The Pentacyano Complexes of Cobalt(III). IV. Kinetics and Mechanism of the Substitution of Water in $Co(CN)_5OH_2{}^{2-}$ by Pyridine, Ammonia, Hydrazine, and Hydrazinium Ion[1]

By ROBERT BARCA,[2] JOHN ELLIS, MAAK-SANG TSAO, AND W. K. WILMARTH

A study has been made of the displacement of H_2O in $Co(CN)_5OH_2{}^{2-}$ by pyridine, hydrazine, hydrazinium ion, and ammonia. At low concentration of $Co(CN)_5OH_2{}^{2-}$ and 0.05–1.0 M concentration of a given ligand X, the rate law for each reaction is pseudo first order in $Co(CN)_5OH_2{}^{2-}$ and may be described by a rate constant k. For each ligand the quantity $k/[X]$ is a constant independent of the X concentration. The numerical values of $k/[X]$ are 52×10^{-5}, 10.0×10^{-5}, 14.7×10^{-5}, and 20.6×10^{-5} M^{-1} sec^{-1} for py, N_2H_4, $N_2H_5{}^+$, and NH_3, respectively. The acidity quotient of $Co(CN)_5N_2H_5{}^-$ has been measured.

Introduction

In our earlier studies of the rate of substitution of H_2O in $Co(CN)_5OH_2{}^{2-}$ by $N_3{}^-$ and SCN^-, evidence was presented which suggested that the reaction occurred by a limiting type of SN1 mechanism.[3] One of the pieces of evidence presented in support of this mechanism was the decrease in the ratio $k/[X^-]$ with increasing X^- concentration, where k is the pseudo-first-order rate constant for the reaction and X^- is the substituting ligand under consideration. The decrease in the quantity $k/[X^-]$ was found to be largest with $N_3{}^-$, the most reactive nucleophile, a phenomenon to be expected in a limiting type of SN1 mechanism.

In the present work, we chose to study the rate of reaction of $Co(CN)_5OH_2{}^{2-}$ with various amine ligands. These ligands were chosen for investigation, in part, because it was hoped that their relatively large basicity and the absence of the unfavorable electrostatic interaction present with X^- ligands would lead to relatively rapid reactions. The ligands also enabled us to make other interesting comparisons of the factors which may be correlated with reaction rate in the present system. Pyridine, hereafter designated py, was found to be more reactive than the more basic NH_3 ligand, possibly because of the greater ability of py to form metal to ligand π bonds in the activated complex. The study of N_2H_4 provided a test of the importance of the α effect, *i.e.*, the effect of having an unshared pair of electrons on the atom α to the reacting atom.[4] Finally, the studies revealed the rather remarkable observation that $N_2H_5{}^+$ was as reactive a nucleophile as the enormously less basic N_2H_4 ligand.

Experimental Section

Reagents.—Baker and Adamson reagent grade pyridine and Matheson Coleman and Bell hydrazine hydrate were purified by the selection of the center fraction of the distillate obtained using an all-glass, 15-plate, Oldershaw perforated-plate fractionating column. Stock solutions approximately 2.0 M were prepared and protected from unnecessary exposure to light. Purified hydrazine was handled only in an N_2 atmosphere. Stock solutions of $N_2H_5ClO_4$ and pyHClO_4 were prepared by slowly adding the appropriate amount of the purified amine to a solution of $HClO_4$. Stock $NaClO_4$ solutions were prepared by neutralizing reagent grade sodium carbonate with $HClO_4$.

Stock solutions of $Co(CN)_5OH_2{}^{2-}$ were prepared by the very rapid reaction of $Co(CN)_5N_3{}^{3-}$ and HNO_2

$$Co(CN)_5N_3{}^{3-} + HNO_2 + H^+ \longrightarrow Co(CN)_5OH_2{}^{2-} + N_2 + N_2O$$
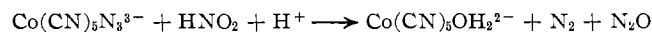
Solid $K_3Co(CN)_5N_3$ was weighed and transferred to a volumetric flask with a small amount of water. The solution was photosensitive and was exposed only to dim light for short periods of time. A 10% excess of dilute $HClO_4$ was added to the flask and the nitrous acid was generated by the dropwise addition of a standardized solution of $NaNO_2$. During the dropwise addition, the solution in the flask was vigorously shaken. After reaction, the excess acid was neutralized with $NaOH$ and the concentration adjusted to 0.01 M by the addition of water. No extensive study of the rate of polymerization was carried out. However, tests indicated that a 0.01 M stock solution could be stored for at least 2 weeks without detectable polymerization occurring.[5]

Preparation of the Complexes.—$[Co(NH_3)_5N_3]Cl_2$ was prepared by the method[6] of Linhard and Flygare by aerial oxidation of an ammoniacal solution containing $CoCl_2 \cdot 6H_2O$ and NaN_3. The purity of the product was established by comparison of the molar absorbancy indices with those previously reported.[6]

$K_3Co(CN)_5N_3$ was prepared by reaction of $Co(NH_3)_5N_3{}^{2+}$ and CN^-, a reaction which is catalyzed by Co^{2+} and presumably involves the inner-sphere redox reaction

$$Co(NH_3)_5N_3{}^{2+} + Co(CN)_5{}^{3-} \longrightarrow Co(CN)_5N_3{}^{3-} + Co(NH_3)_5{}^{2+}$$
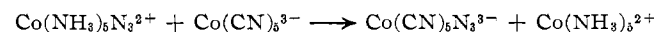
The reaction was carried out by adding 35 ml of a solution containing 11.25 g of KCN and 0.050 g of $CoCl_2 \cdot 6H_2O$ to a well-stirred slurry of 8.2 g of $[Co(NH_3)_5N_3]Cl_2$ in 49 ml of water. After the rapid reaction had occurred, solid $K_3Co(CN)_5N_3$ was precipitated by addition of 125 ml of ethanol and cooling of the solution to 0°.

$K_2Co(CN)_5py$ was formed by keeping a 100-ml solution 0.02 M in $K_2Co(CN)_5OH_2$, 0.02 M in $KClO_4$ (formed in the preparation of $K_2Co(CN)_5OH_2$ from $K_3Co(CN)_5N_3$), and 7.2 M in py at 40° overnight. The solution was then evaporated to 5–10 ml, cooled to 0°, and filtered to remove solid $KClO_4$. A 10-ml amount of py was added and the solution again was evaporated to a volume of approximately 5 ml to ensure complete conversion of $Co(CN)_5$-$OH_2{}^{2-}$ to $Co(CN)_5py^{2-}$. The solid $K_2Co(CN)_5py$ was then pre-

(1) This work was supported by the Atomic Energy Commission.
(2) Based in part on a thesis submitted by R. Barca to the Graduate School of the University of Southern California in partial fulfillment of the requirements for the M.S. degree.
(3) A. Haim and W. K. Wilmarth, *Inorg. Chem.*, **1**, 573 (1962).
(4) J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, **84**, 16 (1962).
(5) A. Haim and W. K. Wilmarth, *ibid.*, **83**, 509 (1961).
(6) M. Linhard and H. Flygare, *Z. Anorg. Chem.*, **262**, 328 (1950).

cipitated by addition of 80 ml of propanol, filtered, washed with propanol, washed with ether, and dried under vacuum.

Anal. Calcd for $K_2Co(CN)_5py$: C, 34.65; H, 1.47; N, 24.25; Co, 17.00. Found: C, 34.54; H, 1.66; N, 24.35; Co, 16.84.

$Ag_2Co(CN)_5N_2H_4$ was prepared by reaction of $Co(CN)_5OH_2^{2-}$ with N_2H_4, isolation of the sodium salt, and reprecipitation of the silver salt. The N_2H_4 reaction was carried out at 40° in a solution 0.2 M in $Co(CN)_5OH_2^{2-}$ and 0.4 M in both N_2H_4 and N_2H_5-ClO_4. After reaction, enough concentrated KOH solution was added to convert the $N_2H_5ClO_4$ to N_2H_4 and also to precipitate solid $KClO_4$ which was removed by filtration. The volume of the solution was reduced as quickly as possible to 10–20 ml with a rotary vacuum evaporator. The pH of the solution was then adjusted to 2.0 with $HClO_4$ and absolute ethanol was added until the solution was approximately 80% ethanol. The addition of ethanol caused the separation of a small amount of oil. Precipitation of the solid sodium salt, perhaps mixed with a small amount potassium salt, occurred when the solution containing the oil was allowed to stand in the refrigerator for 3 days. In earlier experiments it was established that a solid prepared by the above procedure contained both sodium and potassium ions. However, in the preparation under consideration, 0.80 g of the solid dissolved completely in 6.0 ml of $HClO_4$, indicating that the solid was largely the sodium salt, since there was no precipitate of $KClO_4$. The solid silver salt was precipitated with aqueous $AgNO_3$, filtered, washed with water until the filtrate was neutral, finally washed with alcohol and ether, and dried at room temperature for 4 hr under vacuum.

Anal. Calcd for $Ag_2Co(CN)_5N_2H_4$: C, 13.75; N, 22.47; H, 0.92; Ag, 49.4. Found: C, 13.82; N, 22.18; H, 0.93; Ag, 50.4.

It should perhaps be noted that the $Ag_2Co(CN)_5N_2H_4$ was precipitated from 1.0 M acid where 99% of the complex would have been present in the form of the conjugate acid $Co(CN)_5N_2H_5^-$. By contrast, in earlier experiments where precipitation of the mixed sodium and potassium salt was carried out in much less acidic solution, the solid was found by acid–base titration to contain appreciable amounts of the conjugate acid. These poorly understood results may mean either that there is a reversal in the relative solubility of the basic complex in going from the silver to the alkali salts or that rate of nucleation determines whether the precipitate contains the acidic or basic form of the complex. No detailed study was made of this phenomenon.

Apparatus.—Absorbancy measurements were carried out using a Cary Model 14 PM recording spectrophotometer and a Beckman Model DU quartz spectrophotometer. A Beckman Model G pH meter was used for pH measurements. The saturated KCl in the reference electrode was removed and replaced by 3.0 M NaCl, a procedure which prevented plugging of the electrode by precipitation of $KClO_4$ when measurements were made in solutions containing ClO_4^-.

Kinetic Measurements of the Ligation Reactions.—In each kinetic measurement a solution with the desired concentration of reactants, pH, and ionic strength was prepared from stock solutions and placed in a thermostat regulated to ±0.02°. At suitable time intervals an aliquot was withdrawn and diluted when necessary, and the absorbancy was measured. The choice of wavelength used in a given spectrophotometric analysis was dictated by the absorption spectra of the reactants and products. The py reaction was followed at 355 $m\mu$ where $Co(CN)_5py^{2-}$ has an absorption maximum with a molar absorbancy index of 267 and $Co(CN)_5OH_2^{2-}$ has a molar absorbancy index of 183. The NH_3 reaction was followed at 380 $m\mu$ where the molar absorbancy indices of $Co(CN)_5OH_2^{2-}$ and $Co(CN)_5NH_3^{2-}$ are 295 and 80, respectively. The reaction with N_2H_4 and $N_2H_5^+$ was studied at 400 $m\mu$ where $Co(CN)_5OH_2^{2-}$ has a molar absorbancy index of 215; at this wavelength $Co(CN)_5N_2H_4^{2-}$ and $Co(CN)_5N_2H_5^-$ have molar absorbancy indices of 29 and 38, respectively.

Equilibrium in the $Co(CN)_5py^{2-}$ System.—It was possible to obtain only semiquantitative values for the equilibrium quotient for formation of $Co(CN)_5py^{2-}$.

$$Co(CN)_5OH_2^{2-} + py \underset{}{\overset{K_a}{\rightleftharpoons}} Co(CN)_5py^{2-} + H_2O \quad (A)$$

Neutral solutions of $Co(CN)_5py^{2-}$ containing no added py showed no detectable change in absorbancy in a period of 40 hr at the desired temperature of 40°, an indication either that the rate of aquation of $Co(CN)_5py^{2-}$ was extremely slow or that the per cent aquation at equilibrium was too small to detect. Similar results were obtained in 1.0 M $HClO_4$ solutions at 40°. At 80° in the acidic solution, appreciable reaction was observed in a few hours, but useful quantitative information could not be obtained because of a side reaction which produced an unidentified product having an absorption maximum at 400 $m\mu$.

An attempt was made to obtain the desired equilibrium constant for reaction A indirectly by attempting to study the equilibrium constant for reaction B

$$Co(CN)_5N_3^{3-} + py \underset{}{\overset{K_b}{\rightleftharpoons}} Co(CN)_5py^{3-} + N_3^- \quad (B)$$
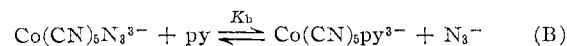
Since the equilibrium quotient, K_c, for formation of $Co(CN)_5$-N_3^{3-} is known, K_a can, in principle, be evaluated from the relationship $K_a = K_bK_c$. Again, it was found that neither the forward nor reverse reaction was measurable at 40°. At 70 and 90°, equilibrium was approached from either reactants or products at an appreciable rate, but the side reaction mentioned above prevented an accurate measurement of the equilibrium constant. However, the side reaction was somewhat slower than the rate of approach to equilibrium from either direction and lower limit values of K_a of 51 and 144 were obtained for 70 and 90°, respectively.

Measurement of Acidity Quotients.—Acidity quotients were determined spectrophotometrically and by acid–base titration using a pH meter. In both measurements the basic equation relating concentrations of the conjugate acid and its base, HA and A^-, was

$$\log \frac{[A^-]}{[HA]} = \log K_{acid} + pH \quad (C)$$

Values of H^+ were obtained from pH readings in the manner indicated above. In the spectrophotometric measurements it can be shown that

$$\log \frac{[A^-]}{[HA]} = \log \left[\frac{A - [Co(III)]\epsilon_{HA}}{[Co(III)]\epsilon_A - A} \right] \quad (D)$$

In this equation [Co(III)] represents the total concentration of the Co(III) complex, A is the measured absorbancy, and ϵ_{HA} and ϵ_A are the molar absorbancy indices of the acid and its conjugate base, respectively. The log K values were obtained from the linear plot of the right-hand side of the equation *vs.* pH. In the acid–base titrations, the pK values were again obtained graphically from the linear plot of log $[[A^-]/[HA]]$ *vs.* pH. The concentrations of HA and A^- were calculated at each point of the titration from the measured pH, the known total Co(III) concentration, and the amount of added $HClO_4$ or NaOH solution.

Results

Unless other conditions are specified, the kinetic studies reported in this paper were carried out at 40° and unit ionic strength, the conditions employed in our earlier work. In any given experiment the rate of approach of the system to equilibrium was characterized by a rate constant k, obtained from the linear slope of a plot of log $(A_\infty - A_t)$ *vs.* time, where A_t and A_∞ are the absorbancies of the solution at time t and after a time long enough for the system to reach equilibrium, respectively.

Reaction E was studied using solutions containing 0.05–1.0 M pyridine, (1–6) × 10^{-3} M $Co(CN)_5OH_2^{2-}$, 0.048 M pyridine perchlorate, and sufficient $NaClO_4$ to

$$Co(CN)_5OH_2^{2-} + py \rightleftharpoons Co(CN)_5py^{2-} + H_2O \quad (E)$$
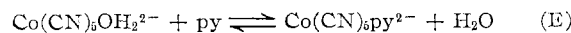
adjust [Na$^+$] to unity. The presence of the pyridinium ion, hereafter designated pyH$^+$, reduced the alkalinity of the system so that the pH of the system never appreciably exceeded 7, a condition which prevented appreciable formation of the kineticly inactive Co(CN)$_5$OH^{3-}.[7] The results are presented in Figure 1 as a plot of 10$_4$k vs. the py concentration. The significance of the curved lines in the figure will be discussed below.

In experiments carried out at 0.048 M pyH$^+$ and pH 2, an acidity which repressed any significant ionization of pyH$^+$, it was established that pyH$^+$ did not react with Co(CN)$_5$OH$_2$$^{2-}$ at an appreciable rate. However, the rate of the py reaction was found to increase somewhat when Na$^+$ was replaced by pyH$^+$, even when unit ionic strength was maintained. At 0.3 M py, unit ionic strength, and 0.048, 0.16, and 1.0 M pyH$^+$, the numerial values of k were 15.5 (two experiments), 18.2, and 24.1 sec^{-1}, respectively.

In our studies of reaction F, it was necessary to work at relatively high concentrations of N$_2$H$_5$$^+$ to reduce the basicity of the medium and prevent extensive

$$Co(CN)_5OH_2{}^{2-} + N_2H_4 \rightleftharpoons Co(CN)_5N_2H_4{}^{2-} + H_2O \quad (F)$$
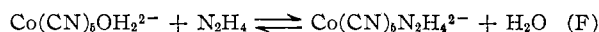
formation of Co(CN)$_5$OH^{3-}. Early exploratory work revealed that both N$_2$H$_4$ and N$_2$H$_5$$^+$ were nucleophiles of comparable reactivity. Consequently, further studies were made of the reactivity of both species. For simplicity, we will first describe the experiments at relatively low pH where only the reaction of N$_2$H$_5$$^+$ is of importance

$$Co(CN)_5OH_2{}^{2-} + N_2H_5{}^+ \rightleftharpoons Co(CN)_5N_2H_5{}^- + H_2O \quad (G)$$
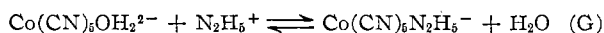
The experiments involving only N$_2$H$_5$$^+$ were carried out in solutions also containing NaClO$_4$ to adjust the ionic strength to unity. The pseudo-first-order rate constants obtained at various N$_2$H$_5$$^+$ concentrations are represented by points lying along the lower line in Figure 2. In these experiments the rate at pH 1.5 was found to be the same as at pH 3.0, an indication that the small amount of N$_2$H$_4$ formed by hydrolysis of N$_2$H$_5$$^+$ did not contribute appreciably to the rate, a conclusion which would also be reached by comparison of the rate constants for reactions F and G.

In the studies carried out at variable N$_2$H$_4$ concentration, the solutions also contained 0.39 M N$_2$H$_5$$^+$ to reduce the alkalinity and prevent formation of Co-(CN)$_5$OH^{3-}. However, at the higher N$_2$H$_4$ concentrations the reduction was not quite adequate, and, at 1.0 M N$_2$H$_4$, the highest concentration used, approximately 10% of the Co(CN)$_5$OH$_2$$^{2-}$ was converted to Co(CN)$_5$OH^{3-}, a species which experiments showed did not react with N$_2$H$_4$ at an appreciable rate.

The results obtained at 0.39 M N$_2$H$_5$$^+$ and variable N$_2$H$_4$ are presented as the points which lie along the upper curve of Figure 2. At the three highest concentrations of N$_2$H$_4$, the experimental values of k', which lie below the arrows, were corrected for the presence of inactive Co(CN)$_5$OH^{3-} by application of

(7) Earlier work has established the value 2 × 10^{-10} for the acidity constant of Co(CN)$_5$OH$_2$$^{2-}$.
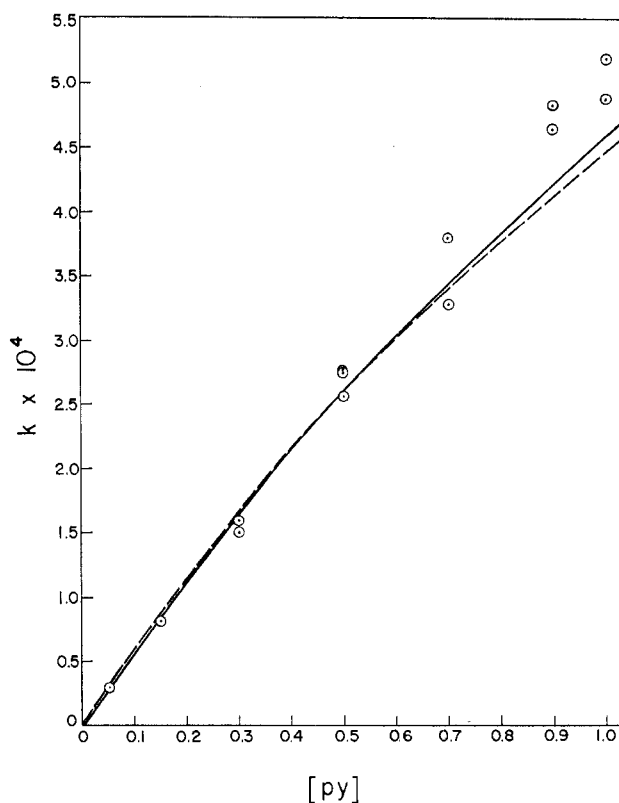

Figure 1.—A plot of the pseudo-first-order rate constant vs. the py concentration for reaction at 40° and unit ionic strength.
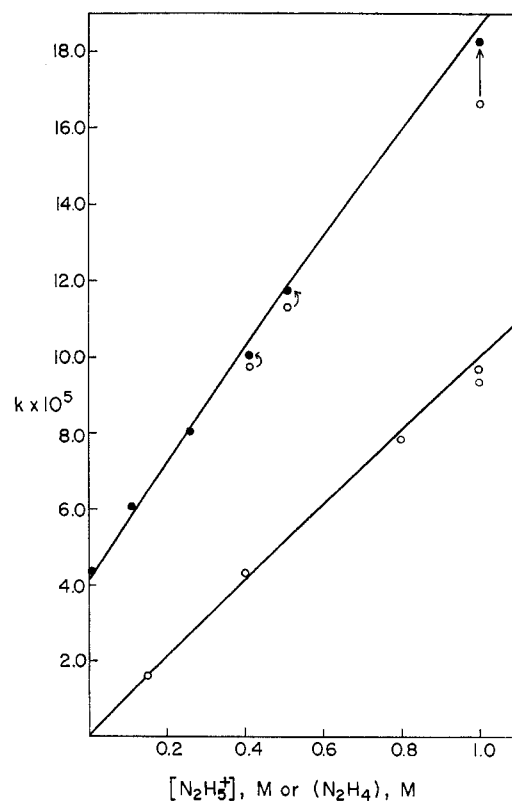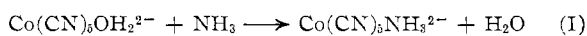

Figure 2.—Lower curve: a plot of the pseudo-first-order rate constant vs. the N$_2$H$_5$$^+$ concentration. Upper curve: a plot of the pseudo-first-order rate constant vs. the N$_2$H$_4$ concentration. All experiments with N$_2$H$_4$ were carried out at 0.39 M N$_2$H$_5$$^+$. Both series of experiments were carried out at 40° and unit ionic strength.

$$k = k'\left[\frac{[H^+] + (2 \times 10^{-10})}{[H^+]}\right] \qquad (H)$$

In eq H, k' is the observed value of the pseudo-first-order rate constant, k the corrected value, and 2×10^{-10} the acidity quotient of $Co(CN)_5OH_2{}^{2-}$. The magnitude of the correction can be seen by inspection of the figure, since the lower, uncorrected points and the upper, corrected points are included.

The data obtained in the spectrophotometric and acid–base titration studies of the acidity quotient of $Co(CN)_5N_2H_5{}^-$ are presented in Figure 3 as a plot of log $[[A]/[HA]]$ *vs.* pH. For both studies, a line of unit slope has been drawn through the points so that it closely approximates the data at log $([A]/[HA]) = 0$, the midpoint of the titration. The line through the solid circles falls within the limit of error of the measurements and corresponds to a pk value of 4.35. This value should closely approximate the thermodynamic constant, since the measurements were made in dilute, unbuffered solutions in the pH range 3.0–5.0. In the acid–base titration, represented by the open circles, there are appreciable deviations from the line of unit slope, perhaps because of the change in ionic strength during the titration. The line drawn through the points corresponds to a pk of 3.90. If this value is corrected to zero ionic strength using the equation log $f = 0.5Z^2\sqrt{\mu}/(1 + \sqrt{\mu})$ and the ionic strength of 0.07, which existed at the midpoint of the titration, the pk value 4.32 is obtained, a result in good agreement with that obtained in the spectrophotometric study.

The pseudo-first-order rate constants for reaction I obtained at 0.30 and 0.60 M NH_3 were 5.56×10^{-5} and 11.0×10^{-5} sec^{-1}, respectively. In these two experi-

$$Co(CN)_5OH_2{}^{2-} + NH_3 \longrightarrow Co(CN)_5NH_3{}^{2-} + H_2O \qquad (I)$$

ments the NH_4NO_3 concentration was equal to the NH_3 concentration in order to maintain a constant pH. The ionic strength was adjusted to unity using $NaNO_3$, the change from $NaClO_4$ being necessary to avoid precipitation of NH_4ClO_4. When these rate constants are corrected by eq F for the approximately 10% of the total $Co(CN)_5OH_2{}^{2-}$ present as $Co(CN)_5OH^{3-}$, values of 6.14×10^{-5} and 12.4×10^{-5} sec^{-1} are obtained for the 0.30 and 0.60 M NH_3 experiments, respectively.

Discussion

If the studies of the substitution of H_2O in $Co(CN)_5OH_2{}^{2-}$ were limited to those of the present paper, the results would justify only the tabulation of the second-order rate constants for reaction of $Co(CN)_5$-$OH_2{}^{2-}$ with the various amines under consideration. The numerical values of these second-order rate constants are 52×10^{-5}, 10.0×10^{-5}, 14.7×10^{-5}, and 20.6×10^{-5} M^{-1} sec^{-1} for reaction of py, N_2H_4, $N_2H_5{}^+$, and NH_3, respectively. However, our earlier studies with more reactive nucleophiles strongly suggest a limiting type of S_N1 mechanism.[8] With the possible

Figure 3.—A plot of log $([A]/[HA])$ *vs.* pH, where A is Co-$(CN)_5N_2H_4{}^{2-}$ and HA the corresponding conjugate acid. The solid circles refer to measurements made in very dilute unbuffered solution in the pH range 3.0–5.0. The experiments represented by the open circles correspond to an ionic strength of 0.07 at the midpoint of the titration. All measurements were at room temperature $(23 \pm 2°)$.

exception of py studies, which will be discussed below, the kinetic data obtained in the amine systems are also entirely consistent with this S_N1 mechanism, even though they provide no independent support for it. Consequently, the present data will also be discussed in terms of this mechanism.

The S_N1 mechanism may be formulated in terms of eq 1 and 2, where X represents the nucleophile under discussion

$$Co(CN)_5OH_2{}^{2-} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Co(CN)_5{}^{2-} + H_2O \qquad (1)$$

$$Co(CN)_5{}^{2-} + X \overset{k_3}{\longrightarrow} Co(CN)_5X^{2-} \qquad (2)$$

Computer calculations using the $N_3{}^-$ and SCN^- data yield a numerical value for k_1 of $(1.47 \pm 0.10) \times 10^{-3}$ sec^{-1}.[9] This mechanism requires that the pseudo-first-order constant k be related to the concentration of the nucleophile X and the other kinetic parameters by

(8) For a review of this work see the paper by A. Haim, R. J. Grassi, and W. K. Wilmarth, Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 31.
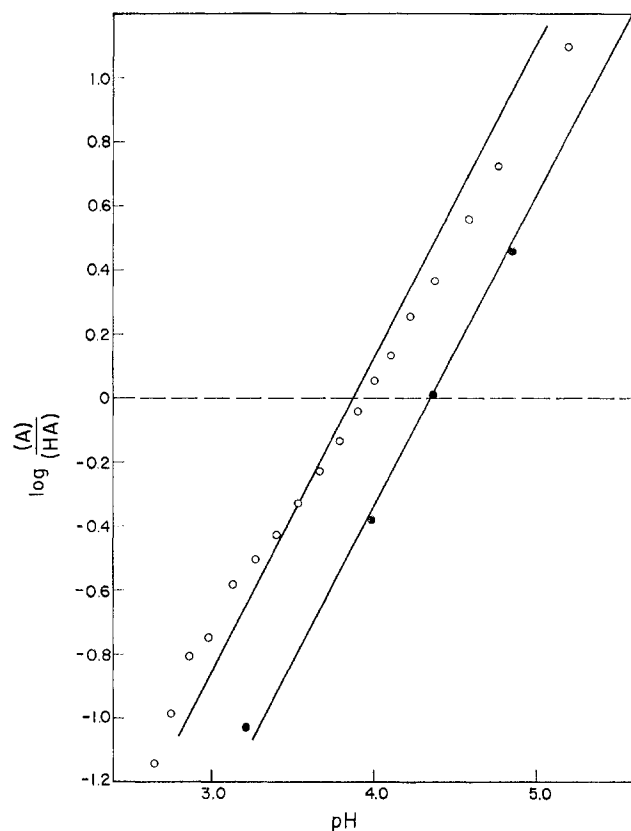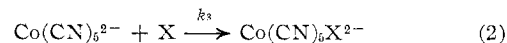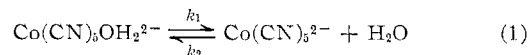
(9) We are indebted to Dr. T. W. Newton of the Los Alamos Scientific Laboratory for carrying out early computations. More recently, with his help, we have obtained the programs described in Los Alamos Scientific Laboratory Report LA-2367, Oct 1959, by R. H. Moore and R. K. Zeigler and obtainable from the U. S. Department of Commerce, Washington, D. C., No. 225. Since the $N_3{}^-$ and SCN^- data are believed to be most suitable for evaluating k_1, both because of the greater accuracy of the data and also because of the relatively high reactivity of these nucleophiles, these data have been used in the evaluation. Further details may be found in the paper by R. Grassi, A. Haim, and W. K. Wilmarth, *Inorg. Chem.*, **6**, 237 (1967).
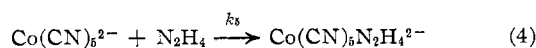
$$k = \frac{k_1[X]}{(k_2/k_3) + [X]} \qquad (3)$$

In deriving eq 3, it has been assumed that reaction 2 proceeds essentially to completion, a valid approximation in the ligation studies under discussion. Equation 3 implies that a plot of k vs. $[X]$ should be curved, with the extent of the curvature increasing with increasing nucleophile reactivity. In the present work only py is reactive enough so that detectable curvature should have been present in such a plot.

The data obtained using the nucleophile $N_2H_5{}^+$ will be discussed first. Apart from the unexpected rapidity, substitution by $N_2H_5{}^+$ in reaction G appears to be straightforward and requires little comment. Use of the value $k_1 = 1.47 \times 10^{-3}$ in the least-squares treatment of the data yields a value of $k_2/k_3 = 13.7 \pm 0.03$, with the recorded uncertainty here and elsewhere representing the standard deviation. In this and in the other least-squares computations presented in this paper, the numerical values of k were weighed by the factor $1/k^2$, a weighting which assumes that the probability of a given percentage error is the same for all values of k.

The lower line in Figure 2 was calculated using these kinetic parameters and deviates from the experimental data by a mean deviation of 3.25% and a maximum deviation of 3.54%. In actual fact, larger deviation from theory would not have been surprising, since the variation in $[N_2H_5{}^+]$ was achieved by replacing Na^+ by $N_2H_5{}^+$, a procedure which might have produced an appreciable medium effect[10] in a reaction involving a dinegative and unipositive ion.

When the reaction involves the simultaneous substitution by both N_2H_4 and $N_2H_5{}^+$, it is necessary to include reaction 4 in the mechanism and to calculate the kinetic parameter k_5/k_3 from eq 5.

$$Co(CN)_5{}^{2-} + N_2H_4 \xrightarrow{k_5} Co(CN)_5N_2H_4{}^{2-} \qquad (4)$$

$$k = \frac{k_1\{[N_2H_5{}^+] + k_5[N_2H_4]/k_3\}}{(k_2/k_3) + [N_2H_5{}^+] + k_5[N_2H_4]/k_3} \qquad (5)$$

Again assuming the value of k_1 listed above, the least-squares computation yields the value $k_5/k_3 = 1.56 \pm 0.04$. The upper line in Figure 2 calculated using this value of k_5/k_3 lies within the limit of error of the experimental data (after correction for the unreactivity of $Co(CN)_5OH^{3-}$ by eq H). In this instance, the mean deviation is 1.82% and the maximum deviation is 4.34%. For purposes of comparison it is perhaps preferable to express the hydrazine reactivity in terms of the quantity k_2/k_5. The numerical value of 8.8 may be directly compared with the values of k_2/k_3 listed for the other nucleophiles.

The data obtained using NH_3 as a nucleophile yield a value of $k_2/k_3 = 6.71 \pm 0.02$. Calculated rate constants using this kinetic parameter show a maximum deviation of 2.7%.

The least-squares calculation using the py data yields a value of $k_2/k_3 = 2.33 \pm 0.08$. The dotted line in Figure 1 was calculated using this value of k_2/k_3.

(10) A. R. Olson and T. R. Simonson, *J. Chem. Phys.*, **17**, 1167 (1949).

Inspection of the figure indicates that, in part, the relatively large mean deviation of 9.04% and the maximum deviation of 14.8% arise from the scatter of the points caused by apparently unavoidable inaccuracies in the measurements. However, most of the deviations arise from the failure of $k/[py]$ to decrease at the larger py concentrations in the manners predicted by eq 3 for a relatively reactive nucleophile.

In view of the above conflict between theory and experiment, consideration was given to the approximations involved in deriving eq 3. It is readily evident that a very questionable approximation in this derivation does exist when the equation is applied to neutral nucleophiles. The approximation in question involves the assumption that the activity of H_2O is independent of the ligand concentration. With uninegative nucleophiles such as $N_3{}^-$ or SCN^- this approximation may be valid, since increase in concentration of the nucleophile may be made by substituting it for $ClO_4{}^-$, a process which does not appreciably change the H_2O content of the solvent. By contrast, an increase in py concentration may be achieved only by dilution of the H_2O content of the solvent, a procedure which would favor reaction 2 in its competition with the reverse of reaction 1 and lead to a decrease in the curvature of a plot such as that of Figure 1.

In the Brønsted–Bjerrum formulation of medium effects, eq 3 should be replaced by eq 6, where the symbol $Co(CN)_5$ is replaced by the symbol R and charges of the ions have been omitted to simplify the equation

$$k = \frac{k_1[X]\gamma_{ROH_2}{}^*/\gamma_{ROH}}{\dfrac{k_2\gamma_{H_2O}\gamma_{RX}{}^*}{k_3\gamma_X\gamma_{ROH_2}{}^*} + [X]} \qquad (6)$$

It seems likely that the ratio $\gamma_{ROH_2}{}^*/\gamma_{ROH_2}$ and perhaps the ratio $\gamma_{RX}{}^*/\gamma_{ROH_2}{}^*$ are relatively insensitive to the py concentration, since both ratios represent activity coefficients of dinegative ions. By contrast, it may be anticipated that the ratio γ_{H_2O}/γ_X will change with a change in the concentration of H_2O in the solvent. To a first approximation this change in H_2O concentration may be included in the mechanism by replacing eq 3 by

$$k = \frac{k_1[X]}{\dfrac{k_2[H_2O]}{k_3[H_2O]^0} + [X]} \qquad (7)$$

In eq 7, $[H_2O]^0$ and $[H_2O]$ are the weights of water per liter of solution in absence and presence of py, respectively. The solid curved line in Figure 1 was calculated using this equation and the least-squares value of $k_2/k_3 = 2.42 \pm 0.07$. The agreement is better than that which would have been obtained with eq 3, but the points at high $[py]$ still deviate by slightly more than the estimated limit of error. Perhaps this is not surprising, since the activity coefficients in the py–H_2O system are far from ideal,[11] and the approximations made in obtaining eq 7 may be rather poor ones.

(11) Unfortunately the activity coefficient data of N. Ibon, G. Dandlicher, and G. Trümpler, *Helv. Chim. Acta*, **37**, 1661 (1954), do not cover the relatively dilute solutions of interest in the present paper.

Alternately, it might be argued that the substitution reaction does not proceed by an S$_N$1 mechanism, at least when the substituting nucleophile is py. Completion of studies of the rate of exchange of Co(CN)$_5$-OH$_2{}^{2-}$ with O^{18}-labeled H$_2$O should clarify this point.

The present studies considerably extend our knowledge of the factors which parallel nucleophilic reactivity in the displacement of H$_2$O in Co(CN)$_5$OH$_2{}^{2-}$. The NH$_3$ ligand, with an experimental value of $k_2/k_3 = 6.4$, is appreciably more reactive than N$_2$H$_4$, an indication that an unshared pair of electrons on the atom α to the reactive site does not result in exceptional reactivity in the present system.[4] Basicity is also apparently not of major importance. The py molecule is much more reactive than NH$_3$, despite its lower basicity, presumably because of its ability to form metal-to-ligand π bonds in the activated complex, a phenomenon which may also contribute to the reactivity series I$^-$ > Br$^-$ > Cl$^-$. A comparison of the relative reactivity of N$_2$H$_4$ and N$_2$H$_5{}^+$ also demonstrates the lack of correlation of basicity and reactivity and suggests that electrostatics may play an appreciable role in determining nucleophilicity. Alternately, the unexpected reactivity of N$_2$H$_5{}^+$ may arise from especially favorable hydrogen bonding in the activated complex.

It is of interest, finally, to compare the acid properties of Co(CN)$_5$N$_2$H$_5{}^-$ with those of structurally related ions. It is generally recognized that substitution of a proton by a Co(III) linkage is acid weakening, particularly when the Co(III) is present in a complex with a negative charge. A pertinent example is a comparison of the acidity of H$_3$O$^+$ with that of Co(CN)$_5$OH$_2{}^{2-}$, with the latter species having a pK of 9.8. It might be anticipated, therefore, that the acidities of N$_2$H$_6{}^{2+}$ and Co(CN)$_5$N$_2$H$_5{}^-$ would be related in an analogous fashion, with the latter species being much less acidic in agreement with prediction.[12] The effect of substitution on the N$_2$H$_6{}^{2+}$ ion is, as expected, less than that in H$_3$O$^+$, because the substitution in N$_2$H$_6{}^{2+}$ presumably occurs on an atom in the α position to that bearing the acidic proton. In an alternative comparison of acidity, it may be noted that the addition of Co(CN)$_5{}^{2-}$ to the basic nitrogen atom of N$_2$H$_5{}^+$ decreases the pK of the latter species from 8.0 to 4.35.

(12) At ordinary acidities N$_2$H$_6{}^{2+}$ dissociates completely to form N$_2$H$_5{}^+$ and H$^+$. The data of G. Schwarzenbach, *Helv. Chim. Acta*, **19**, 178 (1936), reported as basicity constant, correspond to an acidity constant of 1.0 $\times$ 10^2.

The Replacement of Thiocyanate Ion in the *trans*-Dithiocyanatotetraammineplatinum(IV) Cation by Chloride Ion[1]

By W. Roy Mason, III, Eugene R. Berger, and Ronald C. Johnson

The predominant paths for the stepwise replacement of the two thiocyanate ions in *trans*-Pt(NH$_3$)$_4$(SCN)$_2{}^{2+}$ by chloride ion have third-order rate laws with rate dependences on the reactant platinum(IV) complex, Pt(NH$_3$)$_4{}^{4+}$, and chloride ion, The third-order rate constants at 25.0° are 1.8 $\times$ 10^2 and 2.7 M^{-2} sec^{-1}, respectively. The thiocyanate ions in both *trans*-Pt(NH$_3$)$_4$(SCN)$_2{}^{2+}$ and the intermediate product *trans*-Pt(NH$_3$)$_4$(SCN)Cl^{2+} were found to be S bonded. These results are explained in terms of a bridged inner-sphere redox mechanism in which the sulfur atom of a thiocyanate ion links the platinum(II) and platinum(IV) complexes. Activation parameters for the reactions are reported. The equilibrium constants for the stepwise replacement of thiocyanate ions are 0.084 and 0.0028 at 35.0°.

Introduction

A variety of substitution reactions of *trans*-dihalo-tetraammineplatinum(IV) cations are catalyzed by the tetraammineplatinum(II) cation.[2-5] The rate behavior of these reactions is consistent with a mechanism proposed by Basolo and Pearson, which involves an inner-sphere, two-electron redox process, eq 1–3. The four

$$\text{Pt}^{2+} + \text{Z}^- = \text{Pt–Z}^+ \qquad (1)$$
$$\text{Y–Pt–X}^{2+} + \text{Pt–Z}^+ = \text{Y–Pt–X–Pt–Z}^{3+} \qquad (2)$$
$$\text{Y–Pt–X–Pt–Z}^{3+} = \text{Y}^- + \text{Pt}^{2+} + \text{X–Pt–Z}^{2+} \qquad (3)$$

ammonias in the plane of each complex are omitted; X, Y, and Z are halogens. Studies in this laboratory have been aimed at a detailed investigation of this mechanism and its applications in the chemistry of platinum(IV).

In terms of this mechanism, an intriguing situation can be visualized for the ambidentate thiocyanate ligand. A thiocyanate situated in the bridging position of the activated complex (group X in eq 2) might
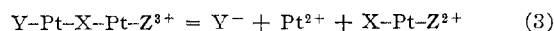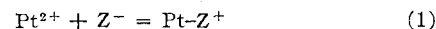
(1) Based on part of the Ph.D. Dissertation of W. R. M., Emory University, 1966.

(2) F. Basolo, M. L. Morris, and R. G. Pearson, *Discussions Faraday Soc.*, **29**, 80 (1960).

(3) F. Basolo and R. G. Pearson, *Advan. Inorg. Chem. Radiochem.*, **3**, 35 (1961).

(4) R. R. Rettew and R. C. Johnson, *Inorg. Chem.*, **4**, 1565 (1965).

(5) R. C. Johnson and E. R. Berger, *ibid.*, **4**, 1262 (1965).