symmetry about the nickel atom are the result of attractive forces when explanatory repulsive forces are so obviously present. Repulsion explains the additional distortion in the monoclinic structure where the Cl(4)···N(32′) distance is also short (3.17 A). Also it appears, from the similarity of their ultraviolet–visible spectra,[6] that the two crystalline forms of $[Ni(etu)_4Br_2]$ are isostructural with the chlorine complexes; there halogen–nitrogen hydrogen bonds are less likely to exist.

The short S···N distances in the triclinic structure connect ethylenethiourea rings in different molecules which, though related by centers of symmetry, are not coplanar, being separated normally by about 0.5 A. The possibility of hydrogen bonding in this case cannot be ruled out although it seems unlikely.

In an independent infrared investigation one of us (S. L. H.) has found evidence that there is less hydrogen bonding in monoclinic $[Ni(etu)_4Cl_2]$, and more in triclinic $[Ni(etu)_4Cl_2]$, than in the free ligand. Wheatley, however, considered that there was no real evidence for N–H···S hydrogen bonds in the crystalline free ligand because there were other nonbonded interatomic distances that were abnormally short. This conclusion seems valid in the present work.

It is evident from Table V and the figures that the Ni–S–C bond angle is rather flexible and that an ethylenethiourea ligand can rotate easily about its S–C bond. Both factors help to explain why $[Ni(etu)_4Cl_2]$ molecules can form stable crystals with similar densities but different molecular environments.

Finally, it is to be noted that the nickel atom lies close (0.2 A) to the best least-squares planes through the individual ethylenethiourea ligands of monoclinic $[Ni(etu)_4Cl_2]$ but 0.8 to 2.0 A away from these planes in triclinic $[Ni(etu)_4Cl_2]$. Thus the geometry around the sulfur atoms does not indicate any special interaction of d orbitals on nickel and sulfur.

Acknowledgments.—The authors wish to thank Dr. R. L. Carlin for his interest in this work and also Dr. P. Main, of Purdue University, for his generous help with the extensive least-squares refinement calculations. A version of Figure 2 (monoclinic structure) at an early stage of refinement[16] was prepared by Dr. C. K. Johnson. The use of his program[17] and computing facilities provided by Dr. J. Ibers at Northwestern University made it possible to present stereoscopic illustrations with this paper.

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(16) C. K. Johnson, "Stereoscopic Drawings of Some Crystal Structures Presented at the Joint Meeting of the American Crystallographic Association and the Mineralogical Society of America, June 27–July 2, 1965, Gatlinburg, Tenn."

(17) C. K. Johnson, "ORTEP, a Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations," Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

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The Rate of Displacement of H_2O in $Co(CN)_4(SO_3)OH_2^{3-}$ by CN^- and the Formation Quotient of $Co(CN)_4(SO_3)NH_3^{3-}$ from $Co(CN)_4(SO_3)OH^{4-}$ and NH_3[1]

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A kinetic study has been made of the rate of displacement of OH^- in $Co(CN)_4(SO_3)OH^{4-}$ by CN^-. All experiments were at 25°, at unit ionic strength, and in the presence of a large excess of CN^-. In each experiment pseudo-first-order kinetic behavior was observed and characterized by a rate constant. The rate data are in agreement with a rate law given by

$$\frac{d\ln\{[Co(CN)_4(SO_3)OH_2^{3-}] + [Co(CN)_4(SO_3)OH^{4-}]\}}{dt} = \frac{1.73(CN^-)}{0.028 + (CN^-)}\,\frac{1}{1 + 776(OH^-)}$$

and are discussed in terms of a limiting type of SN1 mechanism. A numerical value of 98 ± 3 is reported for the equilibrium quotient for formation of $Co(CN)_4(SO_3)NH_3^{3-}$ by reaction of $Co(CN)_4(SO_3)OH^{4-}$ and NH_3.

Introduction

This paper is the first of a series dealing with the ligation reactions of $Co(CN)_4(SO_3)OH_2^{3-}$. In the present paper we report kinetic studies of the rate of displacement of H_2O in $Co(CN)_4(SO_3)OH_2^{3-}$ by CN^-, a process which occurs very rapidly by a limiting type of SN1 mechanism. In addition, a value is reported for the formation quotient of $Co(CN)_4(SO_3)NH_3^{3-}$, produced by the reaction of $Co(CN)_4(SO_3)OH^{4-}$ with aqueous NH_3.

The results are discussed in terms of the assumption that the SO_3^{2-} ligand has a remarkable *trans*-labilizing effect in Co(III) complexes. This assumption has been used to explain the results of earlier preparative studies[2,3] and, more recently, kinetic studies involving octahedral Co(III) complexes.[4,5]

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(1) This work was supported by the Atomic Energy Commission.

(2) J. C. Bailar, Jr., and D. F. Peppard, *J. Am. Chem. Soc.*, **62**, 105 (1940).

(3) A. V. Bobaeva and I. B. Boranovskii, *Russ. J. Inorg. Chem.*, **7**, 404 (1962).

(4) J. Halpern, R. A. Palmer, and L. M. Blakley, *J. Am. Chem. Soc.*, **88**, 2877 (1966).

(5) H. H. Chen, M. S. Tsao, R. W. Gaver, P. H. Tewari, and W. K. Wilmarth, *Inorg. Chem.*, **5**, 1913 (1966).

Experimental Section

Reagents.—All commercial inorganic chemicals were of reagent grade and were used without further purification. The preparation of $Na_5[Co(CN)_4(SO_3)_2]\cdot 3H_2O$ and $Na_4Co(CN)_5SO_3\cdot 2H_2O$ has been described previously.[5]

The stock solutions of $Co(CN)_4(SO_3)OH^{4-}$, which were used in the kinetic studies, were prepared in the following manner and used within a period of a few hours, a time interval in which no appreciable decomposition occurs.[6] First, $Co(CN)_4(SO_3)_2^{5-}$ was converted to $Co(CN)_4(SO_3)OH_2^{3-}$ and SO_2 by dissolving solid $Na_5[Co(CN)_4(SO_3)_2]\cdot 3H_2O$ in water containing enough $HClO_4$ to adjust the pH to 1.0 after reaction. At this pH, aquation of one SO_3^{2-} ligand occurs within a matter of seconds and further aquation of $Co(CN)_4(SO_3)OH_2^{3-}$ is very slow. The SO_2 was then removed by bubbling N_2 through the solution for 1 hr at room temperature, a time which exploratory tests showed was more than adequate. To obtain efficient purging of the SO_2, the N_2 was passed through a sintered-glass disk which served as the bottom of the vessel containing the solution. The size of the disk was chosen so that the depth of the solution above the disk was only a few centimeters. After purging, the solution was diluted with NaOH and $NaClO_4$ solutions at concentrations such that conversion of $Co(CN)_4(SO_3)OH_2^{3-}$ to $Co(CN)_4(SO_3)OH^{4-}$ occurred and the final solutions had the composition desired for the kinetic experiments.

Apparatus.—Spectrophotometric measurements were made using a Beckman DU or a Cary Model 14 spectrophotometer. The stopped-flow apparatus was purchased from Atom-Mech Machine Co. and has been described in detail elsewhere.[7] A Beckman Research Model pH meter equipped with an E3 glass electrode and a fritted reference electrode No. 39071 was used in the pH measurements. The saturated KCl solution in the reference electrode was removed and replaced by 3.0 M NaCl, a procedure which prevented clogging of the fritted disk by precipitation of $KClO_4$ when measurements were made in solutions containing ClO_4^-.

Kinetic Procedures.—In solutions which were 0.25 M or greater in OH^-, the reaction was slow enough so that conventional mixing procedures could be used. Under these conditions the appropriate stock solutions, which had been brought to 25 ± 0.02°, were rapidly mixed and placed in the 1.0-cm quartz cell contained in the cell compartment of a Beckman DU spectrophotometer equipped with thermal spacers. Absorbancy measurements were made at appropriate time intervals without removal of the absorption cell from the cell compartment. In solutions less basic than 0.25 M OH^-, the solutions were mixed and absorbancy measurements obtained using the stopped-flow apparatus. In these measurements the total optical transmittance change in the absorption tube during reaction was kept below 3%. To a very good approximation under these conditions the change in transmittance is proportional to the change in optical density and hence to the concentration change of the absorbing species. As a result of this the vertical scale of the oscilloscope was linear in the concentration of the absorbing species, and the oscillograms could be treated as ordinary concentration–rate plots.

In the kinetic studies at 0.25 M OH^- and above, the hydroxide ion concentration was calculated directly from the composition of the various stock solutions used in the experiment. In the stopped-flow experiments at lower alkalinity the pH of the solution was measured after reaction was complete. The pH values were converted to OH^- concentrations by using a calibration curve obtained by measurement of the pH of solutions of unit ionic strength containing known amounts of OH^- in the range 1.0 to 1.0×10^{-4} M OH^-.

When the conventional mixing procedure was used, the absorbancy was measured at 305 mμ where the molar absorbancy indices of $Co(CN)_4(SO_3)OH^{4-}$ and $Co(CN)_5SO_3^{4-}$ are 2255 and 689, respectively. The solutions used in these measurements were so alkaline that the absorbancy of $Co(CN)_4(SO_3)OH_2^{3-}$ was negligible. The stopped-flow measurements were made at 320 mμ, a more favorable wavelength for this apparatus. The molar absorbancy indices of $Co(CN)_4(SO_3)OH^{4-}$, $Co(CN)_4(SO)_3OH_2^{3-}$, and $Co(CN)_5SO_3^{4-}$ are 770, 2030, and 431, respectively, at this wavelength.

The Formation Quotient of $Co(CN)_4(SO_3)OH_2^{3-}$.—Spectrophotometric measurements were carried out at λ 240 mμ where the molar absorbancy indices of $Co(CN)_4(SO_3)OH^{4-}$ and $Co(CN)_4(SO_3)NH_3^{3-}$ are 8.37×10^3 and 2.90×10^3, respectively.

Results

The displacement of OH^- in $Co(CN)_4(SO_3)OH^{4-}$ by CN^- was studied at 25°, unit ionic strength, and with the Na^+ concentration also fixed at unity.

$$CO(CN)_4(SO_3)OH^{4-} + CN^- \longrightarrow CO(CN)_5SO_3^{4-} + OH^-$$

In all experiments the reaction proceeded to completion. In any given experiment the rate was characterized by a pseudo-first-order rate constant k, defined by the expression $-d \ln\,[(Co(CN)_4(SO_3)OH_2^{3-}) + (Co(CN)_4(SO_3)OH^{4-})]/dt$. Numerical values of k were obtained from the linear plot of log $(A_t - A_\infty)$ *vs.* time, where A_t and A_∞ are the absorbancies of the solution at a time t and after a time long enough for the system to reach equilibrium, respectively. Pseudo-first-order behavior was observed in all experiments because the concentration of CN^- was always very large compared to the total Co(III) concentration.

In one series of experiments, all of which were carried out at 0.5 M CN^-, the OH^- concentration was varied over the range from 0.5 to 5×10^{-4} M. These results are presented in Figure 1 as a semilogarithmic plot of k *vs.* $-\log\,(OH^-)$. These experiments were carried out in triplicate, but the scale of the figure is such that the size of each single point more than covers the range in variation of k for each of the three replicate experiments.

Two other series of experiments were carried out, one at 0.50 M OH^- and the other at 1.10×10^{-2} M OH^-. In each series the CN^- concentration was varied from 0.50 to 0.02 M or less. The results of both series of experiments are presented in Figure 2 as a plot of k *vs.* the CN^- concentration. The numerical value of the ordinate to the right of the figure refers to the solid circles, the results obtained at 0.5 M CN^-. The ordinate values to the left of the figure refer to the open circles representing data obtained at 1.10×10^{-2} M OH^-. In all of this latter series of experiments there is the possibility that there is an appreciable error not present in the other experiments in the tabulated value of OH^- concentration.

Six experiments not included in Figures 1 or 2 were carried out at 0.25 M CN^-, three at 0.75 M OH^-, and three at 0.25 M OH^-. The observed values of 10^3k were 2.83, 2.87, 2.63 sec^{-1} for the experiments in 0.75 M alkali and 7.60, 7.45, and 7.90 sec^{-1} for the 0.25 M alkali experiments.

The equilibrium quotient for the displacement of OH^- in $Co(CN)_4(SO_3)OH^{4-}$ by NH_3 was determined over the ranges of 9×10^{-5} to 9×10^{-6} M and 0.002

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(6) After standing a number of hours the $Co(CN)_4(SO_3)OH_2^{3-}$ is converted, apparently without loss of CN^- or SO_3^{2-}, to a complex ion which reacts only very slowly with CN^-. Present evidence indicates that this is a conversion of the complex from the *trans* to the *cis* configuration.

(7) G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963).

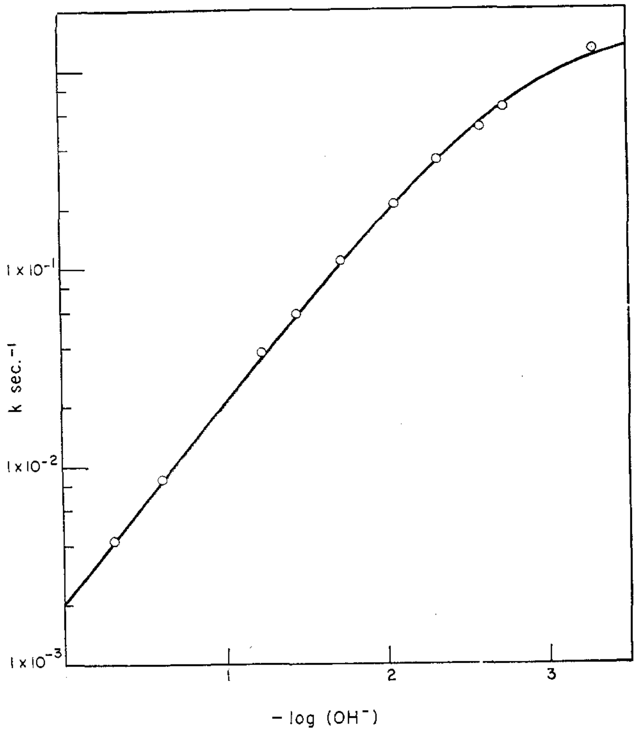

Figure 1.—The variation of k with OH^- concentration in the reaction of $Co(CN)_4(SO_3)OH^{4-}$ with CN^-.

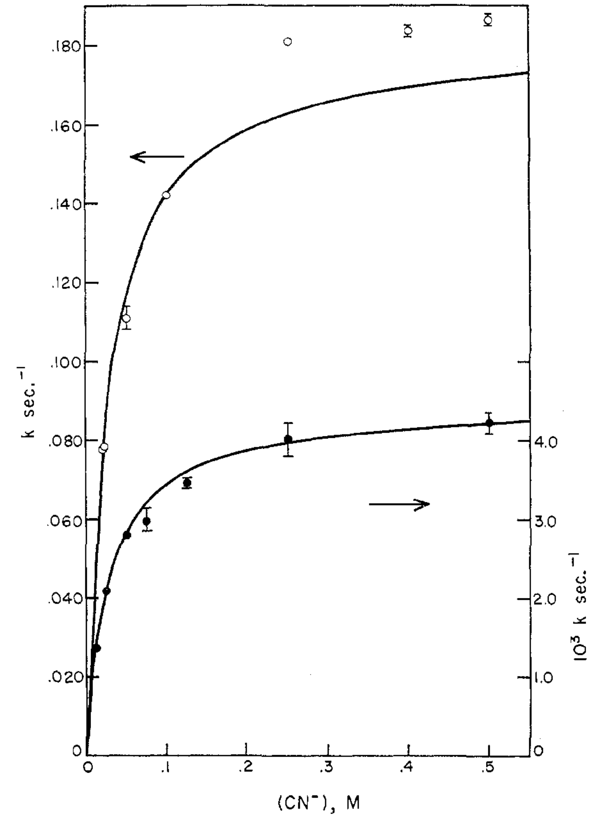

Figure 2.—The variation of k with CN^- concentration in the reaction of $Co(CN)_4(SO_3)OH^{4-}$ with CN^-.

to 0.5 M in the concentrations of Co(III) and NH_3, respectively.

$$Co(CN)_4(SO_3)OH^{4-} + NH_3 \overset{k_1}{\rightleftharpoons} Co(CN)_4(SO_3)NH_3^{3-} + OH^- \quad \text{(A)}$$

All experiments were at 25°, 0.5 M OH^-, and unit Na^+ concentration, with the ionic strength adjusted to unity with $NaClO_4$. The equation as written represents the net reaction at 0.5 M OH^- since conversion of $Co(CN)_4(SO_3)OH_2^{3-}$ to $Co(CN)_4(SO_3)OH^{4-}$ is essentially quantitative at this alkalinity. At equilibrium, the relationship between A_0, A_∞, ϵ_{RNH_3}, ϵ_{ROH}, K_1, and [Co(III)] is given by the following well-known equation, where A_∞ is the absorbancy at equilibrium at the specified NH_3 concentration, A_0 is the absorbance of a solution of $Co(CN)_4(SO_3)OH^{4-}$ at the same total Co(III) concentration, [Co(III)] is the total concentration of Co(III) in all forms, K_1 is the formation quotient for $Co(CN)_4(SO_3)NH_3^{3-}$, l is the length of the light path, and ϵ_{ROH} and ϵ_{RNH_3} are the molar absorbancy indices for $Co(CN)_4(SO_3)OH^{4-}$ and $Co(CN)_4(SO_3)NH_3^{3-}$, respectively.

$$\frac{A_0 - A_\infty}{[Co(III)]l} = \frac{(\epsilon_{ROH} - \epsilon_{RNH_3})K_1(NH_3)/(OH^-)}{l + K_1(NH_3)/(OH^-)}$$

The results of the spectrophotometric study are given in Figure 3 as a plot of $(A_\infty - A_0)/[Co(III)]l$ *vs.* the NH_3 concentration. The line drawn through the points represents the best nonlinear least-square fit[8] of the data and corresponds to a value of K_1 of 98 ± 3, where the indicated uncertainty is the standard deviation.

$$\frac{[Co(CN)_4(SO_3)NH_3^{3-}](OH^-)}{[Co(CN)_4(SO_3)OH^{4-}](NH_3)} = K_1$$

The average per cent deviation between theory and experiment in the 30 experiments is 4.5 and the maximum deviation is 14.9%, the latter occurring in an experiment at very low NH_3 concentration where the experimental error is relatively large.

Discussion

The rate of displacement of OH^- in $Co(CN)_4(SO_3)OH^{4-}$ by CN^- conforms to the following limiting type of SN1 mechanism

$$Co(CN)_4(SO_3)OH_2^{3-} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Co(CN)_4SO_3^{3-} + H_2O \quad (1)$$

$$Co(CN)_4(SO_3)OH_2^{3-} + OH^- \overset{K_2}{\rightleftharpoons} Co(CN)_4(SO_3)OH^{4-} + H_2O \quad (2)$$

$$Co(CN)_4SO_3^{3-} + CN^- \xrightarrow{k_3} Co(CN)_5SO_3^{4-} \quad (3)$$

To explain the kinetic results it is necessary to assume that the reactive intermediate $Co(CN)_4SO_3^{3-}$ generated in reaction 1 has a lifetime long enough to exhibit a selective reactivity pattern toward the various nucleophiles in the system. We are inclined to believe that $Co(CN)_4SO_3^{3-}$ is pentacoordinated, but the available evidence does not preclude the possibility of rearrangement to a configuration in which SO_3^{2-} acts as a bidentate ligand. In the present system, H_2O and CN^- compete for $Co(CN)_4SO_3^{3-}$ in the reverse of reactions 1 and 3, the latter being an irreversible process. As Figure 2 indicates, CN^- competes so effectively that

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(8) The least-square computer program was developed by and obtained from R. H. Moore and R. K. Zeigler and is described in Los Alamos Scientific Laboratory Report LA-2366, Oct 1959, obtainable from the U. S. Department of Commerce, Washington, D. C.

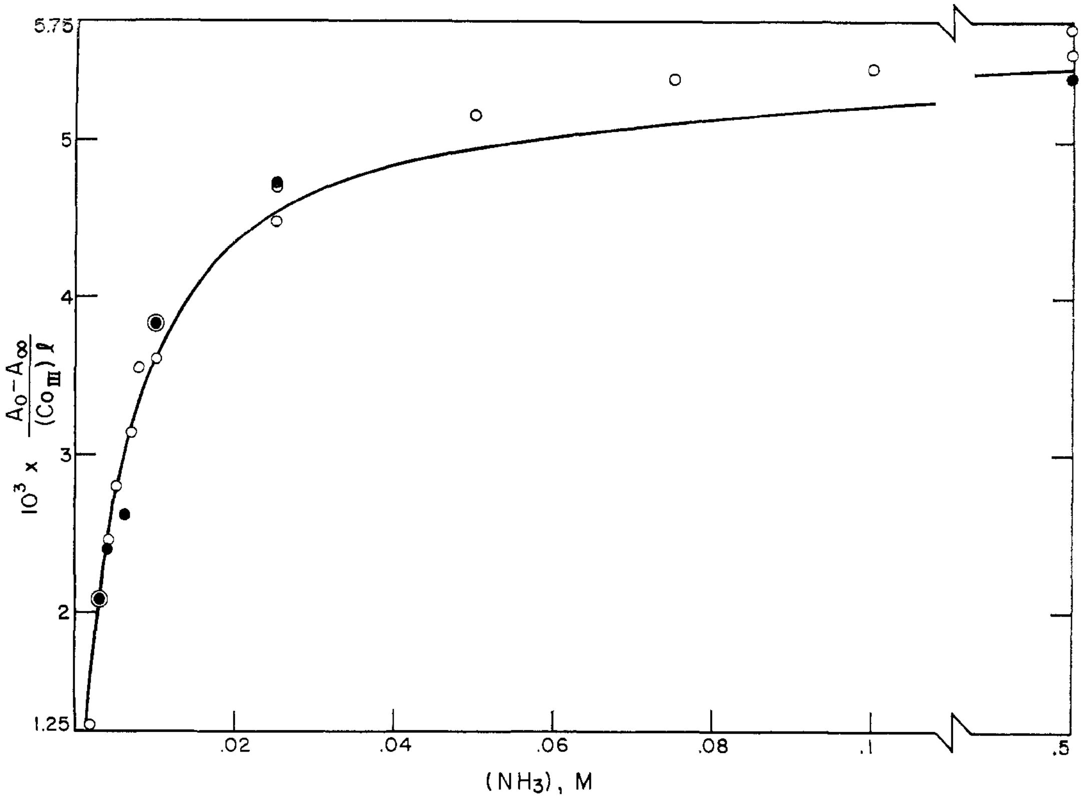

Figure 3.—Data used in the evaluation of the formation quotient of $Co(CN)_4(SO_3)NH_3^{3-}$.

the rate becomes zero order in CN^- at concentrations greater than 0.25 *M*. Under these conditions reaction 1 is rate determining and proceeds irreversibly.

The reaction mechanism based on eq 1–3 requires that the pseudo-first-order rate constant k be related to the kinetic and equilibrium parameters by

$$k = \frac{k_1(CN^-)}{(k_2/k_3) + (CN^-)} \frac{1}{1 + K_2(OH^-)} \qquad (4)$$

Equation 4 leads to the prediction that values of k measured at constant CN^- should vary inversely with the first power of the OH^- concentration as long as $K_2(OH^-) >> 1$, a condition which implies negligible protonation of $Co(CN)_4(SO_3)OH^{4-}$. This is the kinetic behavior observed in Figure 1 in experiments carried out at OH^- concentrations greater than 10^{-2} *M*. At sufficiently low OH^- concentration where protonation is complete and $K_2(OH^-) \ll 1$, the rate should become zero order in OH^-. The experimental results in Figure 1 at the lower OH^- concentrations begin to approach this limiting condition, as the curvature in the line indicates. Studies at lower OH^- concentrations would have been very desirable, since they would have increased the accuracy with which k_1 and K_2 could have been determined. However, these experiments were not feasible, since a further decrease in pH would have led to substantial conversion of CN^- to HCN.

The evaluation of k_2/k_3 is achieved most readily by carrying out a series of experiments at constant OH^- concentration under conditions where k decreases with decreasing CN^- concentration. Two such series of experiments are presented in Figure 2.

The solid lines of Figures 1 and 2 represent calculated values of k using eq 4 and the procedure of nonlinear least-square curve fitting. In the calculation the individual values of k were weighted as $1/k^2$, a weighting which assumes that all values of k are subject to the same per cent error. The least-square curve fitting yielded the values of $k_1 = 1.73 \pm 0.07$ sec^{-1}, $k_2/k_3 = (2.84 \pm 0.10) \times 10^{-2}$ *M*, and $K = 776 \pm 34$, where listed uncertainties are the standard deviations. In the total of 69 experiments, the average per cent deviation between the calculated and observed values of k was 4.4 and the maximum deviation was 11.5%. With one possible exception, the signs of the deviations were random and showed no trend with increasing OH^- or CN^- concentration, an indication that the deviations did not arise from an incorrect assignment of rate law. The possible exception may be seen by examining the upper curve in Figure 2 where there is a tendency for the calculated values of k to be considerably less than the experimental values at CN^- concentrations of 0.25 *M* or greater. These points include almost all of the deviations between theory and experiment which are greater than 6%. The values of the rate constants in this series of experiments are believed to be accurate, but there is reason to believe the recorded value of the OH^- concentration of 1.10×10^{-2} *M* may be subject to considerable error.

In terms of physical significance, the numerical value of k_1 implies a half-life for reaction 1 of 0.40 sec, a remarkably rapid substitution process for a diamagnetic Co(III) complex. The value of k_2/k_3, when corrected for the concentration of H_2O in the solution, corresponds to a reactivity ratio[9] of $CN^-/H_2O = 1.9 \times 10^3$ in their competition for $Co(CN)_4SO_3^{3-}$. The value of K_2 may be used to calculate an acidity quotient for $Co(CN)_4(SO_3)OH_2^{3-}$ at 25° and unit ionic strength of 1.6×10^{-11}. This may be compared with the structurally similar but less highly charged $Co(CN)_5OH_2^{2-}$ which has an acidity quotient of 1.6×10^{-10} under comparable conditions.[10]

In addition to the work under discussion, preliminary studies have been made of the rate of displacement of OH^- in $Co(CN)_4(SO_3)OH^{4-}$ by various other ligands. In the NH_3 system, NH_3 has a scavenger efficiency in its reaction with $Co(CN)_4SO_3^{3-}$ very similar to that of CN^-, but an accurate measurement of k_2/k_3 is complicated by the fact that formation of $Co(CN)_4(SO_3)NH_3^{3-}$ is not quantitative at low NH_3 concentrations. A tentative value of k_2/k_3 of 0.67 has been obtained for the SO_3^{2-} ligand, an indication that SO_3^{2-} is a much less efficient scavenger than CN^- or NH_3.

In the above discussion, it has been assumed that neither $Co(CN)_4(SO_3)OH^{4-}$ nor $Co(CN)_4(SO_3)OH_2^{3-}$ undergoes polymerization in solution, a reaction which does occur slowly in concentrated solutions[11] of $Co(CN)_5OH_2^{2-}$. Spectrophotometric studies carried out over the concentration range 3.8×10^{-4}–3.8×10^{-6} M provided no evidence for polymerization in that Beer's law was obeyed to within the limit of error of the measurements. In addition, the study of the equilibrium with NH_3 in reaction A seems to provide quite compelling evidence that $Co(CN)_4(SO_3)OH^{4-}$ is present primarily as a monomeric unit. If eq A were replaced by eq 5, then the appropriate mass action expression[12] would be

$$[Co(CN)_4SO_3]_x{}^{3-} + xNH_3 \rightleftharpoons xCo(CN)_4(SO_3)NH_3{}^{3-} \quad (5)$$

$$\frac{(Co(CN)_4(SO_3)NH_3)^x}{([Co(CN)_4SO_3{}^{3-}]_x)(NH_3)^x} = K \quad (6)$$

Theory and experiment are in reasonable agreement only when x is assumed to be unity. The equilibrium data do not rule out the possibility that $Co(CN)_4(SO_3)OH_2^{3-}$ undergoes polymerization, since it is present only at very low concentrations in the solutions at 0.5 M OH^- which were used in the equilibrium studies. However, the observation that the rate of the CN^- substitution reaction varies inversely with the OH^- concentration over the range 1.0×10^{-2} to 0.50 M OH^- implies a simplicity of mechanism which does not seem compatible with the existence of extensive polymerization of $Co(CN)_4(SO_3)OH_2^{3-}$.

Recently it has been reported that the displacement of OH^- in $Co(NH_3)_4(SO_3)OH$ by various ligands also proceeds by a limiting type of S$_N$1 mechanism.[4] However, in this system reaction 7 appears to be a major path for generation of the reactive intermediate.

$$Co(NH_3)_4(SO_3)OH \rightleftharpoons Co(NH_3)_4SO_3^+ + OH^- \quad (7)$$

To test whether an analogous path was of importance in our system, least-square calculations were made using eq 9, an equation consistent with a mechanism based on eq 1, 2, 3, and 8. The calculation yielded

$$Co(CN)_4(SO_3)OH^{4-} \underset{k_6}{\overset{k_5}{\rightleftharpoons}} Co(CN)_4SO_3^{3-} + OH^- \quad (8)$$

$$k = \frac{[k_1 + k_5K_2(OH^-)](CN^-)}{(k_2/k_3) + [k_6(OH^-)/k_3] + (CN^-)}\,\frac{1}{1 + K_2(OH^-)} \quad (9)$$

values of k_1, k_2/k_3, and K_2, which did not differ significantly from those listed above, and the negative value of $k_5 = -1.33 \times 10^{-4}$. It must be concluded any contribution to the generation of $Co(CN)_4SO_3^{3-}$ by reaction 8 is within the limit of error of our data, since negative values of rate constants are without physical significance.

Quite apart from the least-square calculation, it is possible to see merely by inspection of the kinetic data that reaction 8 is not of major importance in our system. The simple dependence of rate upon pH shown in Figure 1 is obviously that predicted by eq 4 and not the more complex behavior given by eq 9. Inspection of Figure 2 leads to the same conclusion. Equation 4 predicts that the shape of the two curves obtained at varying CN^- concentration should be very similar in the sense that the increase in k with increasing CN^- and the appearance of a rate zero order in CN^- should appear at the same CN^- concentration. By contrast, if eq 8 was of appreciable importance, eq 9 would predict that the upper curve should rise to its plateau value at much lower CN^- concentrations than the lower curve does. The two curves are obviously almost identical in shape.

At 0.75 M alkali, the most alkaline solution which was studied, a calculation based on the numerical value of K_2 listed above yields the concentration ratio $[Co(CN)_4(SO_3)OH^{4-}]/[Co(CN)_4(SO_3)OH_2^{3-}] = 580$. In the studies of the substitution of H_2O in $Co(NH_3)_4(SO_3)OH_2^+$, it was possible to make the concentration ratio $[Co(NH_3)_4(SO_3)OH]/[Co(NH_3)_4(SO_3)OH_2^+]$ much greater than 580 because of the acidity quotient of $Co(NH_3)_4(SO_3)OH_2^+$ is considerably greater than that of $Co(CN)_4(SO_3)OH_2^{3-}$, a factor which facilitates detection of reaction 7. However, it is not merely this difference in concentration ratio which leads to different rate laws in the two systems. Detailed calculations indicate that the value of k_5/k_1 in our system must be smaller than the corresponding ratio in the $Co(NH_3)_4(SO_3)OH_2^+$ system by at least a factor of 10^3.

In the Introduction it was suggested that the unusual kinetic behavior of $Co(CN)_4(SO_3)OH_2^{3-}$ was caused by the SO_3^{2-} ligand labilizing the H_2O ligand *trans* to itself. For this explanation to be applicable, it is necessary to assume that $Co(CN)_4(SO_3)OH_2^{3-}$ does have a *trans* configuration. The evidence supporting this assumption is reasonably strong, but not unambiguous. It is

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[9] The calculation is based in the assumption that the concentration of H_2O in the solution is 55 M.

[10] On making the calculation it is necessary to assume a value for the ionization quotient of H_2O at unit ionic strength, since an experimental value does not appear to be available for $NaClO_4$ solutions. The assumed value of 2×10^{-14} is consistent with that observed in NaCl solution.

[11] A. Haim and W. K. Wilmarth, *J. Am. Chem. Soc.*, **83**, 509 (1961).

[12] Polymerization would presumably occur through displacement of H_2O or OH^- in $Co(CN)_4(SO_3)OH_2^{3-}$ or $Co(CN)_4(SO_3)OH^{4-}$ by a bridging CN^- ligand. A polymeric Co(III) complex containing bound NH_3 is deemed unlikely.

known that $Co(CN)_4(SO_3)OH_2^{3-}$ is generated by aquation of $Co(CN)_4(SO_3)_2^{5-}$, a complex known to have a *trans* configuration, and that *trans*-$Co(CN)_4(SO_3)_2^{5-}$ is regenerated in the reaction of $Co(CN)_4(SO_3)OH_2^{3-}$ with SO_3^{2-}. If these processes occur with retention of configuration, then the assumption under consideration is valid. Indirect evidence for a *trans* configuration is also provided by the similarity in kinetic behavior of $Co(CN)_y(SO_3)OH_2^{3-}$ and $Co(NH_3)_4(SO_3)_x$, where x may be one of a variety of ligands.[4] In the complex where x is NH_3, exchange studies using $N^{15}H_3$ have established that labilization does occur only in the *trans* position.

The kinetic behavior of $Co(CN)_4(SO_3)OH_2^{3-}$ and $Co(NH_3)_4(SO_3)OH^{4-}$ is remarkable in two respects. First, reactions 1 and 7 occur with unusual rapidity, an indication that the presence of the SO_3^{2-} ligand lowers the free energy of activation for formation of an activated complex which presumably still has a coordination number of six. Of even greater importance from the standpoint of mechanistic interpretation of the kinetic data is the fact that the active intermediate generated by these complexes reacts much more readily with NH_3, CN^-, and other ligands than it does with H_2O, a species present at much higher concentration. An unpublished study of the displacement of H_2O in $Co(DH)_2(SO_3)OH_2^+$ by SCN^- suggests that, at least for SCN^-, this latter behavior may vary considerably, depending upon the ligands other than SO_3^{2-} present in the complex. Preliminary experiments[13] for this system at 25° and unit ionic strength yield the numerical values of $k_1 = 11\ \text{sec}^{-1}$ and $k_2/k_3 = 0.85\ M$.

In view of the sparsity of data, any detailed discussion of the origin of the kinetic behavior under discussion is probably premature. However, it may be noted that Ballhausen and Gray have predicted that the kinetic phenomenon known as the *trans* effect should be observed in octahedral complexes where a ligand undergoes strong metal-to-ligand π bonding.[14,15] It is possible that π bonding of this sort is of importance, but the rather extensive organic literature of the SO_3^- functional group suggests that other ligands such as NO_2^- or CN^- would accept electrons much more effectively in this type of bonding. A limiting type of S_N1 mechanism has been proposed for the displacement of H_2O in $Co(CN)_5OH_2^{2-}$, but *trans* activation by the CN^- ligand in this complex[16] is certainly less effective than that found in the sulfite complexes. In addition, it may be noted that the rate of exchange[17] of the axial CN^- ligand in $Cr(CN)_5NO^{2+}$ with labeled CN^- is only a factor of 14 greater than with the equational CN^-. This result is of some importance, since the prediction of *trans* activation by Ballhausen and Gray was based, in part, upon a consideration of the spectral properties of $Cr(CN)_5NO^{2-}$. A factor of 14 is, of course, not insignificant, but it hardly provides an overwhelming confirmation of the theory.

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[13] This work and analogous studies of the substitution reactions of $Co(DH)_2(NO_2)OH_2$ and $Co(DH)_2(CN)OH_2$ are being carried out by Hon-Gee Tsiang.

[14] C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **2**, 426 (1963). The SO_3^{2-} ligand is effective in *trans* activation of square-planar complexes, but it is generally assumed that these reactions involve an S_N2 mechanism.

[15] By contrast, C. K. Ingold, R. S. Nyholm, and M. L. Tobe, *Nature*, **187**, 477 (1960), have suggested that metal-to-ligand π bonding promotes S_N2 reaction mechanisms.

[16] A summary of this work has been published by A. Haim, R. J. Grossi, and W. K. Wilmarth, Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 31.

[17] R. B. Spencer and R. J. Myers, *J. Am. Chem. Soc.*, **86**, 522 (1964).

CONTRIBUTION FROM THE NATIONAL CHEMICAL RESEARCH
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Kinetics of Aquation of Aquopentachlororhodium(III) and Chloride Anation of Diaquotetrachlororhodium(III) Anions

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The kinetics of the reactions

$$RhCl_5(H_2O)^{2-} + H_2O \underset{k_4}{\overset{k_3}{\rightleftharpoons}} RhCl_4(H_2O)_2^- + Cl^-$$

were investigated. The process of equilibration is described by the rate law

$$\frac{-d[RhCl_5(H_2O)^{2-}]}{dt} = k_3[RhCl_5(H_2O)^{2-}] - k_4[RhCl_4(H_2O)_2^-][Cl^-]$$

Values for k_3 and k_4 were obtained at several temperatures in perchloric–hydrochloric acid media of ionic strength $\mu = 4.00$. At 30°, $k_3 = 8.0 \times 10^{-5}\ \text{sec}^{-1}$ and $k_4 = 6.4 \times 10^{-4}\ M^{-1}\ \text{sec}^{-1}$. The Arrhenius energies of activation, E_a, are 26 and 22 kcal/mole, respectively. The corresponding PZ factors are $1.6 \times 10^{14}\ \text{sec}^{-1}$ and $3.7 \times 10^{12}\ M^{-1}\ \text{sec}^{-1}$.

Introduction

A paper by Johnson, Basolo, and Pearson[1] on the reactions of acidoamminerhodium(III) complexes suggested that some of the reactions of rhodium(III) conformed more to an S_N2 type of mechanism than do

[1] S. A. Johnson, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 1741 (1963).