumed model with given rate constants, according to the Runge-Kutta computation


0.04
0.03
0.02
0.01
0
CONCENTRATION (M)
V^{2+}
$CrCl^{2+}$
Cl^-
Cr^{3+}
V^{3+} AND Cr^{2+}
0
1000
2000
TIME (SEC)

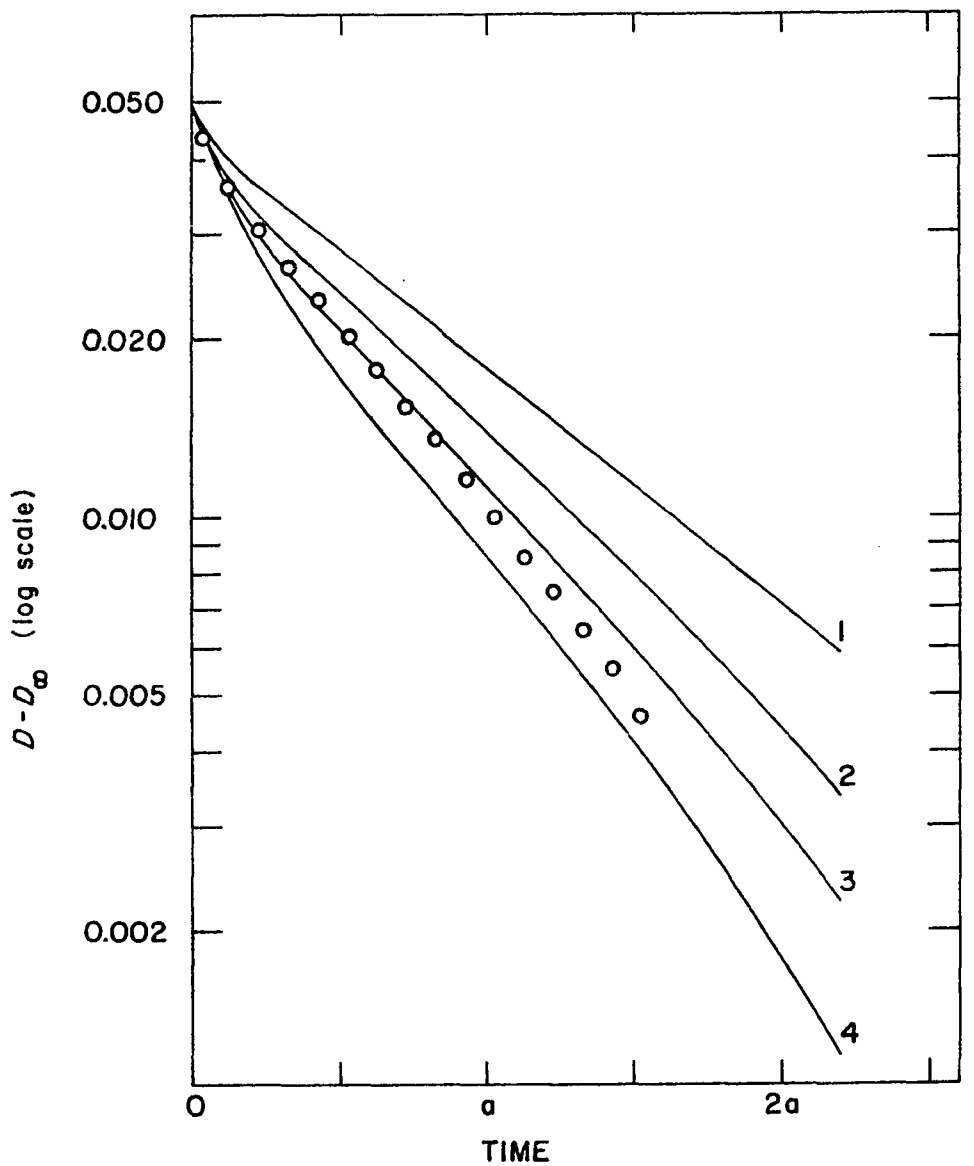
maximum values, past this point, and except for the final stages of reaction, plots of ln $(D_t - D_\infty)$ *vs.* time should be nearly linear, as observed.

In the early portion of each experiment, when $[V^{3+}]$ and $[Cr^{2+}]$ were yet increasing, $[V^{2+}]$ was decreasing substantially. The decrease in $[V^{2+}]$ would alone account for the unexpected curvature in the pseudo-first-order plots. The affect was accentuated in the absorbance values; gradual conversion of V^{2+} (ϵ 3.3) to V^{3+} (ϵ 5.4) caused the apparent rate constant to decrease with time. Very late in the run, $-d[Cr^{2+}]/dt$ became of the same order of magnitude as $-d[CrCl^{2+}]/dt$, accounting for the downward curvature noted near the end of each run.

It is interesting to note that the computer treatment of the nonsteady-state behavior predicted an induction period in the rate of formation of chromium(III). Its rate then paralleled the rate of formation of chloride ion but $[Cr^{3+}]$ always lagged behind $[Cl^-]$ because of the induction period. The concentration of vanadium(II) reached a minimum early in the reaction and then was slowly replenished as the reaction proceeded to completion.

The absorbance-time pattern observed in experiments over the previously stated concentration ranges agreed rather closely with the computer-calculated values. A comparison of four experiments at varying $[V^{2+}]$ is given in Figure 19, where the time scale has been normalized to compensate exactly

Figure 19. Observed and calculated absorbance values (2 cm optical path) in a nonsteady state experiment on $V^{2+} + CrCl^{2+}$ plotted as $(D - D_\infty)$ (log scale) versus time. Conditions: $[CrCl^{2+}]_0 = 0.0403$ at $[H^+] = 1.00$ M and 25.0°. Calculated lines are given for three other nonsteady state-runs at different $[V^{2+}]$ successively higher by a factor of 2: (1) 0.0103, (2) 0.0205, (3) 0.0410 (data depicted), (4) 0.082. The time scales are successively shorter by factors of 2, the values of a in runs 1-4 being 3200, 1600, 800, and 400 sec.


0.050
0.020
0.010
0.005
0.002
D - D∞ (log scale)
0
a
2a
TIME
1
2
3
4

for variation in $[V^{2+}]$ (i.e. were the steady-state approximation valid, all 4 plots would be linear and would coincide precisely). In addition, the data for one experiment are shown superimposed on the theoretical line. A comparison of the theoretical behavior under nonsteady-state conditions is most instructive.

The amount of vanadium(II) "catalyst" converted to V^{3+} is much less when the initial concentration of $[V^{2+}] = 0.0103$ as compared with 0.0821 M, but the fraction of vanadium(II) as intermediate is signficantly larger. Consider two runs with these values of $[V^{2+}]_0$ and with $[CrCl^{2+}]_0 = 0.0403$. The maximum concentration of V^{3+} intermediate were 3.4×10^{-3} and 9.3×10^{-3} M. These represent decreases of 33% and 11% from $[V^{2+}]_0$.

Chloride ion increased the rate at which intermediates reacted by the k_2 pathway. It is useful to consider its effect in the nonsteady-state experiments. In two experiments with $[CrCl^{2+}]_0 = 0.0403$, $[V^{2+}]_0 = 0.0821$, and $[H^+] = 1.00$ M, having $[Cl^-]_0 = 0$ and $[Cl^-]_0 = 0.100$ M respectively, it was observed that there was greater curvature in the first-order plot for the run with added chloride ion. Initial rates in the two experiments were quite close, but the run with added chloride slowed down considerably more than the other. Again, the computer calculation based on the proposed mechanism agreed with this observation. This again is easily understood in

terms of the proposed mechanism: at higher $[Cl^-]$ a greater fraction of the intermediates reverted to $CrCl^{2+}$ thus delaying net aquation.

The computer program could be applied quite effectively to the previously cited data at the $CrCl^{2+}$ - Cr^{3+} isosbestic point, 580 nm. The use of the known molar absorptivities appropriate to this wavelength yielded a computed absorbance-time trace with a minimum similar to that observed. Using the following absorptivities at λ = 580 nm:

V^{2+}	3.8	Cr^{3+}	13.1
V^{3+}	5.6	$CrCl^{2+}$	13.1
Cr^{2+}	2.3		

in a run with $[CrCl^{2+}]_0$ = 0.0200, $[V^{2+}]_0$ = 0.0820, $[Cl^-]_0$ = 0 and $[H^+]$ = 1.00 M, the observed $[Cr^{2+}]_{max}$ was 0.0051 M at ca. 210 sec, compared to the computed value of 0.0058 M at 220 sec. (Estimated error in experimental $[Cr^{2+}]_{max}$ and t max are 10% and 20 sec.) In the identical experiment but with added chloride, $[Cl^-]_0$ = 0.400, observed $[Cr^{2+}]_{max}$ 0.0036 M at ca. 160 sec, and calculated $[Cr^{2+}]_{max}$ = 0.0040 M at 180 sec.

With regard to the general pattern of the reaction, several of the Runge-Kutta computations were performed for runs which presumably met the steady-state criterion. The experiments had added V^{3+} or Cr^{2+}, and the experimental absorbance values followed pseudo-first-order kinetics quite closely. The effect of adding one of these intermediates was considered

above. The predictions were borne out by these computations, and the fit of observed and calculated absorbance readings was again quite excellent. The latter computation had no merit in its own right; it served merely as a cross-check between the steady-state reasoning presented earlier and the correct formulation of the computer program.

Effect of $[H^+]$ on the various rate constants In the original study of the reaction of V^{3+} and Cr^{2+} in perchlorate solution (34), the apparent second-order rate constant k_3 was found to vary with $[H^+]$ according to Equation 71. The data obtained here differ from the earlier in that they were obtained

$$k_3 = q/(r + [H^+]) \qquad (71)$$

at a higher ionic strength. A plot of $1/k_3$ vs. $[H^+]$ is linear, and leads to the values $q = 1.09\ sec^{-1}$ and $r = 0.12$ M at 25.0°, $\mu = 2.5$ M, compared to $q = 0.624\ sec^{-1}$ and $r = 0.108$ M at $\mu = 0.65$ M (34).

The values of the rate constants k_1 and k_2 in the rate terms $k_1[CrCl^{2+}][V^{2+}]$ and $k_2[V^{3+}][Cr^{2+}][Cl^-]$ represent reactions with the same activated complex. The functional dependence of k_1 upon $[H^+]$ is given by the relation $k_1 = e + f/[H^+]$ and $k_2 = g + h/[H^+]$. In fact, the interpretation offered above is that the two reactions are the reverse of one another. If such is the case, then the principle of microscopic reversibility requires that $k_1/k_2 = e/g = f/h$. The observed values of $10^2 \times k_1/k_2$ are: 0.92, 0.92, 0.89, 1.00, 0.84 M at $[H^+] = 0.100$,

0.133, 0.200, 0.500, and 1.00 M. Except for the value at $[H^+]$ = 0.500 M, which was the condition where the anomalously low value of k_2 was obtained, the rate constant ratio seems to be satisfactorily constant with varying $[H^+]$.

Greater precision was achieved for k_1 than k_2. A plot of k_1 vs. $1/[H^+]$ (see Figure 20) was used to evaluate e and f, with the result that the following relation was found: k_1 (M^{-1} sec^{-1}) = $0.038_4 + 0.0025/[H^+]$. Likewise a plot of k_2 vs. $1/[H^+]$ led to the relation $k_2(M^{-2}\ sec^{-1}) = 4.3 + 0.27/[H^+]$.

Effect of temperature on k_2 A few measurements of k_2 were carried out at other temperatures. These are listed in Tables 51 and 52. At a single hydrogen ion concentration, 1.00 M, values of k_2 are as follows: 5.0°, 0.90, and 15.0°, 2.21 M^{-2} sec^{-1}. Since k_2 represents a composite rate constant, meaningful activation parameters cannot be computed from these data. The value of k_2 is largely the contribution of the hydrogen ion independent term g at $[H^+]$ = 1.00 M, however, and at least approximate values for the activation parameters of rate constant g can be computed to be $\Delta H^{\ddagger}$ = 13 kcal/$mole^{-1}$ and $\Delta S^{\ddagger}$ = -11 cal/$mole^{-1}$ deg^{-1}. Considering the low precision which we were able at present to evaluate k_2, it did not appear useful to carry out a detailed investigation of temperature effects.

Equilibrium involving $CrCl^{2+}$ formation A value for the stability quotient of $CrCl^{2+}$ at the ionic strength in question

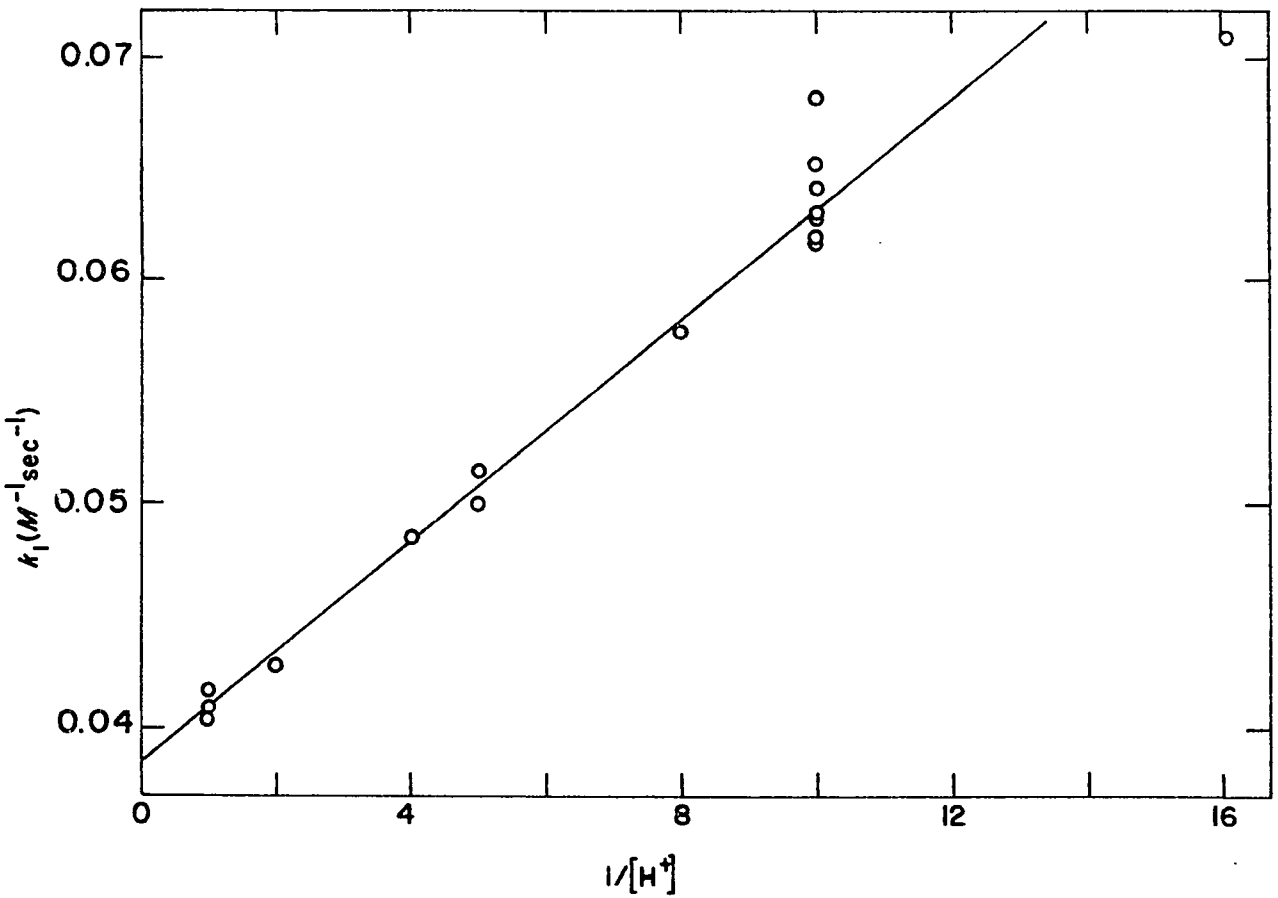


Figure 20. Illustrating the dependence of k_1 upon $[H^+]$ in a plot of k_1 versus $1/[H^+]$

Table 51. Rate constants for the reaction of Cr^{2+} and V^{3+}

Conditions: 5.0°, μ = 2.50 M perchlorate and chloride solution, λ = 574 nm, $[H^+]$ = 1.00 M

Exp.	$[Cl^-]$	$10^2[Cr^{2+}]_0$	$10^2[V^{3+}]_0$	k_{obs} (M^{-1} sec^{-1})
1	0	8.58	1.42	0.178
2	0	8.58	1.42	0.195
3	0	8.58	1.42	0.188
4	0.250	9.58	0.790	0.389
5	0.250	9.58	0.790	0.414
6	0.500	9.58	0.790	0.630
7	0.500	9.58	0.790	0.624
8	0.500	5.31	0.839	0.683
9	0.750	6.07	0.790	0.934
10	0.750	6.07	0.790	0.903
11	0.750	5.31	0.829	0.838
12	0.750	5.31	0.829	0.838
13	0.947	6.07	0.790	1.07
14	0.947	6.07	0.790	1.11
15	0.947	5.31	0.829	1.03
16	0.947	5.31	0.829	1.13

Table 52. Rate constants for the reaction of Cr^{2+} and V^{3+}

Conditions: 15.0°, μ = 2.50 M perchlorate and chloride solution, λ = 574 nm, $[H^+]$ = 1.00 M

Exp.	$[Cl^-]$	$10^2[Cr^{2+}]_0$	$10^2[V^{3+}]_0$	k_{obs} (M^{-1} sec^{-1})
1	0	3.26	0.940	0.374
2	0	3.26	0.940	0.387
3	0.202	3.26	0.940	0.749
4	0.202	3.26	0.940	0.756
5	0.399	3.26	0.940	1.32
6	0.399	3.26	0.940	1.37
7	0.601	3.26	0.940	1.63
8	0.601	3.26	0.940	1.77
9	0.947	5.21	0.792	2.19
10	0.947	5.21	0.792	2.19
11	0.947	5.21	0.792	2.26

was not available. Baltisberger and King (35) and Hale and King (72) had reported values for $Q_1 = [CrCl^{2+}]/[Cr^{3+}][Cl^-]$. Values of Q_1 extrapolated to 25.0° are 0.105, 0.072, 0.094, and 0.32 $\underline{M}^{-1}$ at μ = 0.19, 0.96, 0.98, and 4.0 $\underline{M}$, respectively.

Because of the previous rate measurements, it was necessary to evaluate Q_1 at μ = 2.50 $\underline{M}$ and 25.0°. A total of 17 solutions was studied, 11 of which started with Cr^{3+} (0.04-0.1 $\underline{M}$), Cl^- (0.05-0.5 $\underline{M}$) and the remaining 6 with $CrCl^{2+}$ (0.1-0.2 $\underline{M}$). The latter series also contained added Cl^- (0.05-0.5 $\underline{M}$). Table 53 presents these results. The average equilibrium quotient is $Q_1 = 0.060 \pm 0.007$ $\underline{M}^{-1}$ when all experiments are considered. The precision of experiments 2, 3, 10-17 is higher due to the ease of analyzing the higher concentrations of $CrCl^{2+}$. The average of these experiments is $Q_1 = 0.058 \pm 0.003$ $\underline{M}$.

Table 53. Evaluation of the equilibrium quotient, Q_1, for the equilibrium involving Cr^{3+}, Cl^- and $CrCl^{2+}$ μ = 2.50 M, 25.0°

Exp.	$10^2[Cr^{3+}]_0$	$10^2[Cl^-]_0$	$10^2[CrCl^{2+}]_0$	$10^2[CrCl^{2+}]_{eq}$[a]	10^2Q_1 (M^{-1})[a,b]
1	3.96	10.0		0.297	7.57
2	3.96	50.3		0.111	5.76
3	3.96	50.3		0.121	6.25
4	3.96	5.03		0.0162	8.16
5	3.96	5.03		0.0134	6.78
6	9.98	10.0		0.0464	4.69
7	9.98	10.0		0.0484	4.90
8	3.96	10.0		0.0273	6.96
9	3.96	10.0		0.0241	6.12
10	9.98	50.0		0.218	5.39
11	9.98	50.0		0.256	5.30
12	9.98	9.87	20.0	0.487	5.61
13	9.98	9.87	20.0	0.520	6.01
14	9.98	50.0	10.0	0.628	5.47
15	9.98	50.0	10.0	0.653	5.70
16	9.98	5.04	10.0	0.178	6.07
17	9.98	5.03	10.0	0.179	6.09

[a]Two separate determinations of $[CrCl^{2+}]_{eq}$ per experiment.

[b]$Q_1 = [CrCl^{2+}/[Cr^{3+}][Cl^-]$.

INTERPRETATION AND DISCUSSION

Vanadium(II) - Copper(II) Reaction

Activation parameters The rate constants were fit to the Eyring relation using a computer program to find values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ that best fit the observed rate constants. The values of the activation parameters so obtained are $\Delta H^{\ddagger}$ = 11.3 ± 0.1 kcal/mole and $\Delta S^{\ddagger}$ = -14.1 ± 0.5 cal/mole-deg. With these parameters the observations are reproduced to an average deviation of 3.0% and with a maximum deviation of 8.6%. The calculated values of k are 13.1 ± 0.16, 26.4 ± 0.15, and 50.7 ± 0.4 $\underline{M}^{-1}$ sec^{-1} at the three temperatures studied.

Following the procedure of Newton and Rabideau (73), the following equation for the net activation process can be written,

$$Cu^{2+} + V^{2+} = [CuV^{4+}]^{\ddagger} \qquad (72)$$

Based on the known molar entropy $\bar{S}^0$ = -23.6 eu for Cu^{2+} (74) and the estimated value $\bar{S}^0$ = -23 eu for V^{2+} (75), the molar entropy of the transition state is -61 ± 3 eu. Newton and Baker (76) have pointed out the close correlation of the overall charge on a transition state and its entropy for a variety of reactions covering many different metal ions and a considerable range of observed $\Delta S^{\ddagger}$ values. The entropy

computed here, -61 eu, lies in the range -60 to -80 eu in which almost all of the entropies of transition states with 4+ charge lie.

Reaction mechanism The net equation suggests that the mechanism is a simple one electron process. Other mechanisms are consistent with the kinetic data but the 1- equivalent reaction between the hydrated cations seems the more probable mechanism, since it produces the desired products in a single step. No experimental evidence for the presence of an intermediate was obtained.

Does the reaction proceed by an inner-sphere or outer-sphere mechanism? The question of whether one water molecule occupies the primary coordination sphere of both cations in the transition state cannot be answered directly, since the products exchange with solvent at a rate high compared to that of oxidation-reduction. The question of mechanism in this case is a very subtle one. Conclusions drawn from these arguments depend upon the weight given to the various lines of evidence.

A very plausible argument can be advanced in favor of an outer-sphere mechanism. The lack of an appreciable reaction path involving a hydroxo complex has been cited in previous cases as one characteristic of many processes (6, 77-79) known to follow an outer-sphere mechanism, in contrast to the dominance of the hydroxo path in reactions that proceed by inner-sphere mechanisms. The lack of a dependence of the

Cu^{2+}-V^{2+} reaction rate upon $[H^+]$ stands in sharp contrast to the result found for the reduction of Cu^{2+} by Cr^{2+}, where the rate term varying as $1/[H^+]$ predominates. The stoichiometry of the latter reaction is parallel to the present reaction, but there are two independent transition states $[CrCu^{4+}]^{\ddagger}$ and $[Cr(OH)Cu^{3+}]^{\ddagger}$, with the latter making the more important contribution even at $[H^+] = 1$ M.

The reaction studied here has a rate constant (26.4 M^{-1} sec^{-1} at 25.0°) considerably higher than that for the analogous term in the Cr^{2+}-Cu^{2+} reaction (0.17 M^{-1} sec^{-1} at 25.0°). The rate ratio is thus ~150. Sutin has recently applied the Marcus relations to rate comparisons of a similar nature with considerable success (3). The equation for the comparison of two reactions with a species in common is

$$k_{12}/k_{13} = [(k_2/k_3)K_{23}]^{1/2} \qquad (73)$$

where k_2, k_3 represent the electron exchange rates and K_{23} the equilibrium constant. The rate ratio so calculated is $\geq$ 0.56, using second-order exchange rate constants of 1.0 x 10^{-2} M^{-1} sec^{-1} for V^{2+}-V^{3+} (80) and $\leq$ 1.90 x 10^{-5} M^{-1} sec^{-1} for Cr^{2+}-Cr^{3+} (81) and an equilibrium quotient of 1/1700 which is the value obtained in the V^{2+}-$CrCl^{2+}$ reaction. If the exchange rate for the Cr^{2+}-Cr^{3+} is some 250 times smaller than the minimum cited above, then the rate ratios are in good accord. The generalization has frequently been made

that for reactions of similar mechanisms the more favorable reaction generally proceeds at the higher rate. Use of the reverse trend observed here as evidence for the mechanisms being different is not very convincing when the rate ratio calculations are considered.

The identification of the products of the electron transfer process has shown directly and unambiguously that the reactions of vanadium(II) with $CrSCN^{2+}$ (77), VO^{2+} (82), cis-$Co(en)_2(N_3)_2^+$ (83), and $Co(NH_3)_5(C_2O_4)^+$(84) proceed mainly by inner-sphere mechanisms. The rate constants for these reactions range from 1.6 to 45 $\underline{M}^{-1}$ sec^{-1}. The rate of formation of V^{3+} and Cu^+ in this case is quite similar to the previously cited rates and the rate of H_2O exchange on $V(H_2O)_6^{2+}$, which has been variously estimated at 10-120 $\underline{M}^{-1}$ sec^{-1} (77). Sutin has suggested, that in some processes at least, the rate of entry of a bridging ligand to the coordination sphere of V^{2+} is a major factor in dictating the rate. At least a part of the evidence for this proposal is that in many cases the rate of oxidation-reduction has proven to be quite close to the estimated V(II) - solvent exchange rate. Table 54 lists several examples of rates of substitution and of electron transfer reactions involving vanadium(II) which are in the range 1-50 $\underline{M}^{-1}$ sec^{-1}. The case in question, $V^{2+} + Cu^{2+}$, appears to be quite consistent with the other cited examples. If an inner-sphere mechanism is thus obtained, two points remain to be answered. (1) Why

Table 54. Rates of substitution and of electron transfer reactions involving vanadium(II)

Conditions: 25.0°, μ = 1.00 M

Reaction	k(M^{-1} sec^{-1})	$\Delta\bar{H}^{\ddagger}$ (kcal)	$\Delta\bar{S}^{\ddagger}$ (cal/deg)	Ref
V^{2+} + SCN^-	15[a]----28[b]	13.5	-2	85,86
V^{2+} + Cu^{2+}	26.4	11.3	-14.1	
V^{2+} + $CrSCN^{2+}$	7.1	12.5	-12	77
V^{2+} + VO^{2+}	1.6[c]	12.8	-16.5	82
V^{2+} + cis-$Co(en)_2(N_3)_2^+$	32.9			83
V^{2+} + RX^{2+}				
X = azide	13	11.7	-14	5
binoxalate	12.5	12.2	-13	84
oxalate	45			84
glyoxalate	8.2	11.0	-17	84
pyruvate	10.2	11.6	-15	84
trimethylpyruvate	2.1	11.9	-17	84
oxamate	20.7	11.6	-14	84

[a] 24°.

[b] μ = 0.84 M.

[c] μ = 2.0 M.

is the rate of $V(H_2O)_6^{2+}$ substitution relevant in dictating the rate of formation of the inner-sphere complex when the substitution rate of $Cu^{2+}(aq)$ is so high? (2) Why is the hydroxide bridged path an unimportant reaction path in this case?

Considerable precedent exists for assuming that the bridging ligand must originate from the oxidizing agent. The basis of this contention is that in all inner-sphere reactions, insofar as the author is aware, the bridging ligand is coordinated to the oxidizing agent prior to formation of the transition state, and not to the reducing agent. The observation however may be due to the difficulty of finding systems with an inert reducing agent and a labile oxidizing agent that reverse labilities after electron transfer. The assumption of the origin of the bridging ligand on the oxidizing agent is not a trivial one. If this is a necessary condition for inner-sphere mechanisms the two points previously mentioned are quite easily answered. (1) The substitution rate of $V(H_2O)_6^{2+}$ will be the maximum rate of the oxidation process when the bridging, H_2O, ligand originates on $Cu^{2+}(aq)$. (2) The absence of an inverse acid term is thus expected after the following consideration. The hydroxide bridged path would be represented by the following sequence

$$Cu^{2+} + H_2O \rightleftharpoons CuOH^+ + H^+ \quad K_a \qquad (74)$$

$$V^{2+} + CuOH^{+} \overset{k_{OH}}{\rightleftharpoons} [V(OH)Cu^{3+}]^{\ddagger} \rightarrow VOH^{2+} + Cu^{+} \quad (75)$$

according to which the total rate, including the aquo path, would be

$$k' = k_{H_2O} + k/[H^+] = k_{H_2O} + k_{OH} K_a/[H^+] \quad (76)$$

Since $K_a \sim 10^{-7}$ M, and since k_{OH} has a maximum value of 120 M^{-1} sec^{-1} (the inner-sphere rate being limited by V(II) - H_2O exchange), so that the resulting rate constant would be

$$k = 26.4 + 1.2 \times 10^{-5}/[H^+] \quad (77)$$

The second term would contribute a negligible part to the observed rate; for all practical purposes, the rate would appear to remain independent of $[H^+]$. Thus the failure of an inner-sphere reaction to exhibit the expected large k_{OH}/k_{H_2O} ratio arises from the leveling of k_{OH} and k_{H_2O} by the V(II) - H_2O exchange rate.

It is of interest in this regard that Dodel and Taube (87) based part of their argument for an outer-sphere mechanism for $V^{2+} + Co(NH_3)_5OH_2^{3+}$, on the lack of an inverse acid term. Using the following calculations involving rate constants and the acid dissociation constant for ROH^{2+} (88), it is apparent that in an inner-sphere mechanism the k_{OH} term would not be detectable. In an inner-sphere reaction the bridging ligand must originate on ROH_2^{3+} due to the inertness

of this complex to oxygen exchange. The hydroxide bridged path would therefore result from $ROH^{2+} + V^{2+}$ and the apparent rate constant would be $k = k_{OH} K_a$. Using the recently determined value (87) of the acid dissociation constant for ROH_2^{3+}, $pK_a = 6.216$, the following is obtained. The composite rate constant, Equation 78, has the values; $k_{H_2O} = 0.53\ \underline{M}^{-1}\ sec^{-1}$ (87), and

$$k' = k_{H_2O} + k/[H^+] \qquad (78)$$

$k \leq 7 \times 10^{-6}\ sec^{-1}$. According to this point of view the lack of a large k_{OH}/k_{H_2O} values does <u>not</u>, in this instance, constitute an indication of an outer-sphere mechanism, but rather is attributed to a leveling of the two rate values by the substitution rate of $V(H_2O)_6^{2+}$.

Vanadium(III) - Copper(II) Reaction

<u>Reaction scheme</u> Because of the complexities of this system, considerable evidence supporting the reaction scheme has been obtained. The proposed mechanism is a one electron transfer producing the intermediate, Cu^+, at a steady-state concentration, followed by a rapid reaction between the intermediate and the oxidizing agent. This reaction scheme is outlined in Equations 79, 80, and 81.

$$Cu^{2+} + V^{3+} \underset{2}{\overset{1}{\rightleftharpoons}} Cu^{+} + V(IV) \quad (79)$$

$$Cu^{+} + \text{Oxidant} \xrightarrow{ox} Cu^{2+} + \text{Products} \quad (80)$$

$$\text{net reaction: } V^{3+} + \text{Oxidant} = V(IV) + \text{Products} \quad (81)$$

This mechanism demands the following general rate expression

$$\frac{-d[V^{3+}]}{dt} = \frac{k_1 k_{ox}[Cu^{2+}]_0[V^{3+}][Ox]}{k_2[V(IV)] + k_{ox}[Ox]} \quad (82)$$

which simplifies to

$$-d[V^{3+}]/dt = k_1[Cu^{2+}]_0[V^{3+}] \quad (83)$$

with the restriction that $k_{ox}[Ox] \gg k_2[V(IV)]$.

There are seven major points that support the proposed reaction scheme. (1) The observed rate law, Equation 83, is valid over an extensive range of concentration variations of Cu^{2+}, oxidant, and V^{3+}. (2) The observed rate law and rate constant is not a function of the oxidant used, as was observed with Fe^{3+} (32), RBr^{2+}, RCl^{2+} and <u>trans</u>-$Co(en)_2Cl_2^{+}$. This is true in general with the restriction that $k_{ox}[Ox] \gg k_2[V(IV)]$ as was the case in these examples;

$$k_{Fe} = 1.61 \times 10^{-5}/[H^{+}]\ \underline{M}^{-1}\ sec^{-1},\ \mu = 1.00\ \underline{M}\ (LiClO_4);$$

$$k_{RBr} = 7.2 \times 10^{5}\ \underline{M}^{-1}\ sec^{-1},\ \mu = 1.00\ \underline{M}\ (LiClO_4);$$

$k_{RCl} = 1.13 \times 10^5\ \underline{M}^{-1}\ sec^{-1}$, $\mu = 3.00\ \underline{M}$ ($LiClO_4$);

$k_{trans} \geq 1 \times 10^7\ \underline{M}^{-1} sec^{-1}$, $\mu = 0.20\ \underline{M}$ ($LiClO_4$).

The observation that $RNCS^{2+}$ resulted in the formation of a precipitate of CuNCS is also consistent with the proposed detailed scheme. (3) The observed two stage absorbance traces when $[RBr^{2+}]_0 < [V^{3+}]_0$ also supports the sequence proposed. Independent treatment of the data from both stages yielded values for k_1 that were in good agreement with other observations. (4) The direct measurement of the rate of reaction of V^{3+} and Cu^{2+} and the resulting k_1 is very convincing evidence that the catalytic rate studies measure k_1 also. (5) The retarding effect of high concentrations of added V(IV), removing the previously cited inequality, is completely consistent both qualitatively and quantitatively. (6) The form of the rate law when corrected for medium effects is compatible with the form of the rate law for the reaction of Cu^+ and V(IV) as demanded by microscopic reversibility. Conclusions regarding medium effects are discussed in the next section. (7) The comparison of activation parameters and $\overline{\Delta H}^0$, $\overline{\Delta S}^0$ for reaction show the investigated rate process to be the reverse of the reaction between Cu^+ and V(IV). Computations of this are discussed later.

With regard to point two, the agreement between the data of Higginson and Sykes (32) in $\mu = 3.00\ \underline{M}$ ($NaClO_4$) and this

work with μ = 3.00 $\underline{M}$ ($LiClO_4$) is considered good. Table 55 lists a comparison of these results.

Table 55. A comparison of k_{app} ($\underline{M}^{-1}$ sec^{-1}) with data of Higginson and Sykes[32]

	25.0°			15.0°		
H+	Li^+ [a]	Na^+ [a]	Na^+ [b]	Li^+ [a]	Na^+ [a]	Na^+ [b]
0.70	0.498	0.444	0.405	0.150	0.131	0.13
1.00	0.352	0.322	0.300	0.108	0.0954	0.090
1.80	0.205	0.196	0.190	0.0631	0.0582	0.0588
2.67	0.144	0.144	0.145	0.0450	0.0430	0.0445

[a] This work.

[b] Higginson and Sykes, Reference 32.

The precipitation of CuBr(s) was avoided by the low concentration of both Cu^+ and Br^-. Assuming $[Cu^+]$ obeys the steady-state relation, its concentration is given by Equation 84.

$$[Cu^+]_{ss} = k_1[Cu^{2+}]_0[V^{3+}]/k_{RBr}[RBr^{2+}] \qquad (84)$$

The condition for no formation of precipitate is

$$[Cu^+][Br^-] < 5.3 \times 10^{-9}\ \underline{M}^2 \text{ (Reference 68)} \qquad (85)$$

This leads to the following inequality:

$$[Cu^{2+}]_0[V^{3+}][Br^-]/[RBr^{2+}] < 1.5 \times 10^{-3} \qquad (86)$$

at $[H^+] = 0.210$ M.

Experiment number 40, page 57, had conditions that were most favorable to producing a precipitate. After 50% reaction the quantity $[Cu^{2+}]_0[V^{3+}][Br^-]/[RBr^{2+}]$ was equal to 5.2×10^{-5}, thus no precipitate should be formed in any of the experiments, and none was observed.

In the experiments with $RNCS^{2+}$, the conditions for formation of no precipitate are:

$$[Cu^+][NCS^-] < 5 \times 10^{-15} \text{ M}^2 \text{ (Reference 68)} \quad (87)$$

The inequality becomes approximately

$$[Cu^{2+}]_0[V^{3+}][NCS^-]/[RNCS^{2+}] < 1.4 \times 10^{-14} \quad (88)$$

at $[H^+] = 1.00$, using $k_{RNCS} \sim 1\ \text{M}^{-1}\ \text{sec}^{-1}$.

The initial conditions of these experiments were:

$[Cu^{2+}]_0 = 1.60 \times 10^{-2}$ M $[V^{3+}]_0 = 7.5 \times 10^{-5}$ M, $[RNCS^{2+}]_0 = 1.4 \times 10^{-4}$ M, and $[H^+] = 1.00$ M.

Thus after 1% reaction the solubility product was greatly exceeded. The quantity $[Cu^{2+}]_0[V^{3+}][NCS^-]/[RNCS^{2+}]$ would be 1.2×10^{-8} after 1% reaction.

Acid dependence and medium effects Since the rate term $h/[H^+]$ carries the bulk of the reaction, the interpretation of the less important rate term g cannot necessarily be made in terms of a genuine reaction pathway with transition state $[VCu^{5+}]^{\ddagger}$. It is pertinent to consider whether this rate

term could arise from a reasonable medium effect on the rate constant h.

Consider the changes in activity coefficients that may occur when equal concentrations of H^+ and Li^+ or H^+ and Na^+ are traded for one another in a medium that is otherwise constant and that contains ClO_4^- as the only anion. Following Harned's (89) rule, and assuming only a single rate term varying as $1/[H^+]$ is important, the relation becomes

$$k_{app} = \frac{h^0}{[H^+]} \exp(\beta[H^+]) = h^0\beta + h^0/[H^+] \qquad (89)$$

where h^0 represents an intrinsic rate constant in the absence of such medium effects. This relation has the same form as the apparent rate constant, Equation 90, and the rate

$$k_{app} = g + h/[H^+] \qquad (90)$$

constant g is thus, $g = h^0\beta$. It is thus realized that a medium effect can appear as a small apparent rate term in the kinetic expression. Values of h^0 and β are listed in Table 56. The values of β appear to be in reasonable accord with those typical of what one generally finds in a situation similar to this. For a replacement of H^+ by Li^+ in 1.00 M perchlorate solution, a value of 0.1 or less for β represents a reasonable medium effect and 0.2 or less for replacement of H^+ by Na^+. The observation that the activity coefficient of hydrogen ion is more nearly constant in a medium of Li^+

Table 56. Value of h^0 and β for the reaction of Cu^{2+} and V^{3+}

Medium	Temp.	h^0 ($\underline{M}^{-1}$ sec^{-1})	β
Li^+	15.0	0.0999	0.076
Li^+	25.0	0.366	0.054
Li^+	35.1	0.981	0.085
Na^+	15.0	0.0837	0.140
Na^+	25.0	0.284	0.134
Na^+	35.0	0.852	0.130

rather than Na^+ is also consistent with more general observations (90). For these reasons the rate term $g[Cu^{2+}]_0[V^{3+}]$ probably does not represent a genuine reaction path, $[VCu^{5+}]^{\ddagger}$, but may result largely from effects of non-constant activity coefficients.

The true form of the rate law for the reaction of Cu^{2+} and V^{3+} after correction for medium effects is

$$-d[V^{3+}]/dt = h_f[Cu^{2+}]_0[V^{3+}]/[H^+] \qquad (91)$$

At high acid the rate constants determined in $LiClO_4$ and $NaClO_4$ media must agree because of the similarity of the media, the agreement is very good in this respect as shown in Table 57.

Table 57. Comparison of k_{app} ($\underline{M}^{-1}$ sec^{-1}) at high acid in Li^+ and Na^+ media

	25.0		15.0		35.0	
H^+	Li^+	Na^+	Li^+	Na^+	Li^+	Na^+
2.00	0.184	0.178	0.0561	0.0537	0.569	0.533
2.85	0.135	0.139	0.0428[a]	0.0422[a]	0.419	0.408

[a] $[H^+]$ = 2.75 $\underline{M}$.

Microscopic reversibility and equilibrium Shaw and Espenson[6] have shown that reaction 92 does not contain a rate term

$$VO^{2+} + Cu^+ + 2H^+ = V^{3+} + Cu^{2+} + H_2O \qquad (92)$$

of the form $k''_r[VO^{2+}][Cu^+][H^+]^2$. In their study such a term would have carried at least 30% of the reaction at $[H^+]$ = 3.00 $\underline{M}$ and this was definitely not observed. These results are consistent with the conclusions of this study indicating that no true kinetic term $g[Cu^{2+}]_0[V^{3+}]$ exists. It is concluded that the earlier catalytic rate data of Higginson and Sykes (32) contained a term $g[Cu^{2+}]_0[V^{3+}]$ that was a result of medium effects upon exchange of Na^+ for H^+ at constant ionic strength.

The rate expressions, Equations 93 and 94

$$d[V^{3+}]/dt = k_r[V(IV)][Cu^+][H^+] \qquad (93)$$

and

$$-d[V^{3+}]/dt = k_f[Cu^{2+}]_0[V^{3+}]/[H^+] \quad (94)$$

are compatable according to microscopic reversibility and may be used to calculate the equilibrium quotient of reaction 95.

$$V^{3+} + Cu^{2+} + H_2O = VO^{2+} + Cu^+ + 2H^+ \quad (95)$$

where $K = k_f/k_r$. The equilibrium constant so calculated is a function of the medium is a result of the reaction, Cu^{2+} + V^{3+} having a medium effect. For these calculations the rate law, Equation 94, was assumed valid. Three equilibrium constants may be calculated which correspond to the three different media: μ = 3.00 M, $HClO_4$, $LiClO_4$ and $NaClO_4$. In order to make the calculation for a medium of $NaClO_4$, it was necessary to assume that k_r (Shaw and Espenson data[6]) had the same value in a medium of 3.00 M ionic strength maintained with $NaClO_4$ as was experimentally observed in 3.00 M ($LiClO_4$); this is probably valid since the value was the same in 3.00 M $HClO_4$ as in 3.00 M $LiClO_4$. The rate constant h_f was evaluated in a medium of $HClO_4$ by using the value of k_{app} at $[H^+]$ = 2.85 M, h_f was evaluated for a medium of $LiClO_4$ by using the value of K_{app} at $[H^+]$ = 0.210 M ($LiClO_4$) and similarly for a medium of $NaClO_4$. The results are tabulated in Table 58.

Activation and reaction enthalpies and entropies The individual rate constants were fit to the Eyring relation using a nonlinear least-squares computer program (64). The activation parameters from the studies in both $LiClO_4$ and

Table 58. Equilibrium constant for the reaction of V^{3+} and Cu^{2+}, 25.0°

	3.00 M ($HClO_4$)	1.00 M ($HClO_4$)	3.00 M ($LiClO_4$)	3.00 M ($NaClO_4$)
k_f	0.388 ± .006	0.220 ± .002	0.340 ± .007	0.291 ± .004
k_r	384 ± 14	153 ± 2	384 ± 14	384 ± 14
K	$(1.01 \pm .05) \times 10^{-3}$	$(1.44 \pm .03) \times 10^{-3}$	$(0.885 \pm .053) \times 10^{-3}$	$(0.758 \pm .039) \times 10^{-3}$

$NaClO_4$ media, μ = 3.00 M are used in the following calculations. The parameters are:

$\Delta H^{\ddagger}$ = 19.1 ± 0.1 kcal/mole, $\Delta S^{\ddagger}$ = 3.3 ± 0.4 eu, Li^+;

$\Delta H^{\ddagger}$ = 19.7 ± 0.1 kcal/mole, $\Delta S^{\ddagger}$ = 5.1 ± 0.3 eu, Na^+.

The net activation process (73) corresponding to the process under study is given by the following equation:

$$V^{3+} + Cu^{2+} + H_2O = [V(OH)Cu^{4+}]^{\ddagger} + H^+ \qquad (96)$$

The molar entropy of the transition state may be computed from the relation

$$\bar{S}^{\ddagger} = \overline{\Delta S^{\ddagger}} + \bar{S}^0_{react} - \bar{S}^0_{H^+} \qquad (97)$$

The values used are given in Table 59. The scale is adjusted so that $\bar{S}^0(H^+) = 0$ and leads to $\bar{S}^{\ddagger} = -69$ eu, with an estimated uncertainty of ±4 eu.

Newton and Baker (76) have recently tabulated values of $\bar{S}^{\ddagger}$ for many transition states of this general type and have pointed out the close correlation of entropy and ionic charge on the transition state. The value in the present instance lies at the midpoint of the range -60 to -80 eu in which 90% of their examples of this charge type lie. A general limitation of this procedure is that all of the entropies in question will show some dependence on medium; in treatments such as the present this source of variation has been ignored.

Table 59. Thermodynamic quantities

	$\overline{\Delta H}^0$ (ref.)	$\overline{\Delta F}^0$ (ref.)	$\overline{S}^0$ (ref.)
$H_2O(l)$	-68.3 (74)	-56.7 (74)	16.7 (74)
$Cu^+(aq)$	12.4 (74)	12.0 (74)	-6.3 (74)
Cu^{2+} (aq)	15.4 (74)	15.5 (74)	-23.6 (74)
$VO^{2+}(aq)$	-116.0 (91)	-110.0 (91)	-26.0 (91)
$V^{3+}(aq)$	-68.20 [a]	-60.6 (74)	-65.0 (73)

[a] The value for $\overline{\Delta H}^0$ of $V^{3+}(aq)$ was calculated to be -68.2 using $\overline{\Delta G}^0$, (74), and $\overline{S}^0$, (73) for that species.

Added evidence that reactions 93 and 94 are the reverse of each other was obtained by comparing the $\overline{\Delta H}_{react}$ and $\overline{\Delta S}_{react}$ obtained from $\Delta H_f^{\ddagger}$, $\Delta H_r^{\ddagger}$, $\Delta S_f^{\ddagger}$, and $\Delta S_r^{\ddagger}$ [6] with those calculated from the various $\overline{\Delta H}^0$ and $\overline{\Delta S}^0$ values for the different species. The following values of Shaw and Espenson[6] were used:

$\Delta H_r^{\ddagger}$ = 2.15 ± 0.08 kcal/mole, $\Delta S_r^{\ddagger}$ = -41.3 ± 0.3 eu, 1.00 M ($LiClO_4$).

The results are:

	$\overline{\Delta H}_{react}$(kcal)	$\overline{\Delta S}_{react}$(cal/deg)
From $\overline{\Delta H}^0$'s	17.5	39.6
From $\overline{\Delta H}^{\ddagger}$'s ($Li^+$)	17.0±.2	44.6±.7
From $\overline{\Delta H}^{\ddagger}$'s ($Na^+$)	17.5±.2	46.4±.6

The agreement is considered quite good thus demonstrating that the reactions are the reverse of each other.

Reaction mechanism The results obtained from the kinetic study suggest that the following mechanistic step is rate-determining.

$$VOH^{2+} + Cu^{2+} \rightleftarrows [V(OH)Cu^{4+}]^{\ddagger} \qquad (98)$$

According to this scheme the transition state, which may also involve an intermediate of the same composition, is formed from a hydroxo species and an aquo species. A rapidly established protolytic equilibria for V(III) is also involved, as follows.

$$V^{3+} + H_2O \rightleftarrows VOH^{2+} + H^{+} \quad (K_a = 0.002 \text{ ref. } 68) \qquad (99)$$

The value of k_f according to this mechanism is $K_a k$, where k is the forward rate constant of reaction 98. It should be noted that the activation parameters were calculated for k_f and thus no conjecture of mechanism was involved.

This is not the only possible assignment that would make the role of hydrogen ion consistent with the reaction kinetics. It appears most reasonable, however, and the following arguments are advanced in its support.

First, the reaction of VOH^{2+} and Cu^{2+} is preferred since the known reactivity of OH^{-} relative to H_2O, at least in reactions proceeding by inner-sphere mechanisms, is well documented (refer to the section giving the interpretation for the chlorochromium(III) - vanadium(II) reaction). Second,

further support exists for this formation, on the presumption that the mechanism is probably inner-sphere with a bridging hydroxide since the observed reactivity of OH^- relative to H_2O is very high. The question then becomes whether such an inner-sphere transition state originated from $VOH^{2+} + Cu^{2+}$ or from $V^{3+} + CuOH^+$. The latter possibility can be ruled out by computing the second-order rate constant from $V^{3+} + CuOH^+$. Using a value of ca. 10^{-6} M for K_a implies that $k = 3 \times 10^5$ M^{-1} sec^{-1}. Since this value greatly exceeds the known rate constant (92) for substitution on V(III), it cannot be the correct value for an inner-sphere process. Third, for the reverse reaction of Cu^+ and VO^{2+}, a comparison of other reduction reactions of VO^{2+}, for example the reactions with V^{2+} (82) and Cr^{2+} (93), brings out the importance of dinuclear hydroxo-bridged species as intermediates. Although in the present system the high substitution lability of copper(II) precludes detection of such an intermediate, the proposal of such an intermediate (Equation 98) is consistent with the observed kinetics and with the chemistry of related reactions of VO^{2+}.

Effect of Cl^- and Br^- The reaction between Cu^{2+} and V^{3+} has a rate-determining step which involves the net activation process

$$Cu^{2+} + V^{3+} + H_2O \rightarrow [V(OH)Cu^{4+}]^{\ddagger} + H^+ \qquad (100)$$

There is no significant contribution from a path that involves

$$Cu^{2+} + V^{3+} \rightarrow [VCu^{5+}]^{\ddagger} \qquad (101)$$

This result suggests that the reaction proceeds by an inner-sphere mechanism with the hydroxo-bridged activated complex being much more effective in electron transfer than a water-bridged activated complex. The effect of Br^- supports an inner-sphere mechanism. Bromide ion is known to be an effective bridging ligand and in this case the addition of bromide ion allows the aquo path to become a substantial kinetic path (Equation 102).

$$Cu^{2+} + V^{3+} + Br^- \rightarrow [VBrCu^{4+}]^{\ddagger} \qquad (102)$$

Characterization of Copper(I)

It seems pertinent at this point to review and comment on the accumulated evidence for the existence of the metastable species Cu^+_{aq}. Several workers have contributed significant data in this regard. Altermatt and Manahan (22,23) have recently published two different methods of preparing metastable solutions of copper(I) perchlorate. In the first method, the 1,3-cyclooctadiene complex of copper(I) perchlorate was prepared in methanol solution. This solution was added to aqueous 0.1 M $HClO_4$ and the olefin extracted from the suspension with ether. The second method involved dissolving freshly prepared copper(I) hydroxide in 0.1 M $HClO_4$. The authors report the storage of 0.01 M solutions of copper(I) at 0° for up to 10 hours prior to disproportionation.

Considerable kinetic and stoichiometric evidence has been collected in this laboratory supporting the existence of Cu^{+}_{aq}.

The stoichiometric evidence includes both the reduction of Cu^{2+} to Cu^{+} and the subsequent oxidation of Cu^{+} with various oxidizing agents. Botn reductions by Cr^{2+} (Shaw and Espenson (24)) and V^{2+} of Cu^{2+} were shown to have a 1:1 stoichiometry by adding an insufficient quantity of reducing agent to a copper(II) solution. The copper(II) concentration was measured quantitatively both before and after the reduction, and found to correspond closely to the decrease for a 1:1 stoichiometry. Treatment of kinetic data for these two systems was consistent only when a stoichiometric ratio of 1:1 was assumed. A number of the rate runs were carried out under conditions where the excess of Cu(II) was slight, so that pseudo-first-order kinetics were not followed. In such cases, appropriate second-order plots were nicely linear and gave the same apparent rate constant at a particular $[H^{+}]$ as did runs in which pseudo-first-order conditions held. On the other hand, the same experiments when calculated assuming the stoichiometry was such that 0.5 Cu^{0}, and not Cu^{+}, was formed gave nonlinear plots. These results are consistent with the formation of Cu^{+}_{aq}.

The stoichiometry of the subsequent reactions where Cu^{+} was oxidized by Fe^{3+}, RBr^{2+}, RCl^{2+}, and RN_3^{2+} was studied. In

these experiments the metastable species was prepared by adding Cr^{2+} to an excess of copper(II). In all cases an insufficient quantity of the metastable species was added to the oxidizing agent. The concentration of the oxidizing agent was measured quantitatively before and after reduction by the metastable species. The results of the four studies showed a 1:1 stoichiometry of the reducing and oxidizing agents. These results are indicative of a reducing agent of plus one charge if the stoichiometric results of the copper(II) reduction by chromium(II) are accepted.

The calculated formal ionic entropies of the activated complexes and the rate expressions are consistent with Cu^{+}. The entropy of the activated complex, $[V(OH)Cu^{4+}]^{\ddagger}$ was indicative of those with a 4+ charge. The formal entropy of $[Fe(OH)Cu^{3+}]^{\ddagger}$ was consistant with known activated complexes having a 3+ charge. Coupled with the known predominant species of the oxidizing agent and the rate expression, these results imply that the copper species has a charge of 1+.

The Debye-Hückle equation offers a method of determining the charge of the activated complex compared to the reactants. The limiting slope of log k vs: $\sqrt{\mu}$ at infinite dilution (μ = 0.04 to 0.001) is equal to the product of the individual charges on the ions times a physical constant, for a second-order reaction. The theoretical equation (Equation 58) has been previously cited. Thus for the reaction

$$Cu^{+} + Co(NH_3)_5Br^{2+} \xrightarrow{k} \qquad (103)$$

the slope of a plot of log k_{obs} versus $\sqrt{\mu}$ should be $2A\ Z_A\ Z_B$, 2.04 at 25.0°. Such behavior is only to be expected at concentrations where $\mu \leq 0.04$. Studies of the reactions Cu^{+} - RCl^{2+} and Cu^{+} - RBr^{2+} as a function of μ, definitely confirm that the copper species has a charge of 1+. Plots of log k_{obs} vs: $\sqrt{\mu}$ have previously been cited (Figures 14 and 15). The dashed lines represent the limiting slope, 2.04. There can be no doubt that the product of the two reacting species is 2+ and it then follows that Cu^{+} is one of the reacting species.

Reactions that are catalyzed by Cu^{2+} generally involve the proposed intermediate, Cu^{+}, in the reaction scheme. A reaction of particular interest to this study is the Cu^{2+} catalysis of the Fe^{3+} - V^{3+} (32) reaction. The independent preparation of Cu^{+} and the subsequent study of the Cu^{+} - Fe^{3+} and Cu^{+} - VO^{2+} has shown the plausibility of the proposed reaction scheme. In order for the mechanism and observed rate law to be consistent it was necessary for the previous workers (32) to assume that the Fe^{3+} oxidation of the intermediate was rapid relative to the VO^{2+} oxidation. The present study has shown that the assumption is valid. The evidence accumulated on a similar system, catalysis by Cu^{2+} of the RX^{2+}-V^{3+} reaction, has established that the identity of the intermediate is Cu^{+}.

It seems reasonable that little doubt can remain of the existence of the metastable species Cu^{+}_{aq}. The evidence accumulated in this regard seems substantial. Nor can there be much doubt as to the role of Cu^{+} in the catalytic behavior of copper(II). This confirmation on the processes inferred from Cu(II) catalysis may suggest additional processes in which catalysis could bea useful snythetic tool or a useful probe of mechanism.

Iron(III) - Copper(I) Reaction

Reaction mechanism The immediate products of the oxidation-reduction reaction can not be identified owing to the relatively rapid rates of water exchange of the products, $Fe(H_2O)^{2+}_6$ and $Cu^{2+}(aq)$. Thus no direct evidence of the detailed mechanism is possible.

The lack of a rate term (Equation 104) corresponding to a direct path between the aquo ions is strong evidence

$$-d[Cu^{+}]/dt = \{k'/[H^{+}]\}[Fe^{3+}][Cu^{+}] \qquad (104)$$

for an inner-sphere mechanism. The rates of reduction of some hydrolyzed and unhydrolyzed complexes are compared in Table 60. At 25.0°, μ = 1.00 M the observed rate constant is 1.61 x 10^{5} M^{-1} sec^{-1} with an acid independent term of $\leq$ 0.08 x 10^{5} M^{-1} sec^{-1} (estimated to be less than 5% of the observed rate constant a 1 M $[H^{+}]$). Using K_a = 1.65 x 10^{-3} M (96) in the following mechanism

Table 60. Comparison of the aquo and hydroxo paths in electron transfer reactions, conditions: 25°

Reaction	k_{H_2O} ($\underline{M}^{-1}$ sec^{-1})	k_{OH}/k_{H_2O}	Ref.
$Fe^{2+} + Fe^{3+}$	4.0	7.8×10^2	94
$Cr^{2+} + Cr^{3+}$	$\leq 2 \times 10^{-5}$	$\geq 3 \times 10^4$	81
$V^{2+} + V^{3+}$	1.0×10^{-2}	1.8×10^2	80
$Cr^{2+} + Fe^{3+}$	2.3×10^3	1.4×10^3	95,67
$Cu^{+} + Fe^{3+}$	$\leq 8 \times 10^3$	$\geq 1.3 \times 10^6$	
$Cr^{2+} + ROH_2^{3+}$	0.5	3×10^6	79
$V^{2+} + ROH_2^{3+}$	~0.5	$\leq 1 \times 10^5$	79
$Cu^{+} + ROH_2^{3+}$	9.8×10^{-4}	4×10^5	
$V^{2+} + Fe^{3+}$	1.8×10^4	≤ 20	77
$Ru(NH_3)_6^{2+} + ROH_2^{3+}$	3.0	10^{-2}	6
$Cr(bipy)_3^{2+} + ROH_2^{3+}$	5×10^4	10^{-2}	79

$$Fe(H_2O)_6^{3+} = (H_2O)_5FeOH^{2+} + H^{+} \qquad K_a \qquad (105)$$

$$(H_2O)_5FeOH^{2+} + Cu^{+}_{aq} \xrightarrow{k_{OH}} [(H_2O)_5Fe(OH)Cu^{3+}]^{\ddagger} \rightarrow \text{Products} \qquad (106)$$

the rate constant k_{OH} may be computed ($k' = k_{OH}K_a$) to be 1.0×10^8 $\underline{M}^{-1}$ sec^{-1}.

The value may be regarded as a lower limit for the rate of water substitution of Cu^{+} (aq). With regard to Table 60, the following mechanisms are indicated: inner-sphere, Cr^{2+} - ROH_2^{3+}, shown by O^{18} transfer; outer-sphere, Cr^{2+} -

$Cr(bipy)_3^{2+}$ and $Ru(NH_3)_6^{2+}$, substitution inert reducing agents, and V^{2+} - Fe^{3+}, rate of reaction is much higher than the rate of water substitution on either V^{2+} or Fe^{3+}. It is then noted that the observation of a large hydroxide/water ratio indicates that the hydroxide catalyzed reaction is proceeding by an inner-sphere mechanism (79).

Is the origin of the bridging ligand on Fe(III) the only mechanism consistent for the data on this system? On the presumption that the mechanism is inner-sphere with a bridging hydroxide, the rate constant for the reaction $CuOH + Fe^{3+}$ is $k = 1.6 \times 10^{12}$ $\underline{M}^{-1}$ sec^{-1}, ($k' = kK_a$). The value is computed using ca. 1×10^{-7} $\underline{M}$ for the dissociation constant of Cu^+. This value of k exceeds the water substitution rate of Fe^{3+} (280 $\underline{M}^{-1}$ sec^{-1} (97)) and the diffusion limit in an aqueous medium.

The activation parameters were calculated for the observed rate constant, k', and the rate constant k_{OH} pertaining to the reaction of $FeOH^{2+} + Cu^+$. Milburn (98) has determined the equilibrium constants[13] and thermodynamic values for the acid dissociation of Fe^{3+} at $\mu = 1.00$ $\underline{M}$. Table 61 summarizes the calculated activation parameters.

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[13] $K = 1.65 \times 10^{-3}$ $\underline{M}$ at $\mu = 1.00$ $\underline{M}$, 25°; 9.54×10^{-4} $\underline{M}$, 15.8°; 3.81×10^{-4} $\underline{M}$, 1.6°, $\Delta H^0 = 10.2 \pm 0.3$ kcal/mole, $\Delta S^0 = 21.5 \pm 1.0$ eu.

Table 61. Activation parameters for the reaction Fe(III) - Cu(I)

Conditions: μ = 1.00 M		
Rate term	$\Delta H^{\ddagger}$ (kcal/mole)[a]	$\Delta S^{\ddagger}$ (eu)[a]
$k'[Fe^{3+}][Cu^{+}]/[H^{+}]$	12.4 ± 0.2	6.7 ± 0.7
$k_{OH}[FeOH^{2+}][Cu^{+}]$	2.2 ± 0.5[b]	-14.8 ± 1.7[b]

[a]Uncertainties represent standard deviations.

[b]Calculated from the values associated with k' and K.

The $\Delta S^{\ddagger}$ value has been used to estimate the formal ionic entropy of the activated complex (73). For $[Fe(OH)Cu^{3+}]^{\ddagger}$ the molar ionic entropy $\overline{S}^{\ddagger}$ is -52 eu using a value of -70 for $\overline{S}^{0}$ (Fe^{3+}) (73). This value is very close to representative values (-25 to -52 eu) for transition states of similar charge (76).

Cobalt(III) - Copper(I) Reactions

Reaction mechanisms The question of inner-sphere or outer-sphere mechanism for the series of cobalt(III) complexes reduced by copper(I) poses an interesting problem. Ligand transfer cannot be demonstrated in these systems because of the lability of the products, copper(II) and cobalt(II). Several lines of indirect evidence are available, however, and support the conclusion that an inner-sphere mechanism is obtained in these systems.

The following arguments are advanced in support of an inner-sphere mechanism. It has been noted that the observation of a large hydroxide/water ratio indicates that the hydroxide catalyzed reaction is proceeding by an inner-sphere mechanism (79). Table 60 listed some typical results for both inner-sphere and outer-sphere reactions. The rate constant for the reaction of Cu^{+} and ROH^{2+} may be calculated from the known value of the acid dissociation constant of the aquopentaamminecobalt(III) ion ($k_{obs} = k_{OH}K_a$). A recent study by Splinter, Harris and Tobias (88) yielded log K_a = -6.216. Thus the rate constant for the hydroxide path is 380 $\underline{M}^{-1}$ sec^{-1}. The reduction of ROH_2^{3+} and ROH^{2+} by Cu^{+} demonstrates that the hydroxide path is preferred. The observed ratio, k_{OH}/k_{H_2O}, is 4×10^5. This ratio compares with the known inner-sphere reduction of ROH_3^{3+} and ROH^{2+} by Cr^{2+} ($k_{OH}/k_{H_2O} = 3 \times 10^6$) quite well. The outer-sphere reduction of ROH_2^{3+} and ROH^{2+} by $Ru(NH_3)_6^{2+}$ has a ratio, $k_{OH}/k_{H_2O} = 10^{-2}$. These observations are strong evidence for an inner-sphere mechanism for the reduction of the hydrolyzed species. It should not be assumed that the aquo path is also necessarily inner-sphere.

A second point of contention is the large variation in the rates of reduction of the different cobalt(III) complexes. Table 62 lists a comparison of the rates of reduction of various cobalt(III) complexes with six different reducing

Table 62. Rate constants ($\underline{M}^{-1}$ sec^{-1}) for the reduction of various cobalt(III) complexes

Conditions: 25°, μ = 0.20 $\underline{M}$[a]

Oxidant	Reductant					
	$Co(CN)_5^{3-}$	Cr^{2+}	Cu^{+}	V^{2+} [b]	$Cr(bipy)_3^{2+}$[c]	$Ru(NH_3)_6^{2+}$
$Co(en)_3^{3+}$		$\sim 2 \times 10^{-5}$[d]	$\leq 4 \times 10^{-4}$	$\sim 2 \times 10^{-4}$	1.8×10^{2}	
ROH_2^{3+}		0.5[e,f]	9.8×10^{-4}	~ 0.5[f]	5×10^{4}	3.0
ROH^{2+}	9.3×10^{4}	3×10^{6}[f]	3.8×10^{2}		5×10^{2}	4.0×10^{-2}
RF^{2+}	1.8×10^{3}	2.5×10^{5}[c]	1.1	2.6	1.8×10^{3}	
RCl^{2+}	$\sim 5 \times 10^{7}$	6×10^{5}[c]	4.9×10^{4}	~ 5	8×10^{5}	2.6×10^{2}
RBr^{2+}	$>2 \times 10^{9}$	1.4×10^{6}[c]	4.5×10^{5}	25	5×10^{6}	1.6×10^{3}
RN_3^{2+}	1.6×10^{6}	$\sim 3 \times 10^{5}$[b]	1.5×10^{3}	13	4.1×10^{4}	1.2
$RNCS^{2+}$	1.1×10^{6}	19[b]	~ 2	0.3	1.0×10^{4}	
Reference	8, 5	7		5	8	6
Mechanism	R_I	R_I	R_I?	R_I?	R_O?	R_O

[a] μ = 0.2 $\underline{M}$ unless noted.
[b] μ = 1.0 $\underline{M}$.
[c] μ = 0.1 $\underline{M}$
[d] μ = 0.4 $\underline{M}$.
[e] μ = 1.2 $\underline{M}$ (ref. 98)
[f] μ = 1.2 $\underline{M}$ (ref. 79 and 87).

Table 62. (Continued)

Oxidant	Reductant					
	$Co(CN)_5^{3-}$	Cr^{2+}	Cu^{+}	V^{2+} [b]	$Cr(bipy)_3^{2+}$ [c]	$Ru(NH_3)_6^{2+}$
RCN^{2+}		35.8[g]	3.3×10^{-3}	11.0[h]		
Reference	8,5	7		5	8	6
Mechanism	R_I	R_I	R_I?	R_I?	R_O?	R_O

[g] μ = 0.15 M ref. 54.
[h] Ref. 54.

agents. Reductions with Cr^{2+} and $Co(CN)_5^{3-}$ have been shown to be inner-sphere by the ligand transfer criteria. The reductions with $Ru(NH_3)_6^{2+}$ are outer-sphere due to the substitution inertness of both the reduced and oxidized forms. The identity of the ligand, X, in a series of pentaamminecobalt(III) complexes, $Co(NH_3)_5X^{2+}$, has a marked influence on the rate of reduction by Cu^+. The observed variation in the rate constants for these complexes is from 9.8×10^{-4} to 4.5×10^5 $\underline{M}^{-1}$ sec^{-1}. The extent of the rate variations due to the bridging ligand should be influenced by the water substitution rate of the reducing agent. The water substitution rate is thus approximately the upper limit of the rate by which these inner-sphere reactions may proceed. In reductions by V^{2+} the range of rate variations will be small owing to this leveling effect if the reactions proceed by an inner-sphere mechanism. The trend is observed in Table 62, (the water substitution rate of $V(OH_2)_6^{2+}$ is 10 - 120 $\underline{M}^{-1}$ sec^{-1}). This may also be a minor effect in reductions by Cr^{2+} where the water substitution rate is perhaps 10^6 - 10^7 $\underline{M}^{-1}$ sec^{-1}. Reductions by $Co(CN)_5^{3-}$ and Cu^+ should not show this leveling effect and the rate variation is thus very large. The ratio of k_{RBr}/k_{RF} is $>2 \times 10^6$ and 4.0×10^5 for the respective reducing agents, $Co(CN)_5^{3-}$ and Cu^+. These trends are very indicative of inner-sphere reactions.

A third point is the large nonbridging ligand effects that were noted for the Cu^+ reductions. The ratio for the reduction by Cu^+ of trans-$Co(en)_2Cl_2^+$ relative to cis-$Co(en)_2Cl_2^+$ is $\geq$ 500. The ratio for the reduction by Cu^+ of trans-$Co(NH_3)_5(OH_2)CN^{2+}$ relative to $Co(NH_3)_5CN^{2+}$ is 140. The reduction of these two complexes by Cr^{2+} has been studied by Birk and Espenson (54). These workers found a ratio of 41 and cited futher indirect evidence supporting an inner-sphere mechanism for the Cr^{2+} reduction. The corresponding ratio for chromium(II) reduction of trans-$Co(en)_2(H_2O)NCS^{2+}$ relative to $Co(en)_2(NH_3)NCS^{2+}$ is 370 (12,99). These reactions have been shown to proceed via thiocyanate-bridged transition states. This effect has been discussed (100,101) in terms of the higher ligand field strength of NH_3 relative to H_2O; the greater splitting caused by trans NH_3 leads to a larger activation enthalpy and a lower rate. Conclusions drawn from nonbridging ligand effects would be more convincing if comparable data were available for processes that are thought or known to proceed by outer-sphere mechanisms. Studies are needed to examine the effect of such nonbridging ligands for reactions of analogous cobalt(III) complexes with such reducing agents as $Cr(bipy)_3^{2+}$ and $Ru(NH_3)_6^{2+}$ which are thought or known to react by outer-sphere mechanisms (5,6,98).

It is thus very probable that inner-sphere mechanisms are obtained in most of the Co(III) - Cu(I) systems studied. It should not be assumed that all of the reactions proceed by an inner-sphere mechanism. The reaction of $Co(en)_3^{3+}$ necessarily is outer-sphere because of its substitution inertness. The low rate of reduction is cited as being consistent with the conclusion that most of the cobalt(III) complexes are reduced by Cu^+ in an inner-sphere process. The very drastic change in reaction rate when the ligand ethylenediamine is replaced by two chloride ligands is firm indirect evidence for the cis complex proceeding by an inner-sphere mechanism.

Endicott and Taube (6) have concluded that reductions by Cu^+ follow an outer-sphere mechanism. This conclusion was based on a limited number of reductions of cobalt(III) complexes by Cu^+. A more important difficulty with their data was the very small concentrations of Cu^+ generated by equilibrating a copper(II) solution over a clean copper metal. These workers reported a value of $>10^2$ for the reduction rate of ROH_2^{3+}. This value is apparently quite incorrect. A rate of $\sim 10^5 - 10^7$ was reported for the reduction of RBr^{2+}; this value is of the right order of magnitude. The present study has included several preparations of Cu^+ by the method of Endicott and Taube (6). The rate constants obtained in this study with that source of Cu^+ were not significantly

different from those of most experiments; it was not possible to reproduce the published values using their procedure. In view of the extensive evidence accumulated by this study, the results and conclusions of Endicott and Taube are believed to be quite incorrect. It is thus felt that the evidence cited in the previous section warrants the conclusion that inner-sphere mechanisms are obtained in most of the copper(I) reductions of the cobalt(III) complexes.

Vanadium(II) - Chlorochromium(III) Reaction

Mechanism of the reaction of V^{3+} and Cr^{2+} in perchlorate solution

The original study (34) of the V^{3+} - Cr^{2+} reaction mechanism expressed the dependence of the apparent second-order rate constant, k_3, by a 2-parameter relation, Equation 107

$$k_3 = q/(r + [H^+]) \qquad (107)$$

The rate law was originally interpreted (34) in terms of a sequence of consecutive reactions (Equations 108, 109, and 110), mechanism A, in which the empirical parameters are $q = k_1k_3/k_2$ and $r = k_3/k_2$. Haim (102) has very clearly pointed out a type of ambiguity that remains unresolved from a kinetic study of a reaction whose mechanism consists of a single path with consecutive steps. One cannot learn the order in which the steps occur but only the composition of each activated complex. Mechanism B, suggested by Haim (102), is equally consistent with Mechanism A

$$V^{3+} + Cr^{2+} \underset{2}{\overset{1}{\rightleftharpoons}} V(OH)Cr^{4+} + H^{+} \quad (108)$$

$$V(OH)Cr^{4+} \xrightarrow{3} V^{2+} + CrOH^{2+} \quad (109)$$

$$CrOH^{2+} + H^{+} \xrightarrow{\text{rapid}} Cr^{3+} \quad (110)$$

Mechanism B

$$V^{3+} + H_2O \rightleftharpoons VOH^{2+} + H^{+} \text{ (rapid, } Q_a) \quad (111)$$

$$VOH^{2+} + Cr^{2+} \underset{2'}{\overset{1'}{\rightleftharpoons}} V(OH)Cr^{4+} \quad (112)$$

$$V(OH)Cr^{4+} + H^{+} \xrightarrow{3'} V^{2+} + Cr^{3+} + H_2O \quad (113)$$

observed kinetics; in terms of mechanism B, the values of q and r are $q = k_1' Q_a$ and $r = k_2'/k_3'$.

No rigorous method will serve to distinguish these alternatives, but the following indirect argument can be advanced in favor of mechanism B. The reaction involves the intermediate $V(OH)Cr^{4+}$; provided one accepts that its most probable structure is a OH^{-} -bridged species, then the mechanism incorporates an inner-sphere transition state. The pattern of reactivity established for Cr^{2+} inner-sphere reactions with Co(III), Cu(II), Cr(III), and Fe(III) complexes (95,103, 104) is that hydroxide ion is a favored bridging ligand, as evidenced by the major rate terms which are a function of $1/[H^{+}]$. Accepting on a provisional basis that the pattern of reactivity toward aquo and hydroxo complexes consititutes evidence concerning mechanism, B is thus the preferred pathway.

Conclusions based solely on analogy must be regarded as tentative, however.

Reactions in chloride solution Does the detailed mechanism of the reaction of V^{2+} and $CrCl^{2+}$ (Equation 59) involve an inner-sphere transition state? The chlorovanadium(III) substitution equilibrium is established rapidly, and hence the question cannot be answered by experiments on the product distribution. Whatever the mechanism of the $V^{2+} + CrCl^{2+}$ reaction, its reverse, $V^{3+} + Cr^{2+} + Cl^-$, must proceed by an identical transition state.

The mechanisms to be considered are (1) an inner-sphere reaction of VCl^{2+} and Cr^{2+}, and (2) oxidation of $CrCl^+$ by V^{3+}. Processes which lead to the same result (e.g., reduction of an ion pair $V(H_2O)_6^{3+} \cdot Cl^-$ by Cr^{2+}) are indistinguishable and will not be considered as separate mechanisms. A small concentration of VCl^{2+} is in rapid equilibrium with V^{3+} and Cl^-; this does not necessarily implicate VCl^{2+} as a reactant. Moreover, since the Cr(III) product is $CrCl^{2+}$, if VCl^{2+} is a reactant, as in mechanism 1, an inner-sphere mechanism is demanded.

Precedents for both of the mechanisms under consideration are available. Mechanism 1 operates in the reaction of $FeCl^{2+}$ and Cr^{2+} (95), and in the chromium(II) - (III) exchange reaction of $CrCl^{2+}$ and Cr^{2+} (81,103). Each of these processes is accompanied by a parallel pathway involving $M^{3+} + Cr^{2+} + Cl^-$

which amounts to mechanism 2. The ability to establish firmly the existence of parallel pathways in those instances, and not in the present case, arises because the Fe(III) and Cr(III) substitution rates are low relative to the rates of oxidation-reduction. The clear-cut distinction is not possible in the present reaction since substitution on V(III) occurs more rapidly than its reduction. Indirect arguments can be advanced concerning the mechanism, based on comparisons with known cases, as follows.

Actually, the reaction under consideration proceeds along two parallel paths, as shown by the form of the rate expressions for the reaction occurring in the forward and reverse directions, $k_1 = e + f/[H^+]$ and $k_2 = g + h/[H^+]$. Consider first the transition state with the composition $[VCrClOH^{3+}]^{\ddagger}$. It follows that Cl^- is in the primary coordination sphere of chromium in the transition state since the species $CrCl^{2+}$ is involved. It is concluded that the metal atoms in the transition state for reaction are bridged by OH^-, partly on the basis of analogy with reaction of known mechanisms[14], and partly by the precedent set by the V(III) - Cr(II) reaction in ClO_4^- solution, where the high reactivity

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[14] The $[H^+]$ dependence noted here closely parallels the chromium(II)-catalyzed reactions of chromium(III) complexes (9, 105-108). The rates of the reactions of $CrCl^{2+}$ (106) and $CrCl^{2+}$ (107) with Cr^{2+} are of the form $k[CrX^{2+}][Cr^{2+}]/[H^+]$.

of VOH^{2+} and Cr^{2+} in an inner-sphere process has been noted.

A reaction scheme embodying these concepts is given in Equations 114 and 115, in which hydroxide ion is arbitrarily assigned the role of a bridging ligand on the trivalent ion. The rate constants in the mechanism are related to the empirical rate parameters by the equations $f = f'K_a$ and $h = h'Q_a$.

$$CrCl^{2+} \rightleftarrows Cr(OH)Cl^{+} + H^{+} \qquad k_a = 7 \times 10^{-6}\ \underline{M},\ \text{ref. 109} \qquad (114)$$

$$V^{2+} + Cr(OH)Cl^{+} \underset{h'}{\overset{f'}{\rightleftarrows}} VOH^{2+} + Cr^{2+} + Cl^{-} \qquad (115)$$

With regard to the transition state that contains one added proton, reaction 59, the most probable configuration of atoms is <u>not</u> bridging by Cl^-, but either an outer-sphere or a water-bridged transition state. A precedent for parallel inner- and outer-sphere pathways in the same reaction was found in the work of Candlin, Halpern and Nakamura (7). The basis of this conclusion rests on the known relative efficiency of OH^- and Cl^- as bridging anions. The relative rate constants observed here are $f'/e \simeq 10^4$ and $h'/g \simeq 8 \times 10^4$. Since OH^- and Cl^- generally act as bridging groups of roughly equal effectiveness, the low reactivity of chloride compared to hydroxide renders a chloride-bridged mechanism an unlikely feature of reaction.

The equilibrium quotient for reaction of V^{3+} and Cr^{2+} (Equation 116) can be computed from $k_2/k_1\ Q_1$. At 25.0° and 2.50 M ionic strength the value is $k_3/k_4 = 1.7 \times 10^3$. The value computed from electrode potentials that are known only approximately and in different media ca. 10^3. In this regard, Latimer (74) gives the value, $E^o = +0.41$ for $Cr^{2+} = Cr^{3+} + e$. A considerable range of values 0.4 to 0.45 was obtained by Grube and Schlect (110). The value of $E^o = +0.276$ for $V^{2+} = V^{3+} + e$ was reported in reference 111.

The rate constant, k_4, for the reverse reaction (Equation 116)

$$Cr^{2+} + V^{3+} \underset{4}{\overset{3}{\rightleftarrows}} Cr^{3+} + V^{2+} \qquad (116)$$

of the second step of the proposed reaction scheme has previously been neglected. The calculated equilibrium quotient for this reaction may be used to justify the previous omission of k_4. The value of k_4 ($M^{-1}\ sec^{-1}$) so computed ($k_4 = 5.7 \times 10^{-4}/(0.12 + [H^+])$) is small enough that its neglect in the rate equations was justified under all conditions employed here.

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APPENDIX

Computer program for nonsteady-state kinetics

Contents

(1) Introduction

(2) User instructions

(3) Flow diagram

(4) Fortran listings

Introduction This program sets up differential equations for the following reaction scheme, and solves the equations using the Runge-Kutta iteration procedure.

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C + D + E$$

$$C + D \xrightarrow{k_3} E + A$$

The following information is supplied for each computation:

IA, IB,...etc.	Initial concentration of each substance.
EA, EB,...etc.	Molar absorptivity for each substance times optical path length. (If one desires to compute only concentrations and not absorbances, these values are arbitrary.)
R1, R2, R3	Known values of the three rate constants.

The Runge-Kutta method of solving initial-value problems utilizes the differential equations to approximate the slopes over a given interval (112). If the interval is small enough, then $y_{n+1} = y_n + k\Delta t$, $x_{n+1} = x_n + k\Delta t$ and succeeding values of x, y as a function of t can be calculated. The subroutine RNKT calculates four slopes · delt at what would correspond to previous time, p.t. + $\frac{DELT}{2}$, p.t. + DELT. These slopes are then used to calculate the new increments x,y (x-amount of intermediate formed in time DELT, y-amount of product formed in time DELT) by which the various concentrations are changed, TA, TB, ... are always the current value of the concentrations hence the functions are evaluated at (0,0) each time the subroutine is used.

The size of the chosen interval is not critical because a test of the resulting concentration change of A is always made. The value of TINT is automatically divided by 4 at the least, then 8, 12, 18, 24, ... if necessary. The actual evaluation is done over the smaller intervals, but printed values correspond to the interval TINT. The number of times the interval is subdivided is controlled by ITR. If in "ITR" times the convergence test is not met, the program repeats these calculations with the iterations printed option in effect.

User instructions Some definitions are as follows:

NINT- Number of equal time intervals ($\leq$ 49 unless dimensions in program are changed)

ITR- Number of times that a given time interval can be subdivided to obtain convergence; 10-20 is appropriate.

ITP- Iterations printed? 0=no, 1=yes

TINT- Size of each time interval

RKTEST- Fraction of concentration of A that represents a suitable change in an interval; use $1x10^{-3}$.

Input instructions are as follows:

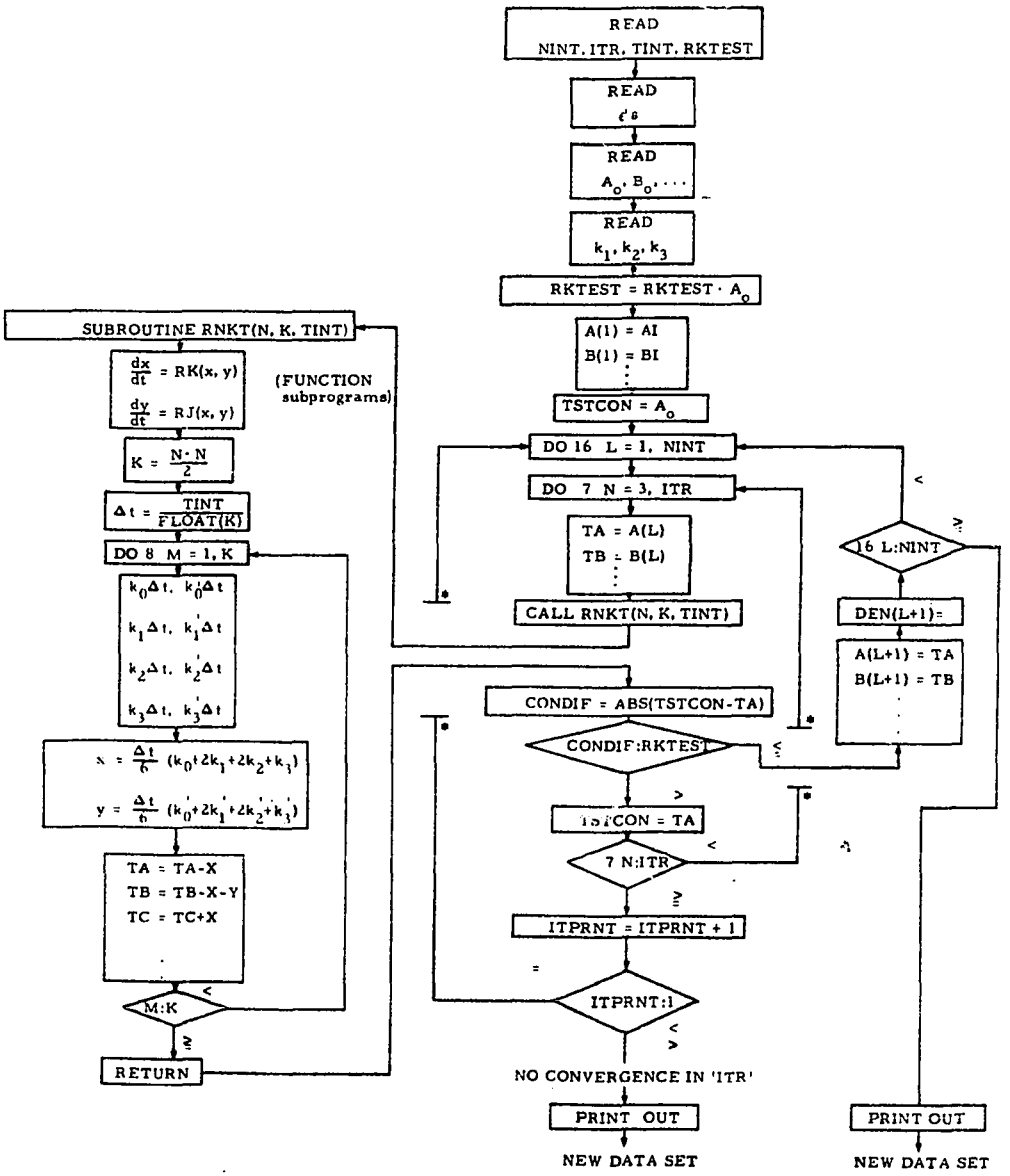
Card 1: 1 in col. 1; Title of particular run in col. 2-72

Card 2: Using format (4I6): 1, NINT, ITR, ITP; format (2E 12.7): TINT, RKTEST

Card 3: Using format (6F 12.7) EA, EB, EC, ED, EE, EF

Card 4: Using format (6F 12.7): IA, IB, IC, ID, IE, IF

Card 5: Using format (3F 12.7): Rate constants R1, R2, R3.


READ
NINT, ITR, TINT, RKTEST
READ
READ
READ
RKTEST = RKTEST · A0
A(1) = AI
B(1) = BI
TSTCON = A0
DO 16 L = 1, NINT
DO 7 N = 3, ITR
TA = A(L)
TB = B(L)
CALL RNKT(N, K, TINT)
CONDIF = ABS(TSTCON-TA)
CONDIF:RKTEST
TSTCON = TA
7 N:ITR
ITPRNT = ITPRNT + 1
ITPRNT:1
NO CONVERGENCE IN 'ITR'
PRINT OUT
NEW DATA SET
16 L:NINT
DEN(L+1)=
A(L+1) = TA
B(L+1) = TB
PRINT OUT
NEW DATA SET
SUBROUTINE RNKT(N, K, TINT)
(FUNCTION subprograms)
K = (N-N)/2
Δt = TINT/FLOAT(K)
DO 8 M = 1, K
TA = TA-X
TB = TB-X-Y
TC = TC+X
M:K
RETURN

```
                                        IBM OS/360 BASIC FORTRAN IV (E) COMPILATION
C    RUNGE-KUTTA SOLUTION TO NON-STEADY STATE PROBLEM
C      A + B = C + D + F  (FORWARD RATE CONSTANT R1,2ND ORDER,)
C      F + C + D = A + B  (FORWARD RATE CONSTANT R2, 3RD ORDER)
C      C + D = A + E      (FORWARD RATE CONSTANT R3, 2ND ORDER)
C      SUBSTANCES C AND D REPRESENT INTERMEDIATES
C      THE OVER-ALL REACTION IS  B = E + F
       COMMON R1,R2,R3,TA,TB,TC,TD,TE,TF
     1 FORMAT(4I6,2E12.7)
     2 FORMAT(6E12.7)
  1001 FORMAT(18A4)
       DIMENSION A(80),B(80),C(80),D(80),TITLE(18),DEN(80),E(80),F(80)
    35 READ (1,1001)(TITLE(I),I=1,18)
       READ (1,1)IPROB,NINT,ITR,ITPRNT,TINT,RKTEST
       IF (IPROB)100,100,37
    37 READ (1,2)EA,EB,EC,ED,EE,EF
       READ (1,2)AI,BI,CI,DI,EI,FI
       READ (1,2)R1,R2,R3
       RKTEST=RKTEST*AI
       A(1)=AI
       B(1)=BI
       C(1)=CI
       D(1)=DI
       E(1)=EI
       F(1)=FI
       DEN(1)=A(1)*EA+B(1)*EB+C(1)*EC+D(1)*ED+E(1)*EE+F(1)*EF
       TSTCON=AI
       IF (ITPRNT-1)39,38,39
    38 WRITE (3,4)R1,R2,R3,RKTEST
     4 FORMAT(1H1,T6,'CRCL+2 - V+2 RXN'/,T6,'R1,R2,AND R3 = ',1P3E12.5/
      1,T6,'RKTEST = ',1PE12.5)
    39 DO 16 L=1,NINT
       DO 7 N=2,ITR
C      TA IS THE CURRENT VALUE OF THE CONCENTRATION OF A,  IB ETC.
       TA=A(L)
       TB=B(L)
       TC=C(L)
       TD=D(L)
       TE=E(L)
       TF=F(L)
       CALL RNKT(N,K,TINT)
       IF (ITPRNT-1)28,27,28
    27 WRITE (3,25)K,TA,TB,TC,TD,TE,TF,L
    25 FORMAT(1HO,T6,'K= ',I2/,T6,'CONC. ARE ',1P6E12.5/,T6,'AFTER RNKUTA
      1 CALC, INT. = ',I2)
    28 CONDIF=ABS(TSTCON-TA)
       IF (CONDIF-RKTEST)13,13,14
    14 TSTCON=TA
     7 CONTINUE
       ITPRNT=ITPRNT+1
       IF (ITPRNT-1)8,39,8
     8 WRITE (3,1001)(TITLE(I),I=1,18)
       WRITE (3,122)R1,R2,R3
   122 FORMAT(1HO,T6,'CRCL+2 - V+2 RXN'/,T6,'R1 = '1PE10.3/,T6,'R2 = '
```

```
      SUBROUTINE RNKT(N,K,TINT)
C     THIS SUBROUTINE DEFINES INTERVALS AND SLOPES FOR RUNGE-KUTTA
      DIMENSION A(80),B(80),C(80),D(80),TITLE(18),DEN(80),E(80),F(80)
      COMMON R1,R2,R3,TA,TB,TC,TD,TE,TF
      K=N*N/2
      DELT=TINT/FLOAT(K)
C     THE FUNCTION X REPRESENTS THE NEXT INCREMENT OF DECREASE IN THE
C     CONCENTRATION OF A, AND THE ACCOMPANYING INCREASE IN CONCENTRATIONS
C     OF C AND D.  Y REPRESENTS SAME QUANTITIES DEFINED FOR B AND E.
      DO 8 M=1,K
      RK1=RK(0.0,0.0)*DELT/2.0
      RJ1=RJ(0.0,0.0)*DELT/2.0
      RK2=RK(RK1,RJ1)*DELT/2.0
      RJ2=RJ(RK1,RJ1)*DELT/2.0
      RK3=RK(RK2,RJ2)*DELT
      RJ3=RJ(RK2,RJ2)*DELT
      RK4=RK(RK3,RJ3)*DELT
      RJ4=RJ(RK3,RJ3)*DELT
C     THE INCREMENTS AND DECREMENTS ARE CALCULATED FROM A PARTICULAR SET
C     OF RUNGE KUTTA COEFFICIENTS.  OTHER EQUATIONS AND COEFFICIENTS
C     ARE SOMETIMES USED.
      X=(2.0*RK1+4.0*RK2+2.0*RK3+RK4)/6.0
      Y=(2.0*RJ1+4.0*RJ2+2.0*RJ3+RJ4)/6.0
      TA=TA-X
      TB=TB-X-Y
      TC=TC+X
      TD=TD+X
      TE=TE+Y
      TF=TF+X+Y
    8 CONTINUE
      RETURN
      END

        SIZE OF COMMON   000036    PROGRAM  003380

                         END OF COMPILATION  RNKT

      FUNCTION RK(X,Y)
      DIMENSION A(80),B(80),C(80),D(80),TITLE(18),DEN(80),E(80),F(80)
      COMMON R1,R2,R3,TA,TB,TC,TD,TE,TF
      RK=R1*(TA-X)*(TB-X-Y)-R2*(TC+X)*(TD+X)*(TF+X+Y)-R3*(TC+X)*(TD+X)
      RETURN
      END

        SIZE OF COMMON   000036    PROGRAM  002830

                         END OF COMPILATION  RK

      FUNCTION RJ(X,Y)
      DIMENSION A(80),B(80),C(80),D(80),TITLE(18),DEN(80),E(80),F(80)
      COMMON R1,R2,R3,TA,TB,TC,TD,TE,TF
      RJ=R3*(TC+X)*(TD+X)
      RETURN
      END

        SIZE OF COMMON   000036    PROGRAM  002764

                         END OF COMPILATION  RJ
```

```
     1)PE10.3/,T6,'R3 = '1PE10.3)
      WRITE (3,15)ITR
   15 FORMAT(1HO,T6,'NO CONVERGENCE IN 'I2,' ITERATIONS')
      WRITE (3,22)CONDIF,RKTEST
   22 FORMAT(1HO,T6,'CONDIF AND RKTEST ARE '1PE12.5,' AND '1PE12.5)
      WRITE (3,10)K,TA,TB,TC,TD,TE,TF
   10 FORMAT(1HO,T6,'K = 'I2/,T6,'TA = '1PE12.5/,T6,'TB = '1PE12.5/,
     1T6,'TC = '1PE12.5/,T6,'TD = '1PE12.5/,T6,'TE = '1PE12.5/,T6,
     1'TF = '1PE12.5)
      GO TO 35
   13 A(L+1)=TA
      B(L+1)=TB
      C(L+1)=TC
      D(L+1)=TD
      E(L+1)=TE
      F(L+1)=TF
C     THE FOLLOWING EQUATION COMPUTES THE VALUE OF ABSORBANCE (DEN)
      DEN(L+1)=A(L+1)*EA+B(L+1)*EB+C(L+1)*EC+D(L+1)*ED+E(L+1)*EE
     1+F(L+1)*EF
   16 CONTINUE
   17 WRITE (3,1001)(TITLE(I),I=1,18)
      WRITE (3,122)R1,R2,R3
      WRITE (3,1222)EA,EB,EC,ED,EE,EF
 1222 FORMAT(1HO,T6,'EA = '1PE10.3/,T6,'EB = '1PE10.3/,T6,'EC = '1PE10.3
     1/,T6,'ED = '1PE10.3/,T6,'EE = '1PE10.3/,T6,'EF = '1PE10.3)
      WRITE (3,24)
   24 FORMAT(1HO,T10,'TIME          A          B          C
     1       D          E          F       ABSORBANCE')
      ZERO=0.0
      WRITE (3,26)ZERO,AI,BI,CI,DI,EI,FI,DEN(1)
   26 FORMAT(1HO,T4,1P8E14.5)
      NINT=NINT+1
      DO 19 L=2,NINT
      TIME=TINT*FLOAT(L-1)
      WRITE (3,26)TIME,A(L),B(L),C(L),D(L),E(L),F(L),DEN(L)
   19 CONTINUE
      GO TO 35
  100 STOP
      END

        SIZE OF COMMON  000036    PROGRAM  005244

                        END OF COMPILATION  MAIN
```

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