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The Pentacyano Complexes of Cobalt(III). I. Kinetics and Mechanism of the Substitution of Water in $Co(CN)_5OH_2^{--}$ by Azide and Thiocyanate Ions and by O^{18}-Enriched Water[1]

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The pseudo-first-order rate constants for substitution of H_2O in $Co(CN)_5OH_2^{--}$ by N_3^- and SCN^- conform to the equation $k = k_1(X^-)/[(X^-) + k_2/k_3]$. At 40°, ionic strength 1.0, and pH 6.4, $k_1 = 1.6 \times 10^{-3}$ sec.$^{-1}$, $k_2/k_3 = 1.9$ for N_3^- and 2.95 for SCN^-. At 20° and ionic strength 5.0, $k_1 = 5.1 \times 10^{-4}$ sec.$^{-1}$, $k_2/k_3 = 3.0$ for N_3^- and 5.0 for SCN^-. The first-order rate constant for aquation of $Co(CN)_5N_3^{-3}$ is 5.5×10^{-7} sec.$^{-1}$ at 40°, ionic strength 1.0, and pH 6.4, and 8.0×10^{-6} sec.$^{-1}$ at 60°, ionic strength 1.0, and pH 6.0 or 0.1 *M* OH^-. The first-order rate constant for aquation of $Co(CN)_5NCS^{-3}$ at ionic strength 1.0 and 0.1 *M* OH^- is 3.7×10^{-7} sec.$^{-1}$ at 40° and 7.8×10^{-6} sec.$^{-1}$ at 60°. The equilibrium constants for the formation of $Co(CN)_5N_3^{-3}$ and $Co(CN)_5NCS^{-3}$ from $Co(CN)_5OH_2^{--}$ are 1530 and 1460, respectively, at 40° and ionic strength 1.0. The pH and N_3^- dependence of the pseudo-first-order rate constant for reaction of $Co(CN)_5OH_2^{--}$ and N_3^- conforms to the equation $k = [k_1(H^+) + k_1'K_a](N_3^-)/[(k_2/k_3) + (N_3^-) + (k_2'/k_3)(OH^-)][K_a + (H^+)]$. At 40° and ionic strength 1.0, K_a, the dissociation constant of $Co(CN)_5OH_2^{--}$, is 2×10^{-10}, $k_1' = 6.5 \times 10^{-4}$ sec.$^{-1}$, and $k_2'/k_3 = 3.0 \times 10^3$. The following tentative limits have been set upon k_{ex}, the first-order rate constant for water exchange between $Co(CN)_5OH_2^{--}$ and solvent: 1.3×10^{-3} sec.$^{-1} > k_{ex} > 1.0 \times 10^{-3}$ sec.$^{-1}$, at 40°, ionic strength 1.0, and pH 6.4. These results yield strong support for a limiting SN1 mechanism involving the pentacoördinated intermediate $Co(CN)_5^{--}$.

Introduction

Most of the substitution reactions of complex ions in aqueous solution involve the participation of water as a reactant (aquation) or as displaced ligand (anation and water exchange).[3] Kinetic studies of anation reactions usually indicate a first-order dependence on both complex ion and substituting anion, but this result alone does not distinguish between an SN1 and an SN2 mechanism.[4] Taube[5] has pointed out that in principle a distinction could be made since in an SN1 process water exchange and complex ion formation compete for the same intermediate, whereas in SN2 processes the reactions are independent. Up to the present, attempts to distinguish between SN1 and SN2 mechanisms on this basis have not been successful because of outer-sphere association between the reactants[6,7] or because of slow rate of anation as compared to water exchange.[8,9]

One possible approach to avoid outer-sphere association between the reactants prior to reaction involves the use of anionic complexes. Aquapentacyanocobaltate(III), whose preparation and properties have been described previously,[10] seemed to provide an interesting choice for a study of anation reactions and exchange of water in an H_2O^{18}-enriched solvent. In this paper we report the rate of the anation reactions for the azide and thiocyanate ions, the corresponding equilibrium constants, the rates of aquation of $Co(CN)_5N_3^-$ and $Co(CN)_5NCS^{-3}$, and a preliminary study of the rate of the water exchange. Subsequent papers in this series will deal with the reactions of $Co(CN)_5OH_2^{--}$ with bromide ion, iodide ion, and a variety of other nucleophiles and with the acid-catalyzed aquation of $Co(CN)_5N_3^{-4}$ (paper II). The over-all results seem to provide strong evidence for a limiting type

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[2] Based in part on a dissertation submitted by A. Haim to the Graduate School of the University of Southern California in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] For a recent review of substitution reactions of complex ions see the chapter by D. R. Stranks in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers Inc., New York, N. Y., 1960.

[4] F. Basolo, *Chem. Rev.*, **52**, 459 (1953).

[5] H. Taube, *Ann. Rev. Nucl. Sci.*, **6**, 284 (1956).

[6] A. C. Rutenberg and H. Taube, *J. Chem. Phys.*, **20**, 823 (1952).

[7] F. A. Posey and H. Taube, *J. Am. Chem. Soc.*, **79**, 255 (1957).

[8] C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1208 (1955).

[9] J. F. Below, R. E. Connick, and C. P. Coppel, *J. Am. Chem. Soc.*, **80**, 2961 (1958).

[10] A. Haim and W. K. Wilmarth, *ibid.*, **83**, 509 (1961).

of SN1 mechanism in which $Co(CN)_5^{--}$, the proposed reactive intermediate, must have a lifetime long enough to discriminate between various nucleophilic ligands which may be present in the solution. It may be noted that this behavior is in marked contrast to many systems where the assignment of an SN1 mechanism is based on data which only imply that bond breaking is more important than bond making in an activated complex whose lifetime need only be of the order of vibrational frequencies.

Experimental

Reagents.—Sodium azide was recrystallized twice from water. Sodium perchlorate, sodium hydroxide, sodium dihydrogen phosphate, sodium thiocyanate, and perchloric acid were of analytical reagent quality. Solutions of potassium aquapentacyanocobaltate(III) were obtained by acidification of potassium μ-peroxodecacyanodicobaltate(III,III) with the theoretical amount of perchloric acid, and the hydrogen peroxide formed was decomposed by heating the solutions to 50°.[10] Potassium azidopentacyanocobaltate(III) was prepared in solution by the reaction of aquapentacyanocobaltate(III) and azide ions, and was isolated by precipitation with ethanol. It was characterized by comparing its absorption spectrum after aquation with that of $Co(CN)_5OH_2^{--}$.

Apparatus.—Absorbancy measurements were carried out with a Cary Model 14 PM recording spectrophotometer and with a Beckman Model DU quartz spectrophotometer. A Beckman Model G pH meter equipped with a Beckman Type E (blue) glass electrode was used for pH measurements.

Kinetic Measurements of the Anation Reactions.—Solutions of the proper concentrations, pH, and ionic strength were prepared and placed in a thermostat at the desired temperature. At appropriate times, aliquots were withdrawn, diluted, and their absorbancies measured. The choice of wave lengths at which the various reactions were followed was dictated by the absorption spectra of reactant and product. The reaction with azide ion was followed at 280 mμ, where $Co(CN)_5N_3^{-3}$ has an absorption maximum with a molar absorbancy index of 7500 and $Co(CN)_5OH_2^{--}$ has a molar absorbancy index of 140. The reaction with thiocyanate ion was followed at 270 mμ, where $Co(CN)_5NCS^{-3}$[11] has a molar absorbancy index of 11,700 and $Co(CN)_5OH_2^{--}$ has a molar absorbancy index of 225. In all measurements, the anion concentration was at least 50 times the concentration of the complex, and all rate constants therefore were obtained as pseudo-first-order rate constants from the slope of plots of log $(D_\infty - D_t)$ *vs.* time. D_t is the absorbancy at time t and D_∞ is the absorbancy after more than 7 half-lives.

Measurements of Hydrogen Ion Concentrations.—The determination of the concentration dissociation constant of $Co(CN)_5OH_2^{--}$ and the interpretation of the pH dependence of the reaction of $Co(CN)_5OH_2^{--}$ with N_3^- required a knowledge of the hydrogen ion *concentration* at 40° and ionic strength 1.0, the experimental conditions usually employed in the present work. Because of the difficulties in interpreting measured pH values in concentrated ionic solutions,[12] the following empirical procedure was devised to correlate measured pH values at 25° with hydrogen ion concentrations at 40°. The pH of 1.0×10^{-1} to 1.0×10^{-4} M perchloric acid solutions and of 1.0×10^{-1} to 5.0×10^{-4} M sodium hydroxide solutions, with the ionic strength adjusted to 1.0 by the use of sodium perchlorate, was measured at 25°. The concentration of H^+ at 40° in the acid solutions was known from the perchloric acid concentration. The concentration of H^+ in the alkaline solutions at 40° was calculated using the known hydroxide ion concentrations and, in the absence of ionic product data for the alkaline sodium perchlorate, assuming that the product of the hydrogen and hydroxide ion concentrations was equal to 5.65×10^{-14}, the known value for 1 M sodium chloride at 40°. The plot of $-\log (H^+)$ *vs.* pH yielded a straight line described by eq. 1, where (H^+) is the hydrogen ion concentration

$$-\log (H^+) = 0.5 + 0.94\ \mathrm{pH} \qquad (1)$$

at 40°, and pH is the measured pH at 25°.

Measurement of the Concentration Dissociation Constant of $Co(CN)_5OH_2^{--}$.—The absorbancies at 300 mμ of $Co(CN)_5OH_2^{--}$ solutions of pH varying from 3 to 13, with sodium perchlorate to adjust the ionic strength to 1.0, were measured at 40° in a thermostated cell using a Beckman spectrophotometer. The concentration dissociation constant was obtained from the expression

$$\log \frac{D_A - D}{D - D_B} = \log K_a - \log (H^+) \qquad (2)$$

D is the absorbancy of the solution at a given hydrogen ion concentration (H^+), D_A and D_B are the absorbancies of $Co(CN)_5OH_2^{--}$ and $Co(CN)_5OH^{-3}$, respectively, at concentrations equal to the total cobalt(III) concentration of the solution under consideration, and K_a is the concentration dissociation constant for reaction 3.

$$Co(CN)_5OH_2^{--} \rightleftharpoons Co(CN)_5OH^{-3} + H^+ \qquad (3)$$

Water Exchange Kinetic Measurements.—Solutions of $Co(CN)_5OH_2^{--}$ were prepared by treating freshly precipitated $Ag_2[Co(CN)_5OH_2]$ with the theoretical amount of sodium bromide, and separating the silver bromide formed.[8] The solution of $Co(CN)_5OH_2^{--}$ and a solution containing the desired amounts of O^{18}-enriched water and sodium perchlorate were separately placed in a thermostat at 40°. After temperature equilibrium was reached, the two solutions were rapidly mixed, and at appropriate times aliquots were withdrawn and delivered into a slight excess of silver nitrate solution. The $Ag_2[Co(CN)_5OH_2]$ that precipitated was filtered, washed with methanol or acetone, and air-dried. It then was placed in a decomposition flask connected to the high vacuum system and evacuated for 45 min. in order to remove the solvent. In order to collect the water from $Ag_2[Co(CN)_5OH_2]$, the decomposition flask was connected to a calibrated sample tube and heated with a Glas-col heating element at ap-

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(11) The complex is formulated as an isothiocyanato complex, although it is not known whether sulfur or nitrogen is bonded to cobalt. The molar absorbancy index of the complex is from optical measurements of solutions in which reaction 5 had proceeded to completion.

(12) R. G. Bates, "Electrometric pH Determinations," John Wiley and Sons, Inc., New York, N. Y., 1954.

proximately 120°, while the sample tube was cooled to liquid nitrogen temperature. Tank carbon dioxide was dried by bubbling through concentrated sulfuric acid and passing through a trap at $-80°$, and then admitted at the desired pressure to the sample tube containing the water. By using the appropriate high vacuum apparatus the carbon dioxide originally trapped in the bore of the stopcock was transferred to the sample tube. The samples were equilibrated for one week at room temperature, and the carbon dioxide then was analyzed with a mass spectrometer constructed in the Department of Chemistry, University of Southern California, under the direction of Professor Sidney W. Benson. N, the ratio of H_2O^{18} to H_2O^{16}, was calculated with the formula given by Hunt and Taube[13]

$$N = \frac{R}{K + R} + \frac{R}{Q(1 + R)} - \frac{R_0}{Q}$$

R is the observed ratio of $CO^{16}O^{18}$ to $CO^{16}O^{16}$; K is the equilibrium constant for the reaction

$$H_2O^{18} + CO^{16}O^{16} \rightleftharpoons H_2O^{16}O^{18} + CO^{16}O^{18}$$

and is equal to 2.078 at 25°; R_0 is the ratio of $CO^{16}O^{18}$ to $CO^{16}O^{16}$ in the carbon dioxide used for the equilibration; Q is the ratio of moles of water to moles of carbon dioxide used in the equilibration. The moles of water were obtained from the weight of the water in the sample tube.[14] The moles of carbon dioxide were obtained from the known volume of the sample tube, the pressure of CO_2, and the temperature.

The fraction of exchange F is defined as $(N_t - N_0)/(N_\infty - N_0)$, where N_t is the measured ratio of H_2O^{18} to H_2O^{16} for the sample of $Ag_2[Co(CN)_5OH_2]$ precipitated at time t, N_∞ is the calculated ratio of H_2O^{18} to H_2O^{16} for $Co(CN)_5OH_2^{--}$ after isotopic equilibrium with the water in the exchange solution is reached, and N_0 is the ratio of H_2O^{18} to H_2O^{16} for $Co(CN)_5OH_2^{--}$ at time 0. In all experiments $N_0 = 1.98 \times 10^{-3}$, the ratio of H_2O^{18} to H_2O^{16} in water of normal isotopic composition. The rate constant k_{ex} for the exchange is related to the fraction of exchange by the formula $\ln(1 - F) = -k_{ex}t$.

Up to the present, all attempts to obtain a quantitative measurement of the rate of exchange between H_2O^{18} and $Co(CN)_5OH_2^{--}$ have been unsuccessful. In view of the unusual nature and great rapidity of this exchange reaction, the experimental results are presented in some detail. For all the experiments, plots of log $(1 - F)$ *vs.* time deviated appreciably from linearity, as shown in Fig. 1. A systematic investigation of the procedure therefore was undertaken in order to isolate the possible sources of error. First, it was established that the general procedure was free from error by collecting the water from the coördination sphere of O^{18}-enriched $[Co(NH_3)_5OH_2]Br_3$,[7] followed by equilibration with CO_2 and mass spectrometric analysis. The analysis yielded values of N within 1% of the ratio of H_2O^{18} to H_2O^{16} calculated from the known O^{18}-enrichment of $[Co(NH_3)_5OH_2]Br_3$. Identical values of N were obtained by drying $[Co(NH_3)_5OH_2]Br_3$ by the method of Posey and Taube[5] or by washing the $[Co(NH_3)_5OH_2]Br_3$ with methanol, followed by pumping under high vacuum for 45 min. prior to collection of the water from the coördination sphere of cobalt. Next, it was established that washing unlabeled $Ag_2[Co(CN)_5OH_2]$ with methanol containing 1% of O^{18}-enriched water resulted in contamination of the water in $Ag_2[Co(CN)_5OH_2]$ with only 2% of the water in the methanol. Since the water content of the methanol used to wash $Ag_2[Co(CN)_5OH_2]$ in the experiments reported in Fig. 1 probably was less than 0.2%, it is concluded that contamination of the water from $Ag_2[Co(CN)_5OH_2]$ with water from the methanol is negligible. In a complementary experiment, unlabeled, freshly precipitated $Ag_2[Co(CN)_5OH_2]$ was left in contact with O^{18}-enriched water for 5 min., and then subjected to the usual procedure. Again the value of N for $Ag_2[Co(CN)_5OH_2]$ indicated less than 2% contamination of the water in $Ag_2[Co(CN)_5OH_2]$ with the O^{18}-enriched water. Finally, it was established that precipitation at 0° of unlabeled $Co(CN)_5OH_2^{--}$ with silver nitrate dissolved in O^{18}-enriched water resulted in 17% induced exchange during precipitation. Furthermore, experiments 1 and 10 in Fig. 1 correspond to 22 and 47% induced exchange, respectively. Attempts to decrease the induced exchange by precipitating $Co(CN)_5OH_2^{--}$ with silver nitrate dissolved in a water–methanol mixture at $-50°$ were not successful, as shown by the experiments numbered 6, 7, 8, and 9 in Fig. 1.

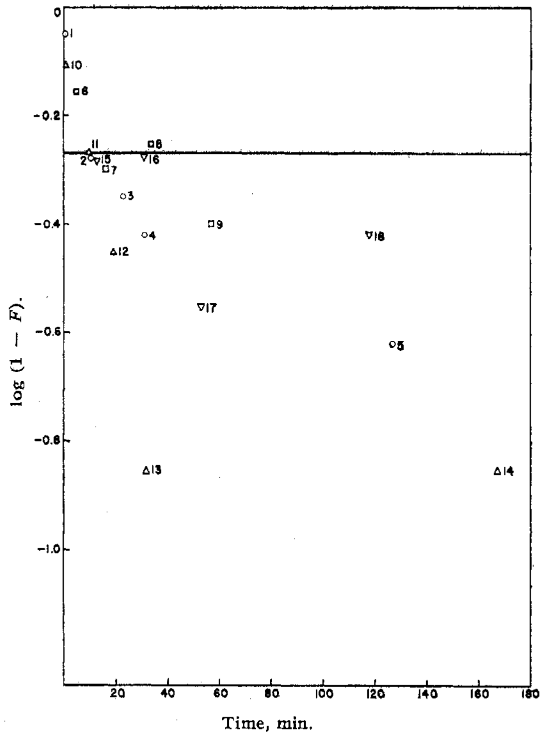

Fig. 1.—Water exchange between $Co(CN)_5OH_2^{--}$ and solvent water at 40° and ionic strength 1.0.

Precipitation of $Co(CN)_5OH_2^{--}$ with Hg_2^{++} did not

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[13] J. P. Hunt and H. Taube, *J. Chem. Phys.*, **19**, 603 (1951).

[14] The weight of water collected usually was 15–20% smaller than the weight calculated from the $Ag_2Co(CN)_6$ remaining in the decomposition flask. It was shown before[10] that pumping on $Ag_2[Co(CN)_5OH_2]$ at room temperature removes the coördination water. In view of the limited accuracy of the measurements, any isotopic fractionation occurring during the initial loss of water would produce only a negligible error.

seem to decrease the induced exchange, as shown by experiments 15, 16, 17, and 18 of Fig. 1. When the precipitate of $Hg_2[Co(CN)_5OH_2]$ was washed with methanol it turned black in color, probably because of formation of mercury. This method of removing surface water therefore was discontinued. Instead, the salt was dried in a vacuum desiccator over sulfuric acid during 15 hr., and then the water from the coördination sphere of cobalt was removed by heating the dry salt at 80°.

Other possible precipitants for $Co(CN)_5OH_2^{--}$ were explored. Some of the heavy metal ions (Fe^{III}, Co^{II}, Cu^{II}, Ni^{II}) yielded precipitates containing water in the coördination sphere of the cation in addition to the water in $Co(CN)_5OH_2^{--}$ and therefore were discarded. The cations $As(C_6H_5)_4^+$, $Pt(NH_3)_4^{++}$, $Co(NH_3)_6^{3+}$, $Co(en)_3^{3+}$, $Co(NH_3)_5Cl^{++}$, $Cr(NH_3)_6^{3+}$, and $Cr(NH_3)_5Cl^{++}$ did not yield any precipitate with 0.1 M $Co(CN)_5OH_2^{--}$ at 0°. $Co(NH_3)SO_4^+$ yielded a somewhat insoluble salt with 0.1 M $Co(CN)_5OH_2^{--}$ at 0°, but the salt contained two molecules of water of crystallization in addition to the water in the coördination sphere of cobalt.

At present attempts to measure the water exchange reaction by precipitation of the salt $[Co(en)_3][Co(CN)_5OH]$ are in progress.

An effort was made to detect the possible ion pair association of $Co(CN)_5OH_2^{--}$ with N_3^- by examining the absorption spectra of the complex in 4.0 M $NaClO_4$ and in 4.0 M NaN_3. In the region between 450 and 290 mμ the absorption spectrum of $Co(CN)_5OH_2^{--}$ was the same in 4.0 M $NaClO_4$ and in dilute aqueous solution; however, between 290 and 250 mμ the molar absorbancy index in 4.0 M $NaClO_4$ was approximately 1.5% higher than in the absence of the $NaClO_4$. In order to obtain the spectrum of $Co(CN)_5OH_2^{--}$ in 4.0 M NaN_3, it was necessary to follow the absorbancy for a period of 10 min. and then to extrapolate the data to zero time, since formation of $Co(CN)_5N_3^{-3}$ is relatively rapid under these conditions. To within the limit of error of the measurements, the molar absorbancy index was the same in the 4.0 M $NaClO_4$ and NaN_3 solutions.

Results

The kinetics of reaction 4 first were studied at 40° and ionic strength 1.0. The pH was adjusted to 6.4 with phosphate buffer in order to prevent hydrolysis of azide ion. Even at the lowest added

$$Co(CN)_5OH_2^{--} + N_3^- \longrightarrow Co(CN)_5N_3^{-3} + H_2O \quad (4)$$

azide ion concentration the absorption spectrum of the solution ultimately approached that of $Co(CN)_5N_3^{-3}$ within the limit of error of the measurement, indicating that reaction 4 proceeded to completion under these conditions. Pseudo-first-order rate constants obtained under various experimental conditions are listed in column 4 of Table I. If the rate of reaction 4 were first-order in azide ion concentration, the values of $k/(N_3^-)$ given in column 3 of Table I should be constant. The significance of the continuous decrease in $k/(N_3^-)$ with increasing azide ion concentration will be discussed below.

TABLE I

THE RATE OF FORMATION OF $Co(CN)_5N_3^{-3}$ AT 40°, IONIC STRENGTH 1.0, AND pH 6.4

$[Co(CN)_5OH_2^{--}]$, $M \times 10^4$	(N_3^-), M	$10^4 \times k/(N_3^-)$, M^{-1} sec.$^{-1}$	$k \times 10^5$, sec.$^{-1}$	$k \times 10^5$, sec.$^{-1}$ (calcd.)
0.86	0.0355	9.30	3.30	2.95
1.72	.071	8.80	6.25	5.78
6.89	.142	7.89	11.2	11.2
6.89	.212	7.48	16.1	16.0
5.32	.45	6.78	30.5	30.6
2.83	.45	6.82	30.7[a]	30.6
1.00	.45	6.85	30.8[a]	30.6
5.67	.725	6.14	44.5[a]	44.4
7.50	.725	6.03	43.7	44.4
5.68	.90	5.61	50.5[b]	51.5
5.70	1.0	5.48	54.8[b,c]	55.2

[a] In these experiments the $Co(CN)_5OH_2^{--}$ was prepared by hydrolysis of $Co(CN)_5Br^{-3}$. [b] Unbuffered perchloric acid solutions at pH 6.7. [c] In this experiment the $Co(CN)_5OH_2^{--}$ was prepared by acid hydrolysis of $Co(CN)_5N_3^{-3}$.

In the absence of added azide ion, the reverse of reaction 4 does not proceed to completion at pH 6.4 and at the concentrations of $Co(CN)_5N_3^{-3}$ necessary to carry out the kinetic measurements. However, at a $Co(CN)_5N_3^{-3}$ concentration of 5×10^{-4} M and pH 6.4, more than 70% aquation occurs. It therefore was possible to obtain the first-order rate constant for aquation from the initial slope of a plot of log $(D_t - D'_\infty)$, with D'_∞ being the absorbancy calculated for complete reaction. At 40°, pH 6.4, and ionic strength 1.0, the first-order rate constant for aquation of $Co(CN)_5N_3^{-3}$ is 5.5×10^{-7} sec.$^{-1}$.[15] The aquation of $Co(CN)_5N_3^{-3}$ also was studied at 0.10 M OH^- concentration, a medium in which the reaction proceeds to completion because of neutralization of the $Co(CN)_5OH_2^{--}$. At 60° and ionic strength 1.0, the rate of aquation of $Co(CN_5N_3^{-3}$ is the same at pH 6.4 and at 0.1 M OH^- concentration, with a first-order rate constant of 8.0×10^{-6} sec.$^{-1}$. The values of ΔH and ΔS^* for the aquation of $Co(CN)_5N_3^{-3}$ calculated from the equation[16]

$$k = \frac{kT}{h} e^{\Delta S^*/R} e^{-\Delta H^*/RT}$$

are 27.3 kcal. and −0.6 e.u., respectively.

Although the detailed interpretation of kinetic

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(15) The rate of the acid-catalyzed aquation of $Co(CN)_5N_3^{-3}$ at pH 6.4 is calculated to be 6.0×10^{-9} sec.$^{-1}$ (A. Haim and W. K. Wilmarth, to be published), which is approximately 1% of the rate for the non-catalyzed reaction.

(16) S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941.

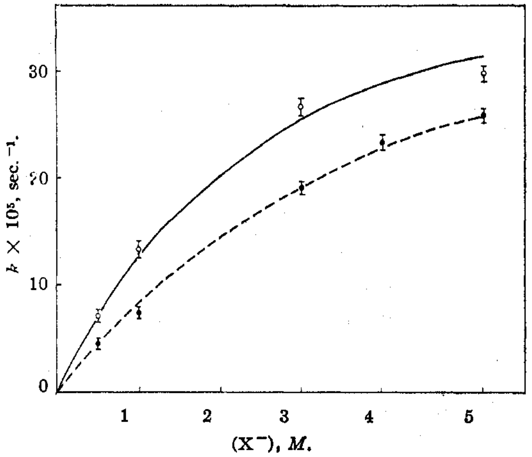

Fig. 2.—Pseudo-first-order rate constants *vs.* anion concentration at 20° and ionic strength 5.0: Φ, azide; ♦, thiocyanate.

studies at high concentrations of reactants is complicated by uncertainties in medium effects as discussed below, the results obtained at ionic strength 1.0 indicated the desirability of extending the studies to higher azide ion concentrations. Therefore, a series of measurements was carried out at an ionic strength of 5.0, with the pH again at 6.4, but at the lower temperature of 20.0°. As shown in Fig. 2, at the higher azide ion concentrations the rate approached a zero-order dependence upon azide ion concentration.

The pseudo-first-order rate constants for reaction 5 are listed in column 4 of Table II. The conditions employed were entirely comparable to those of Table I, except that the solutions

$$Co(CN)_5OH_2^{--} + SCN^- \longrightarrow Co(CN)_5NCS^{-3} + H_2O \quad (5)$$

contained perchloric acid at a pH of 3.4. In all experiments the spectral evidence again indicated that reaction 5 proceeded to completion. The values of $k/(SCN^-)$ listed in column 3 of Table II decrease with increasing thiocyanate ion concentration in a fashion similar to that observed in Table I. The pseudo-first-order rate constants measured at an ionic strength of 5.0 and a temperature of 20.0° are plotted *vs.* thiocyanate ion concentration in Fig. 2. Again the dependence of k upon (SCN^-) became less than first-order at high thiocyanate ion concentration.

TABLE II

THE RATE OF FORMATION OF $Co(CN)_5NCS^{-3}$ AT 40°, IONIC STRENGTH 1.0, AND pH 3.4

$[Co(CN)_5$-$OH_2^{--}]$, $M \times 10^4$	(SCN^-), M	$10^4k/(SCN^-)$, M^{-1} sec.$^{-1}$	$k \times 10^5$, sec.$^{-1}$	$k \times 10^5$, sec.$^{-1}$ (calcd.)
4.00	0.10	5.34	5.34	5.25
2.65	.18	5.10	9.20	9.20
4.00	.20	4.60	9.20	10.1
2.65	.27	4.74	12.8	13.4
4.00	.40	4.75	19.0	19.1
2.65	.45	4.85	21.8	21.2
2.65	.72	4.40	31.6	31.4
4.00	.80	4.40	35.2	34.1
2.96	.90	4.14	37.2[a]	37.5
2.96	.90	4.34	39.0[b]	37.5
2.96	.90	...	33.8[c]	30.9
2.96	.90	...	17.1[d]	13.6

[a] pH 3.1. [b] pH 7.1. [c] pH 9.11. [d] pH 10.11.

Attempts to isolate the sodium or potassium salt of $Co(CN)_5NCS^{-3}$ prepared by the reaction of $Co(CN)_5OH_2^{--}$ and SCN^- were unsuccessful. Therefore, the following procedure was devised to study the rate of the reverse of reaction 5. The reaction of $Co(CN)_5OH_2^{--}$ with SCN^- was allowed to proceed to completion. An aliquot of the solution then was withdrawn and diluted to a known volume with NaOH and $NaClO_4$ to give a OH^- concentration of 0.1 *M* and an ionic strength of 1.0. In the basic solution the equilibrium in reaction 5 was shifted to the left because of neutralization of $Co(CN)_5OH_2^{--}$, and the aquation of $Co(CN)_5NCS^{-3}$ thus could be studied. The first-order rate constants were obtained from the initial slopes of log $(D_t - D'_\infty)$ *vs.* time, since these plots deviated from linearity after 20% reaction because the aquation of $Co(CN)_5NCS^{-3}$ did not proceed to completion under the experimental conditions used. At 40°, 0.1 *M* OH^- concentration, 0.18 *M* SCN^- concentration, and ionic strength 1.0, the first-order rate constant for aquation of $Co(CN)_5NCS^{-3}$ is 3.7×10^{-7} sec.$^{-1}$. Under the same conditions but at the temperature of 60°, the first-order rate constant is 7.8×10^{-6} sec.$^{-1}$. The corresponding values of ΔH^* and ΔS^* are 31.1 kcal. and 11.5 e.u., respectively. The validity of this procedure was tested by using it to study the reverse of reaction 4. At 40°, 0.1 *M* OH^- concentration, 0.18 *M* N_3^- concentration, and ionic strength 1.0, the first-order rate constant for aquation of $Co(CN)_5N_3^{-3}$ is 5.4×10^{-7} sec.$^{-1}$. Under the same conditions, but at the temperature of 60°, the first-order rate constant is 8.3×10^{-6} sec.$^{-1}$. The last two values are in good agreement with the values reported above for the aquation of $Co(CN)_5N_3^{-3}$.

The equilibrium constant for reaction 6 was

$$Co(CN)_5N_3^{-3} + SCN^- \rightleftharpoons Co(CN)_5NCS^{-3} + N_3^- \quad (6)$$

determined by allowing a solution 0.002 *M* in $Co(CN)_5OH_2^{--}$ to reach equilibrium with a mixture of 0.45 *M* SCN^- and 0.45 *M* N_3^-, at 40°, pH 6.4, and ionic strength 1.0, and measuring the optical density of the solution at wave lengths from 430 to 260 mμ, after the appropriate dilutions. It can be shown that, at equilibrium, the optical properties of the system are given by equation 7. *D* is the absorbancy of the solution

$$\frac{D_a - D}{D - D_b} = K\frac{(SCN^-)}{(N_3^-)} \qquad (7)$$

under consideration, D_a and D_b are the absorbancies of solutions of $Co(CN)_5N_3^{-3}$ and $Co(CN)_5NCS^{-3}$, respectively, at the same total cobalt(III) concentration as the solution under consideration, and *K* is the concentration equilibrium constant for reaction 6. The results, presented in Table III, yield an average value of 0.87 for *K*.

TABLE III

THE EQUILIBRIUM CONSTANT AT 40° AND IONIC STRENGTH 1.0 FOR REACTION 6

$(Co^{III}) = 2 \times 10^{-3}$ *M* $(N_3^-) = (SCN^-) = 0.45$ *M*

Wave length, mμ	*D*	$\epsilon_{Co(CN)_5NCS^{-3}}$	$\epsilon_{Co(CN)_5N_3^{-3}}$	*K*
430	0.140	67	201	0.84
420	.203	97	296	.88
410	.275	135	408	.95
400	.358	153	536	.87
390	.430	188	636	.85
380	.460	266	666	.88
370	.441	249	601	.83
360	.375	251	481	.86
350	.310	238	388	1.08
340	.290	222	350	.88
330	.385	228	551	1.06
320	.700	270	1,020	0.74
310	.275	430	2,175	.85
300	.555	985	4,225	.82
290	.195	3,100	6,525	.93
280	.291	7,025	7,500	.73
270	.353	11,700	6,600	.76
250	.306	12,000	3,900	.88
250		5,000	3,320	

The rate of reaction 4 was studied as a function of pH. The pseudo-first-order rate constants measured at 40°, 0.9 *M* N_3^- concentration, and ionic strength 1.0 are listed in column 3 of Table IV. As the pH is increased above 6.7, the pseudo-first-order rate constant first decreases slowly, then more rapidly, and finally becomes inversely proportional to the OH^- concentration above 0.009 *M*. The dependence of the pseudo-first-order rate constant at 40° and ionic strength 1.0 upon N_3^- concentration at 0.009 *M* OH^- concentration and at pH 10.1 is given in Tables V and VI. Column 2 of Table V indicates that at 0.009 *M* OH^- concentration, the pseudo-first-order rate constant increases linearly with the N_3^- concentration.

TABLE IV

THE RATE OF FORMATION OF $Co(CN)_5N_3^{-3}$ AT 40°, 0.9 *M* N_3^-, AND $\mu = 1.0$

$[Co(CN)_5OH_2^{--}]$, $M \times 10^4$	pH[a]	(OH^-)	$k \times 10^5$, sec.$^{-1}$	$k \times 10^5$, calcd.
5.68		0.10	0.18[b]	0.19
5.68		.010	1.84	1.84
6.44		.009	2.05	2.05
6.44	10.1		19.7	19.5
5.68	9.88		29.2	25.6
5.68	9.05		44.5	43.3
5.68	8.65		47.4	48.0
5.68	6.7		50.5	51.5

[a] pH adjusted using phosphate buffers. [b] In this experiment the rate constant was obtained from the initial slope since the reaction did not proceed to completion.

Column 2 of Table VI indicates that at pH 10.1 the dependence of the pseudo-first-order rate constant upon N_3^- concentration becomes less than first-order as the N_3^- concentration increases, but the deviation from linearity is not as pronounced as that observed at pH 6.4. The significance of these results will be discussed later.

The pseudo-first-order rate constant for reaction 5 also decreased with increasing pH. Only two experiments were performed in alkaline

TABLE V

THE RATE OF FORMATION OF $Co(CN)_5N_3^{-3}$ AT 40°, $(OH^-) = 0.009$ *M*, AND $\mu = 1.0$

$[Co(CN)_5OH_2^{--}] = 6.44 \times 10^{-4}$ *M*

(N_3^-), *M*	$10^5k/(N_3^-)$, M^{-1} sec.$^{-1}$	$k \times 10^5$, sec.$^{-1}$	$k \times 10^5$, sec.$^{-1}$ (calcd.)
0.19	2.37	0.43	0.42
.45	2.29	1.03	1.04
.90	2.28	2.05	2.05

TABLE VI

THE RATE OF FORMATION OF $Co(CN)_5N_3^{-3}$ AT 40°, pH 10.1, AND $\mu = 1.0$

$[Co(CN)_5OH_2^{--}] = 6.44 \times 10^{-4}$ *M*

(N_3^-), *M*	$10^4k/(N_3^-)$, M^{-1} sec.$^{-1}$	$k \times 10^5$, sec.$^{-1}$	$k \times 10^5$, sec.$^{-1}$ (calcd.)
0.18	2.67	4.81	4.64
.27	2.49	6.72	6.80
.45	2.36	10.6	10.8
.72	2.29	16.5	16.2
.90	2.19	19.7	19.5

solution, and the results are given in the last two rows of Table II.

As indicated above, a quantitative measurement of the rate of water exchange has not been obtained because of irreproducible induced exchange during separation. The irreproducibility is illustrated by the scatter of the points in Fig. 1, where log $[1 - (N_t - N_0)/(N_\infty - N_0)]$ is plotted *vs.* time. To avoid confusion in the discussion at this point, it might be noted explicitly that N_∞ represents a much larger degree of exchange than that observed for completely induced exchange, because in the medium where completely induced exchange occurs the initial H_2O^{18} content of the solvent has been reduced because of dilution by the silver nitrate solution. The experiments also indicate that the induced exchange is not complete in all the samples since some of the points lie above and some below the values calculated for complete induced exchange represented by the horizontal lines in Fig. 1, a circumstance that permits setting lower and higher limits on the first-order rate constant for the water exchange reaction. Specifically, for point 12 in Fig. 1 the value of N_t of 4.35×10^{-3} corresponds to a rate constant of 1.0×10^{-3} sec.$^{-1}$, N_t being the ratio of H_2O^{18} to H_2O^{16} in the $Ag_2[Co(CN)_5OH_2]$ precipitated at time t. Had induced exchange been complete in this experiment, N_t would have had the value 3.28×10^{-3}. Since the observed value of N_t is larger than 3.28×10^{-3}, any induced exchange could only have lowered the value of N_t. Therefore, the desired value of N_t, free from errors caused by induced exchange, must be at least as large as 4.35×10^{-3}. Correspondingly, the desired rate constant for the exchange cannot be lower than 1.0×10^{-3} sec.$^{-1}$, the value calculated with $N_t = 4.35 \times 10^{-3}$.[17] In a similar manner, a rate constant calculated with a value of N_t smaller than the value calculated for complete induced exchange yields a maximum value for the desired rate constant k_{ex}. In Fig. 1 there are three such values of N_t. Two of these correspond to extremely short reaction times, and the corresponding rate constants do not have any quantitative significance, although they serve to demonstrate that neither the homogeneous exchange nor the induced exchange is immeasurably fast. From experiment 6 it may be concluded that $k_{ex} < 1.3 \times 10^{-3}$ sec.$^{-1}$.[18]

It must be pointed out that the H_2O^{18} content of the solution where exchange is occurring is decreased when silver nitrate dissolved in water of normal isotopic composition is added to precipitate $Ag_2[Co(CN)_5OH_2]$. In calculating the labeling expected for complete induced exchange during precipitation, it was *assumed* that the H_2O^{18} content of $Ag_2[Co(CN)_5OH_2]$ would be that of the solution where exchange was occurring *after* dilution with the silver nitrate solution. Consequently, the limits set on k_{ex} must be considered as tentative values.

Discussion

The results obtained in the study of the substitution of water in $Co(CN)_5OH_2^{--}$ by azide and thiocyanate ions conform to the predictions of an SN1 mechanism.

$$Co(CN)_5OH_2^{--} \underset{k_2}{\overset{k_1}{\rightleftarrows}} Co(CN)_5^{--} + H_2O \quad (8)$$

$$Co(CN)_5^{--} + X^- \xrightarrow{k_3} Co(CN)_5X^{-3} \quad (9)$$

In terms of this mechanism the pseudo-first-order rate constant k listed in Tables I and II should depend upon (X^-), the azide or thiocyanate ion concentration, in the manner indicated by eq. 10.

$$k = \frac{k_1(X^-)}{(X^-) + k_2/k_3} \quad (10)$$

Numerical values of $1/k_1$ and k_2/k_3 were obtained from the intercept, and the ratio of the slope to the intercept of the straight lines defined by the points in plots of $1/k$ *vs.* $1/(X^-)$. For substitution by azide ion at 40° and ionic strength 1.0, $k_1 = 1.4 \pm 0.3 \times 10^{-3}$ sec.$^{-1}$, and for the thiocyanate reaction under the same conditions, $k_1 = 1.8 \pm 0.4 \times 10^{-3}$ sec.$^{-1}$. Although the pseudo-first-order rate constants are reproducible to ±3%, the value of k_1 has a considerably larger uncertainty because of the form of eq. 7 and the long extrapolation involved in obtaining k_1. Nevertheless, there is fairly good agreement between theory and experiment as seen by comparing the two values of k_1 listed above, and also by comparing the values of k (calcd.) with the experimental values in Tables I and II. The values

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(17) The other points in Fig. 1 lying above the complete induced exchange value yield minimum values for k_{ex} smaller than 1.0×10^{-3} sec.$^{-1}$. The latter value is therefore the highest minimum value for k_{ex}.

(18) The rest of the points in Fig. 1 (experiments 2, 7, 8, 11, 15, and 16) have values of N_t within 2% of the complete induced exchange value, and therefore they cannot be used to set any limits on k_{ex}.

of k (calcd.) for the thiocyanate and azide systems were obtained from eq. 10 by using the common value of k_1 of 1.6×10^{-3} sec.$^{-1}$, the average of the two values listed above, and a value of k_2/k_3 of 1.9 for the azide system, and of 2.95 for the thiocyanate system. From the two latter values, it is concluded that, in terms of capture of the pentacoördinated intermediate $Co(CN)_5^{--}$ in reaction 9, azide ion is a better nucleophile than thiocyanate ion by a factor of 1.55. In comparing the competitive efficiencies of the various X^- species with water it perhaps is desirable to divide the ratio k_2/k_3 by 52, an approximate value for the formal concentration of water in 1.0 *M* sodium perchlorate solutions at 40°. If this procedure is adopted, it is found that azide and thiocyanate ions are better nucleophiles than water by the factors 27.4 and 17.6, respectively.

The results obtained at an ionic strength of 5.0 and at 20° seem to provide additional support for the SN1 mechanism. For both azide and thiocyanate ions, plots of $1/k$ *vs.* $1/(X^-)$ are linear and yield the values $k_1 = 4.7 \pm 0.5 \times 10^{-4}$ sec.$^{-1}$ and $k_1 = 5.4 \pm 0.5 \times 10^{-4}$ sec.$^{-1}$, respectively. The agreement between theory and experiment may be seen by comparing the two values of k_1, and also by comparing the theoretical curves with the experimental values in Fig. 2. The theoretical curves for the azide and thiocyanate reactions were calculated from eq. 10 by using the common value of k_1 of 5.1×10^{-4} sec.$^{-1}$, the average of the two values listed above, and a value of k_2/k_3 of 3.0 for azide ion, and of 5.0 for thiocyanate ion. Under these conditions of temperature and ionic strength, azide ion is a better nucleophile than thiocyanate ion by a factor of 1.7.

The SN1 mechanism implies that the rate constant k_{ex} for water exchange between $Co(CN)_5OH_2^{--}$ and the solvent should equal k_1, the limiting rate constant for anation at high anion concentration. As indicated above, a quantitative measurement of the first-order rate constant for the water exchange has not been obtained. Nevertheless, with the assumption that the ratio of H_2O^{18} to H_2O^{16} for complete induced exchange during precipitation corresponds to that of the solution where exchange is occurring *after* dilution with the silver nitrate solution, it has been possible to set these tentative limits on k_{ex} at 40° and ionic strength 1.0: 1.3×10^{-3} sec.$^{-1} > k_{ex} > 1.0 \times 10^{-3}$ sec.$^{-1}$. The values of k_1 obtained in the azide and thiocyanate studies, $1.4 \pm 0.3 \times 10^{-3}$ sec.$^{-1}$ and $1.8 \pm 0.4 \times 10^{-3}$ sec.$^{-1}$, respectively, are compatible with the limits set on k_{ex}, a result which provides further support for the SN1 mechanism.

A mechanism consistent with the azide and thiocyanate data could be formulated in terms of the seven-coördinate intermediate $Co(CN)_5(OH_2)_2^{--}$. Generation of this ion by reaction of $Co(CN)_5OH_2^{--}$ with water would replace reaction 8, and reaction 9 would be replaced by a process in which the two water ligands in the intermediate ultimately would be displaced by a single X^- anion. If the two water molecules in the hypothetical $Co(CN)_5(OH_2)_2^{--}$ intermediate were equivalent, the predicted rate for water exchange would be only one-half k_1. The tentative rate constants obtained for the water exchange data thus favor the $Co(CN)_5^{--}$ formulation, but more reliable measurements are obviously desirable. Such studies are now in progress.

If the mechanism provided by eq. 8 and 9 is accepted for the displacement of water in $Co(CN)_5OH_2^{--}$, then microscopic reversibility restrictions require that the aquation of $Co(CN)_5X^{-3}$ also proceed by an SN1 mechanism. The appropriate reactions for the aquation mechanism are given by eq. 11 followed by the competition of X^- and water for $Co(CN)_5^{--}$ in reaction 9 and the reverse of reaction 8.

$$Co(CN)_5X^{-3} \xrightarrow{k_4} Co(CN)_5^{--} + X^- \quad (11)$$

The mechanism under consideration gains further support from the observation that the rates of the aquation reactions are pH independent. This behavior is entirely analogous to that observed for trityl chloride and other organic halides which undergo solvolyis by well established SN1 mechanisms.[19] By contrast, it may be noted that the rate of aquation of most Co(III) complexes increases with increasing pH.[20]

The internal consistency of the rate and equilibrium data may be verified by calculating the equilibrium constants for reactions 4 and 5 using the kinetic parameters and the relationship $k_1k_3/k_2k_4 = K$. The numerical values of 1530 and 1460 are obtained for the equilibrium con-

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[19] C. K. Ingold, "Structure and Mechanisms in Organic Chemistry," Cornell University Press, Ithaca, New York, 1953, p. 316.

[20] F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 124.

stants at 40° and unit ionic strength for azide ion and thiocyanate ion, respectively. The ratio $1460/1530 = 0.96$ is in good agreement with the experimental value of 0.87 for reaction 6. A single measurement at 0.1 M OH^- concentration, unit ionic strength, and 40° yielded a value of 0.55 for the equilibrium constant of reaction 12.

$$Co(CN)_5OH^{-3} + N_3^- \rightleftharpoons Co(CN)_5N_3^{-3} + H^- \quad (12)$$

The measurement was not of high accuracy, since the position of equilibrium in the experiment was far to the right. Consequently, the result may be considered to be in reasonable agreement with the value 0.43 calculated from the relationship $K_{12} = KK_w/K_a$ using the numerical values of 1530, 5.65×10^{-14}, and 2×10^{-10} for K, K_w, and K_a, respectively.

The observed pH independence of the aquations of $Co(CN)_5N_3^{-3}$ combined with microscopic reversibility restrictions requires that there be no important SN2 path for the reaction of $Co(CN)_5OH^{-3}$ and azide ion. This latter reaction, given by eq. 12, therefore also must proceed by an SN1 mechanism. In this instance two alternative SN1 mechanisms must be considered. In the first alternative it is assumed that $Co(CN)_5OH^{-3}$ is completely unreactive and that at any given pH the azide ion reacts only with the fraction of the complex present as $Co(CN)_5OH_2^{--}$. This mechanism thus involves the pre-equilibrium given by eq. 3, 8, and 9. In this formulation the pH and azide ion dependence of the pseudo-first-order rate constant is given by eq. 13.

$$k = \frac{k_1(H^+)(N_3^-)}{[(k_2/k_3 + (N_3^-)][K_a + (H^+)]} \quad (13)$$

In the second of the alternative SN1 mechanisms the assumption is again made that reactions 3, 8, and 9 occur, but now the further assumption is made that $Co(CN)_5^{--}$ also may be generated by reaction 14.

$$Co(CN)_5OH^{-3} \longrightarrow Co(CN)_5^{--} + OH^- \quad (14)$$

When reaction 14 is included in the mechanism, the expression for the rate constant is given by eq. 15.

$$k = \frac{[k_1(H^+) + k_1'K_a](N_3^-)}{[(k_2/k_3) + (k_2'/k_3)(OH^-) + (N_3^-)][K_a + (H^+)]} \quad (15)$$

The predictions of eq. 13 are not in agreement with the experimental results. First, the rate constants above pH 10 calculated from eq. 13 are 15–20% smaller than the experimentally determined values. A second and perhaps more compelling point is that eq. 13 is not consistent with the observation that with increasing pH k approaches a first-order dependence upon azide ion concentration.

The predictions of eq. 15, unlike those of eq. 13, are in good agreement with experiment, and it therefore is concluded that the mechanism of azide ion substitution in alkaline solution is adequately represented by eq. 3, 8, 9, and 14. It can be seen from inspection of eq. 15 that values of $[K_a + (H^+)]/[k_1(H^+) + k_1'K_a]$ and of $(k_2/k_3) + (k_2'/k_3)(OH^-)$ may be obtained from the intercept and the ratio of the slope to the intercept in the linear plots of $1/k$ *vs.* $1/(N_3^-)$ for the data presented in Table IV. Using these data and the previously evaluated quantities k_1, k_2/k_3, and K_a, we obtain $k_1' = 6.5 \times 10^{-4}$ sec.$^{-1}$ and $k_2'/k_3 = 3.0 \times 10^3$. The excellent agreement between theory and experiment may be seen by referring to Tables III, IV, and V, where experimental values of k may be compared with those calculated from eq. 15. As an alternate way of comparing theory and experiment the value $k_1'/(k_2/k_3) = 2.17 \times 10^{-7}$ sec.$^{-1}$, obtained by use of the numerical values of k_1' and k_2'/k_3, may be compared with the value 2.37×10^{-7} sec.$^{-1}$, the latter value being obtained by substituting appropriate data in the right side of the expression $k_1'/(k_2/k_3) = k_1K_w/K_a(k_2/k_3)$, which results from microscopic reversibility considerations.

To a very good approximation, in strongly alkaline solution eq. 15 may be written in the simplified form $k = k_1'(N_3^-)/(k_2'/k_3)(OH^-)$. At 0.009 M alkali, the condition employed for the experiments reported in Table V, the approximation is valid, and the quantity $k/(N_3^-)$ is independent of the azide ion concentration. Further, at this and higher alkali concentrations the rate constant k is inversely proportional to the alkali concentration. In physical terms this limiting behavior arises because of the extreme inefficiency with which azide ion competes with hydroxide ion for the $Co(CN)_5^{--}$ intermediate, the relative competitive efficiencies at equal concentrations of the two species being given by the quantity $k_2'/k_3 = 3.0 \times 10^3$. The decrease in rate with increasing hydroxide ion concentration is thus an extreme example of what in kinetic studies is commonly termed mass law retardation.

Although the SN1 mechanism adequately describes the kinetics of the substitution of water in $Co(CN)_5OH_2^{--}$ by azide and thiocyanate ions and by O^{18}-enriched water, it is necessary, at this point, to inquire about alternative formulations. In particular, there is the question whether the reaction might not be proceeding by an SN2 mechanism, with the decrease in $k/(X^-)$ with increasing (X^-) merely representing a medium effect arising from the replacement of ClO_4^- by X^-. Medium effects could be attributed either to the usual long range interaction of ions or to ion pairs or triplets having the formulas $Co(CN)_5OH_2^{--} \cdot X^-$ or $Co(CN)_5OH_2^{--} \cdot Na^+ \cdot X^-$. Driving force for the formation of ion pairs presumably would arise from hydrogen bonding of the sort $Co-OH_2 \cdot\cdot X^-$ or from electrostatic interaction of X^- with an incompletely shielded Co(III) ion. Long range interaction does not seem to provide a plausible explanation. In a reaction of two negative ions both theory and experiment seem to indicate that the value of the rate constant is not sensitive to the nature of the negative ions in the solution as long as the positive ion environment is held constant.[21] It also does not seem that ion association can be very important, at least in the solutions of unit ionic strength. An explanation formulated in these terms would require that a very substantial part of the Co(III) be associated with X^- ions. It should be noted, first, that appreciable association of X^- ions with octahedral complex ions has been detected[22] only when the complex ion bears an over-all positive charge of two or greater. In our system the optical studies suggest that there may be a detectable formation of $Co(CN)_5OH_2^{--} \cdot Na^+$, although the studies were not very extensive or conclusive.[23] In view of the unfavorable electrostatic situation, further extensive association with X^- or formation of ion pairs seems quite improbable, though it cannot be conclusively ruled out. Secondly, and perhaps most important, it has been found in unpublished experiments that the decrease in $k/(X^-)$ with increasing X^- occurs only with the more reactive nucleophiles. In studies with the less reactive bromide and iodide nucleophiles there is no detectable variation in the quantity $k/(X^-)$. This behavior and the common value of k_1 found for the more reactive nucleophiles is, of course, the natural consequence of an SN1 mechanism. It could only result by sheer coincidence in an SN2 process. Finally, we note that paper II provides further, very compelling support for our proposed mechanism.

It is of interest to consider whether an SN1 mechanism might have been anticipated in the present system. In organic systems the presence of a highly electronegative cyano substituent would tend to favor an SN2 rather than an SN1 mechanism. Presumably the presence of a single cyano ligand in a positively charged complex ion might have similar mechanistic consequences. However, when the number of cyano ligands is increased to five, the accumulation of negative charge probably produces a relatively high electron density at the cobalt atom, despite the tendency for π-bonding to spread the charge throughout the ligand sphere.[24] Such an accumulation of negative charge at the cobalt atom should lead to a relatively weak $Co-OH_2$ bond, a weakly acidic complex, and a favorable SN1 reaction path. The observed pK of the complex and the relatively rapid water exchange both are consistent with this point of view. There is also at least one other factor which might facilitate an SN1 mechanism. If there is an increase in bond angle in going from the hexacoördinate reactant to the pentacoördinate intermediate, then a stabilization of the intermediate would result from the decrease in electrostatic repulsion of the negatively charged ligands. Lastly, it might be noted that the orientation of the water solvent surrounding a negatively charged complex ion probably will be very different from that surrounding a positively charged complex. The nature of the solvation sphere obviously will be a very important factor in governing the behavior of the $Co(CN)_5^{--}$ intermediate, particularly if the reaction with water in the reverse of reaction 8 is a multimolecular process involving the synchronized action of a number of water molecules.[25]

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[21] See A. R. Olson and T. R. Simonson, *J. Chem. Phys.*, **17**, 1167 (1949), and the chapter entitled "Catalysis in Homogeneous Reactions in a Liquid Phase," by E. L. King in P. H. Emmett, "Homogeneous Catalysis II," Reinhold Publishing Corp., New York, N. Y., 1955.

[22] Recent measurements of the stability of Cr(III) thiocyanate association constants have been reported by A. L. Phipps and R. A. Plane, *J. Am. Chem. Soc.*, **79**, 2458 (1957). Association constants of Co(III) complexes with N_3^- and other anions were reported by M. G. Evans and G. H. Nancollas, *Trans. Faraday Soc.*, **49**, 363 (1953), but later work by E. L. King, J. H. Espenson, and R. E. Visco, *J. Phys. Chem.*, **63**, 755 (1959), indicates that at least in some instances the reported association constants were considerably overestimated.

[23] It is of interest to note that the changes in absorbancy at high sodium ion concentration were opposite in sign to those reported by S. R. Cohen and R. A. Plane, *J. Phys. Chem.*, **61**, 1096 (1957), in their study of the association of $Fe(CN)_6^{-4}$ with various cations.

[24] A referee has pointed out that G. W. Chantry and R. A. Plane, *J. Chem. Phys.*, **35**, 1027 (1961), argue on the basis of Raman spectra measurements that π-bonding is unimportant in the $Co(CN)_6^{-3}$ ion.

[25] For a discussion of the analogous process in the solvolysis of organic halides see section 27d, p. 367 of ref. 19.