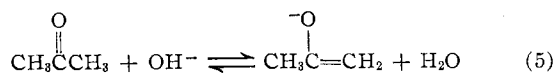rate constant, k (0.39 M^{-2} sec^{-1} at 297°K), is the product of a rate constant for the rate-determining step and the equilibrium quotient for

$$CH_3\overset{O}{\overset{\|}{C}}CH_3 + OH^- \rightleftharpoons CH_3\overset{-O}{\overset{|}{C}}{=}CH_2 + H_2O \qquad (5)$$

Using a pK for propanone of 20,[10] the equilibrium quotient is 10^{-6} and the rate constant for the reaction be-

(10) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p 227.

tween (NC)$_5$FeNO^{2-} and the enolate derived from propanone is about 4.6 $\times$ 10^5 M^{-1} sec^{-1}. Compared with the values of the analogous rate constants for the hydroxide-[2] and hydrogen sulfide ion-[3](NC)$_5$FeNO^{2-} reactions of 0.55 $\pm$ 0.01 and 170 $\pm$ 3 M^{-1} sec^{-1}, respectively, the value of the rate constant for the (NC)$_5$FeNO^{2-}–enolate reaction is large. However, lacking more accurate values of the equilibrium quotient and the enthalpy change for reaction 5, a complete evaluation in terms of the activation parameters is not possible.

The Pentacyano Complexes of Cobalt(III). III.[1] Kinetics and Mechanism of the Substitution of Water in Co(CN)$_5$OH$_2$$^{2-}$ by Iodide, Triiodide, Bromide, and Chloride Ions and Aquation of Co(CN)$_5$I^{3-}, Co(CN)$_5$Br^{3-}, and Co(CN)$_5$Cl^{3-}

BY ROBERT GRASSI,[2] ALBERT HAIM, AND W. K. WILMARTH

A study has been made at 40° and unit ionic strength of the rate of displacement of H$_2$O in Co(CN)$_5$OH$_2$$^{2-}$ by I$_3$$^-$, I$^-$, Br$^-$, and Cl$^-$. The relative rates of reaction are I$_3$$^-$ > I$^-$ > Br$^-$ > Cl$^-$, an order which also characterized the magnitude of the formation constants for Co(CN)$_5$I^{3-}, Co(CN)$_5$Br^{3-}, and Co(CN)$_5$Cl^{3-}. The results are discussed in terms of a limiting type of S$_N$1 mechanism involving the five-coordinate reactive intermediate Co(CN)$_5$$^{2-}$. Rate constants for displacement of the halogen by H$_2$O in Co(CN)$_5$I^{3-}, Co(CN)$_5$Br^{3-}, and Co(CN)$_5$Cl^{3-} are also reported.

Introduction

In earlier papers in this series we have reported kinetic studies of the substitution of water in Co(CN)$_5$-OH$_2$$^{2-}$ by a variety of nucleophiles.[3,4] Various aspects of that work provided evidence that the substitution reactions proceed by a limiting type of S$_N$1 mechanism involving the pentacoordinated Co(CN)$_5$$^{2-}$ as a reactive intermediate.

The present paper contains the results of kinetic studies of the anation of Co(CN)$_5$OH$_2$$^{2-}$ by Cl$^-$, Br$^-$, I$^-$, and I$_3$$^-$ and of the aquation of Co(CN)$_5$Cl^{3-}, Co(CN)$_5$Br^{3-}, and Co(CN)$_5$I^{3-}. The results are discussed in terms of the mechanism indicated above.[5]

The kinetic behavior of these systems has been found to be rather unusual in at least three respects. First, both the rate and equilibrium constants for the reaction of I$^-$ are greater than those for Br$^-$, the order I$^-$ > Br$^-$ > Cl$^-$ being the opposite of that observed for substitution of water in the ammine complexes of Co(III). Second, I$_3$$^-$ is a more reactive nucleophile than I$^-$.

(1) This work was supported by the Atomic Energy Commission.
(2) Based in part on a thesis submitted by R. Grassi 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) A. Haim and W. K. Wilmarth, *ibid.*, **1**, 583 (1962).
(5) A summary of most of the data to be presented in this paper has been published earlier in the Proceedings of the Sixth and Seventh International Conferences on Coordination Chemistry and in Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, pp 31–54.

Third, I$_3$$^-$ (or I$_2$) is an efficient catalyst for the aquation of Co(CN)$_5$I^{3-}.

Experimental Section

Apparatus.—Absorbancy measurements were carried out using either a Cary Model 14 PM recording spectrophotometer or a Beckman Model DU quartz spectrophotometer. A Beckman Model G pH meter was used for pH measurements.

Reagents.—Commercially available chemicals of analytical reagent grade quality, including NaBr, NaOH, NaI, NaH$_2$PO$_4$, I$_2$, NaClO$_4$·H$_2$O, KCN, and CoCl$_2$·5H$_2$O, were used without further purification.

The solutions containing Co(CN)$_5$OH$_2$$^{2-}$ were prepared using solid K$_6$[(NC)$_5$Co·O$_2$·Co(CN)$_5$]·H$_2$O in the manner previously described.[3]

Solid K$_3$Co(CN)$_5$Br was precipitated and recrystallized from aqueous solution at 0° by addition of ethanol. The Co(CN)$_5$-Br^{3-} ion was generated either by reaction of Co(CN)$_5$OH$_2$$^{2-}$ with excess Br$^-$ or by reaction of Co(NH$_3$)$_5$Br^{2+} with cobalt(II) cyanide solutions.[6] Either procedure was found to be satisfactory. The purity[7] of the product was established by a comparison of the spectrum of Co(CN)$_5$OH$_2$$^{2-}$ with that of a solution of Co(CN)$_5$-Br^{3-} which had been quantitatively converted to Co(CN)$_5$OH$_2$$^{2-}$ by aquation.

No entirely satisfactory method has been devised for the preparation of solid K$_3$Co(CN)$_5$I. In the present work the solid was precipitated at 0° by addition of ethanol to a solution in which the Co(CN)$_5$I^{3-} ion had been formed by reaction of Co-(CN)$_5$OH$_2$$^{2-}$ with excess I$^-$. The precipitation procedure fre-

(6) A. W. Adamson, *J. Am. Chem. Soc.*, **78**, 4260 (1956).
(7) In our experience, the results of C and N analyses obtained for Co(III) cyano complexes from commercial laboratories are not very reliable. A similar difficulty has been reported by C. J. L. Lock and G. Wilkins, *J. Chem. Soc.*, 2281 (1964).

quently yielded oils which were difficult to crystallize and which varied in purity over the range 85–100%, the purity being evaluated by the spectroscopic procedure outlined above. Recrystallization proved to be a relatively inefficient purification procedure.

A sample of $K_3Co(CN)_5I$ which was apparently free from impurities was used in the work described below. The purity of the sample was established both by the spectroscopic procedure outlined above and by conversion of the $Co(CN)_5I^{3-}$ to $Co(CN)_5OH_2^{2-}$ by photolysis, a process which proceeds to completion in bright sunlight within 30 min. After photolysis, the concentration of $Co(CN)_5OH_2^{2-}$ was determined spectrophotometrically and found to be that calculated for quantitative conversion of $Co(CN)_5I^{3-}$ to $Co(CN)_5OH_2^{2-}$. As the results presented in Table II indicate, the rate of the thermal aquation of $Co(CN)_5I^{3-}$ was found to be the same in solutions prepared using solid $K_3Co(CN)_5I^{3-}$ as it was in solutions in which the $Co(CN)_5I^{3-}$ was prepared by reaction of $Co(CN)_5OH_2^{2-}$ and I^-, a further test of the purity of the solid.

$K_3Co(CN)_5Cl$ was prepared by the reaction of a suspension of $[Co(NH_3)_5Cl]Cl_2$ with CN^- at 0°, catalyzed by a trace of Co^{2+}. The solid was precipitated by addition of ethanol at 0°, filtered, and washed with ethanol and ether. The purity of the product was determined by two methods. First, it was shown that after aquation, the spectrum of the solution corresponded within the limit of error to that predicted for quantitative formation of $Co(CN)_5OH_2^{2-}$. In the second method a solution of $Co(CN)_5Cl^{3-}$ was passed through an anion-exchange resin (Dowex 1) in the chloride form and the displaced Cl^- was titrated with $AgNO_3$ solution. The observed equivalent weight of 114 is that calculated for the formula $K_3Co(CN)_5Cl$.

Kinetic Procedure.—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 and diluted, and their absorbances were measured. The choice of wavelengths at which the various reactions were followed was dictated by the absorption spectra of the reactant and product. The bromide system was studied at 300 and 290 mμ where $Co(CN)_5Br^{3-}$ has molar absorbancy indices of 720 and 905, the corresponding values for $Co(CN)_5OH_2^{2-}$ being 90 and 95, respectively. The iodide and triiodide reactions were studied at 330 and 340 mμ where $Co(CN)_5I^{3-}$ has molar absorbancy indices of 2960 and 2650, while those of $Co(CN)_5OH_2^{2-}$ are 125 and 140, respectively. The wavelength 280 mμ, which was used in the Cl^- studies, corresponds to smaller molar absorbancy indices for $Co(CN)_5Cl^{3-}$ and $Co(CN)_5OH_2^{2-}$ of 410 and 125, respectively. In the studies involving I_3^-, the I_3^- was reduced to I^- by addition of buffered arsenite solutions before spectrophotometric analysis was carried out.

In handling solutions of $Co(CN)_5I^{3-}$, care must be taken to avoid exposure to sunlight, since the photolytic aquation of the complex is a very efficient process.

Results

Unless other conditions are specified, the kinetic experiments were carried out at 40°, at unit ionic strength, and at unit Na^+ concentration. In all kinetic studies except those of the aquation of $Co(CN)_5I^{3-}$ the rate of approach of the system to equilibrium was characterized by a rate constant k, obtained from the slope of the linear 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.

Let us first consider the replacement of H_2O in $Co(CN)_5OH_2^{2-}$ by I^-

$$Co(CN)_5OH_2^{2-} + I^- \rightleftharpoons Co(CN)_5I^{3-} + H_2O \qquad (1)$$
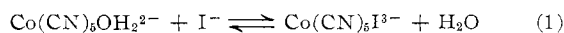
The pseudo-first-order rate constants for the anation

reaction at various I^- concentrations are presented in column 3 of Table I.

The aquation of $Co(CN)_5I^{3-}$, the reverse of reaction 1, was studied under the conditions listed in Table II. In the first two experiments of the table, carried

TABLE I

THE RATE OF REACTION OF $Co(CN)_5OH_2^{2-}$ WITH IODIDE ION AT 40°

$10^3[Co(CN)_5OH_2^{2-}]$, M	$[I^-]$, M	10^5k, sec^{-1}	10^5k, sec^{-1} (calcd)
1.47	1.00	27.3	26.3
1.27	1.00	28.0	26.3
1.23	1.00	27.1	26.3
1.27	1.00	25.5	26.3
1.47	0.70	21.0	19.6
1.27	0.70	21.2	19.6
1.47	0.70	20.0	19.6
1.23	0.50	13.6	14.7
1.47	0.40	12.4	12.1
2.62	0.333	9.68	10.4
2.57	0.100	3.57	3.77
3.36	0.050	2.18	2.27

TABLE II

THE RATE OF AQUATION OF $Co(CN)_5I^{3-}$ AT 40°

$10^3[Co(CN)_5I^{3-}]$, M	T, °C	$[I^-]$, M	$[OH^-]$, M	10^5k, sec^{-1}
0.282	69.9	0.00	1.6×10^{-8}	4.95
0.276	40.0	0.00	1.6×10^{-8}	0.76
0.148	40.0	0.56	0.20	0.73
0.169	40.0	0.63	0.10	0.74

out at 69.9 and 40.0°, the solutions were prepared by dissolving solid $K_3Co(CN)_5I$ and contained no additional iodide ion. Under these conditions, aquation proceeded to only approximately 85% of completion, and the first-order rate constants listed in column 5 were obtained from the initial slopes of the nonlinear plots of log $(A_t - A_\infty')$ vs. time, where A_∞' represents the absorbancy calculated for complete conversion of $Co(CN)_5I^{3-}$ to $Co(CN)_5OH_2^{2-}$. In the remaining two experiments, the $Co(CN)_5I^{3-}$ solutions were prepared by equilibrating solutions containing $Co(CN)_5OH_2^{2-}$ and I^- at concentrations which favored $Co(CN)_5I^{3-}$ formation. By adding alkali to the equilibrated solutions, it was possible to study the aquation reaction, since the alkali shifted the position of the equilibrium of reaction 1 far to the left because of the occurrence of reaction 2

$$Co(CN)_5OH_2^{2-} + OH^- \longrightarrow H_2O + Co(CN)_5OH^{3-} \qquad (2)$$
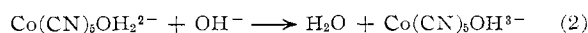
However, even in the presence of excess alkali the reverse of reaction 1 was not quantitative, and the observed values of k must be corrected in the manner indicated in the Discussion section, if they are to be comparable to the result obtained in the second experiment of the table. It is these corrected values of k which appear as the last two entries in Table II.

Use of eq 3 and the range of numerical values of k listed in Table II yielded values of $\Delta H^* = 29.7 \pm 0.5$ kcal and $\Delta S^* = 12.5 \pm 0.6$ eu for the equation of $Co(CN)_5I^{3-}$

$$k = \frac{kT}{h}e^{\Delta S^*/R}e^{-\Delta H^*/RT} \qquad (3)$$

Spectrophotometric measurements of solutions in which reaction 1 had reached equilibrium were used to calculate a numerical value of the equilibrium quotient. The procedure involved the use of eq 4, where A_∞ is the absorbancy of the system at equilibrium at the specified I^- concentration, A_0 is the absorbancy of a solution of $Co(CN)_5OH_2{}^{2-}$ at the same total Co(III) concentration, ϵ_{ROH_2} and ϵ_{RI} are the molar absorbancy indices of $Co(CN)_5OH_2{}^{2-}$ and $Co(CN)_5I^{3-}$, respectively, [Co(III)] is the total concentration of Co(III) in the system, and K is the equilibrium quotient for formation

$$A_\infty - A_0 = \frac{(\epsilon_{RI} - \epsilon_{ROH_2})K[Co(III)][I^-]}{1 + K[I^-]} \qquad (4)$$

of $Co(CN)_5I^{3-}$. The absorbancy[8] of solutions at equilibrium was measured at 330, 340, and 350 mμ over the range 0.02–1.0 M I^-. Use of a computer and a nonlinear least-squares program for curve fitting yielded a value of $K = 36.1 \pm 0.83$, where the listed uncertainty is the standard deviation.[9] The calculated values of $A_\infty - A_0$ for the 18 data points had an average per cent deviation of 2.46 and a maximum deviation of 5.35%.

The anation reaction was also studied in solution containing both I^- and $I_3{}^-$. Under these conditions reaction 5 was found to play an important role in the anation reaction

$$Co(CN)_5OH_2{}^{2-} + I_3{}^- \longrightarrow Co(CN)_5I^{3-} + I_2 \qquad (5)$$
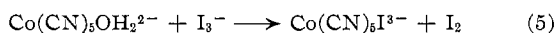
The pseudo-first-order rate constants obtained under these conditions are presented in column 3 of Table III under the heading k', the prime superscript being used to identify the $I_3{}^-$ system. The $I_3{}^-$ concentrations listed in column 2 of the table were calculated assuming that reaction 6 is essentially quantitative, a valid approximation at the 0.5 M I^- concentration employed in all of the experiments. A plot of k' vs.

$$I_2 + I^- \longrightarrow I_3{}^- \qquad (6)$$

[$I_3{}^-$], not included in the present paper, would show appreciable curvature, with the rate being less than linear in the $I_3{}^-$ concentration, an indication that, as with I^-, the data are not compatible with a single rate law involving merely the product of the concentrations of $Co(CN)_5OH_2{}^{2-}$ and $I_3{}^-$.

The rate of formation and aquation of $Co(CN)_5$-Br^{3-} was studied at the Br^- concentration listed in column 3 of Table IV

$$Co(CN)_5OH_2{}^{2-} + Br^- \rightleftharpoons Co(CN)_5Br^{3-} + H_2O \qquad (7)$$
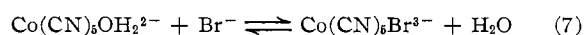
In the absence of added Br^-, the condition employed in the first experiment of the table, the aquation of Co-$(CN)_5Br^{3-}$ proceeded to completion. When kinetic measurements were carried out in the presence of added Br^-, appreciable concentrations of both Co-

(8) The data are available in the M.S. dissertation of R. Grassi. The concentration of I^- was calculated by an iterative procedure when an appreciable fraction of the total I^- was present as $Co(CN)_5I^{3-}$.

(9) The computer program was written by R. H. Moore at the Los Alamos Scientific Laboratory and is described in report LA 2367 (March 4, 1960) and Addenda (Jan 14, 1963).

TABLE III
THE RATE OF REACTION OF $Co(CN)_5OH_2{}^{2-}$ WITH TRIIODIDE
ION AT 40°

$10^4[Co(CN)_5OH_2{}^{2-}]$, M	$[I_3{}^-]$, M	$10^5k'$, sec^{-1} [a]	10^5k, sec^{-1} (calcd)
1.25	0.00	13.8	...
2.97	0.021	15.7	15.9
2.97	0.040	17.3	17.6
3.07	0.060	19.2	19.3
3.07	0.105	22.9	23.0
3.07	0.201	30.2	30.2
3.07	0.246	33.0	33.2
3.07	0.298	36.4	35.3

[a] The rate constant observed for solutions containing 0.5 M I^- and no added $I_3{}^-$.

TABLE IV
RATE OF AQUATION OF $Co(CN)_5Br^{3-}$ AND ANATION OF
$Co(CN)_5OH_2{}^{2-}$ BY Br^-

$10^3 \times$ $[Co(CN)_5Br^{3-}]$,[a] M	$10^{-3} \times$ $[Co(CN)_5OH_2{}^{2-}]$,[a] M	$[Br^-]$, M	10^4k, sec^{-1}	10^4k, sec^{-1} (calcd)[a]
2.75	...	0.00	1.68	1.67
2.75	...	0.20	1.95	1.96
2.75	...	0.50	2.37	2.37
2.75	...	0.80	2.80	2.75
...	4.80	0.50	2.32	2.37
...	1.60	0.80	2.75	2.75

[a] Initial concentrations.

$(CN)_5OH_2{}^{2-}$ and $Co(CN)_5Br^{3-}$ were found to be present at equilibrium. As a comparison of the last four experiments of Table IV will indicate, the numerical values of the pseudo-first-order constants at a given Br^- concentration are the same for solutions in which the reactant was initially present either as $Co(CN)_5$-$OH_2{}^{2-}$ or as $Co(CN)_5Br^{3-}$, the expected result for the kinetic system under investigation.

Pseudo-first-order rate constants for the Br^- anation reaction were also obtained at 20° and at an ionic strength of 5.0. The results obtained at 0.5, 1.0, 3.0, and 5.0 M Br^- may be adequately represented by the equation: $k = [1.2 \times 10^{-5} + 4.9 \times 10^{-5}[Br^-]]$ sec^{-1}. As the form of the equation indicates, a plot of k vs. Br^- concentration would be linear within the error of the measurements.

The equilibrium quotient for formation of $Co(CN)_5$-Br^{3-} at 40° and unit ionic strength was evaluated at a time before computer facilities were available. The equilibrium quotient was determined graphically from the ratio of the slope to intercept of a plot of $1/(A_\infty - A_0)$ vs. the Br^- concentration.[10] The validity of this procedure may be justified by inspection of eq 8, a rearranged form of eq 4

$$\frac{1}{A - A_0} = \frac{1}{(\epsilon_{RBr} - \epsilon_{ROH_2})[Co(III)]} + \frac{1}{(\epsilon_{RBr} - \epsilon_{ROH_2})[Co(III)]K[Br^-]} \qquad (8)$$

Figure 1 is a plot of the data obtained at two wavelengths. The upper two solid lines, representing experiments where the Co(III) is initially present as

(10) At present the data are conveniently available only in graphical form and a nonlinear least-squares calculation is not feasible.
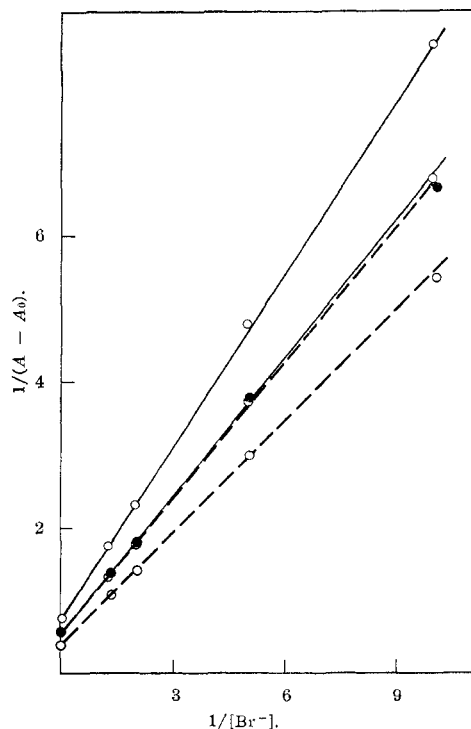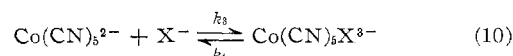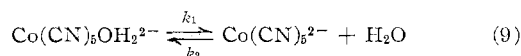
Figure 1.—A plot of $1/(A - A_0)$ *vs.* $1/[Br^-]$. The solid circles represent data at λ 300 mμ; the open circles (which partially overlap the open circles on the central points) data at λ 290 mμ. The solid lines represent experiments in which the Co(III) was initially present as 2.88×10^{-3} M Co(CN)$_5$Br^{3-}; for the dashed lines the Co(III) was initially present as 2.21×10^{-3} M Co(CN)$_5$OH$_2{}^{2-}$. All measurements were carried out at 40° and unit ionic strength.

Co(CN)$_5$Br^{3-}, correspond to formation constants of 0.91 and 0.88. In the remaining two series of experiments, in which the Co(III) was initially present as Co(CN)$_5$OH$_2{}^{2-}$, the dashed lines correspond to values of 0.89 and 0.88.

Only two experiments were carried out in the Co(CN)$_5$Cl^{3-} system. In the first experiment the aquation was found to proceed to completion with a rate constant of 4.5×10^{-4} sec^{-1}. In the second,[11] a pseudo-first-order rate constant of 5.5×10^{-4} sec^{-1} was obtained for the rate of approach to equilibrium of Co(CN)$_5$OH$_2{}^{2-}$ dissolved in 1.0 M NaCl. In the latter experiment the position of the final equilibrium corresponded to a formation quotient for Co(CN)$_5$Cl^{3-} of 0.22.

Discussion

The present results will be discussed in terms of the limiting type of S$_N$1 mechanism adopted on the basis of evidence obtained in earlier studies[3-5]

$$\text{Co(CN)}_5\text{OH}_2{}^{2-} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{Co(CN)}_5{}^{2-} + \text{H}_2\text{O} \qquad (9)$$

$$\text{Co(CN)}_5{}^{2-} + \text{X}^- \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \text{Co(CN)}_5\text{X}^{3-} \qquad (10)$$

The equations for the forward and reverse paths of reactions 9 and 10 serve to define the rate constants k_1, k_2, k_3, and k_4, the symbols being placed over or under

(11) This experiment was carried out by Mr. John Ellis.

the appropriate arrow, with the exception that the concentration of water is incorporated in k_2 in the customary fashion. The formula Co(CN)$_5{}^{2-}$ represents what is believed to be a five-coordinate reactive intermediate with a lifetime long enough to distinguish between various nucleophiles present in the system. The symbol X$^-$ refers to any one of the several nucleophiles under consideration.

If the assumption is made that the changes in activity coefficients caused by replacing NaClO$_4$ by NaX may be neglected, then the usual steady-state treatment leads without further approximation to eq 11, a relationship between the pseudo-first-order rate constant and the other kinetic parameters

$$k = \frac{k_1[\text{X}^-] + k_2 k_4 / k_3}{(k_2/k_3) + [\text{X}^-]} \qquad (11)$$

In our experiments at unit ionic strength, medium effects are expected to be relatively small,[12] since the study involves the reaction of two anions in which the only medium charge is the replacement of one anion by another. Under these conditions k_1 should have a common value for all anions, since reaction 9 does not involve the individual anion. However, to evaluate k_1, it is necessary to have accurate kinetic studies with highly reactive nucleophiles. In our earlier publication, a value of k_1 of 1.60×10^{-3} sec^{-1} was obtained by a graphical procedure using the N$_3{}^-$ and SCN$^-$ anation data, since this was thought to be the most accurate data for our two most reactive nucleophiles. This procedure has also been adopted in the present paper, except that with the recent availability of computer facilities it has been possible to fit the data using a nonlinear least-squares computer program. In this and in other calculations the rate constants were weighted as $1/k^2$, a weighting consistent with the assumption that per cent error is the same in all experiments. The least-squares calculation in which both the N$_3{}^-$ and SCN$^-$ data were used simultaneously to evaluate k_1 yielded a value of $(1.47 \pm 0.05) \times 10^{-3}$ sec^{-1}, with the listed uncertainty corresponding to the standard deviation. Revised values of $k_2/k_3 = 1.68 \pm 0.11$ and 2.71 ± 0.38 were obtained for N$_3{}^-$ and SCN$^-$, respectively.
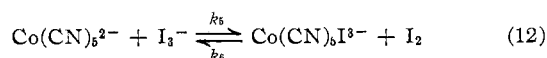
In the present paper the value of $k_1 = 1.47 \times 10^{-3}$ sec^{-1} has been adopted, and nonlinear least-squares curve fitting has been carried out for the various nucleophiles under consideration[13] using eq 11 and the experimental values of k and k_4. Use of the data of Table I and Table IV yielded values of $k_2/k_3 = 4.73 \pm 0.09$ and 8.83 ± 0.11 for I$^-$ and Br$^-$, respectively. The rate constants calculated using these kinetic parameters are listed in the last column of each table and may be compared with the experimental values. For the I$^-$ studies the average per cent deviation between the calculated and measured rate constants was 4.97 and the maximum deviation was 8.19%. De-

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

(13) While I$^-$ is a fairly reactive nucleophile, the data for this ion are believed to be less accurate than those obtained for N$_3{}^-$ and SCN$^-$. Consequently, the I$^-$ data have not been combined with the N$_3{}^-$ and SCN$^-$ data to calculate an alternative value of k_1.

tailed examination of the data at 1.0 and 0.7 M I^-, where replicate experiments are available, indicates that there is a rather large inherent experimental error. However, to some extent it would appear that there is a trend in the difference between the calculated and experimental values of k, with the calculated values being too small at large I^- concentrations and too large at low I^- concentrations. For the Br^- system the corresponding values were 0.83 and 2.03%, respectively. The two data points for the Cl^- system were used to calculate a value of k_2/k_3 of 9.2.

In the measurements carried out in the presence of both I^- and I_3^-, it is necessary to consider an additional reaction path, since the presence of I_3^- considerably enhances the reaction rate. A plausible mechanism, which adequately represents the data, may be based on eq 9, 10, 12, and 13.

$$Co(CN)_5^{2-} + I_3^- \underset{k_6}{\overset{k_5}{\rightleftharpoons}} Co(CN)_5I^{3-} + I_2 \qquad (12)$$

$$I_2 + I^- \rightleftharpoons I_3^- \qquad (13)$$

The pseudo-first-order rate constant may be related to the other kinetic parameters by eq 14, with the symbols k' and k representing the pseudo-first-order rate constants for the solutions containing 0.5 M I^- plus I_3^- and only 0.5 M I^-, respectively.

$$k' = k + \cfrac{\cfrac{k_2 k[I_3^-]}{k_3[I^-]}}{\cfrac{k_3}{k_5}\left[\cfrac{k_2}{k_3} + [I^-]\right] + [I_3^-]} \qquad (14)$$

Least-squares curve fitting using the data of Table III and the kinetic parameters listed above lead to a value of $k_3/k_5 = 0.279 \pm 0.005$ and the calculated values of k listed in the last column of the table. This result indicates that I_3^- is a more efficient nucleophile than I^- by a factor of 36, a rather surprising result.

It is pertinent to comment at this point on several possible sources of ambiguity in the interpretation of the I_3^- data. First, it is possible that I_2 may form a complex with $Co(CN)_5I^{3-}$, just as it does with alkyl iodides in nonaqueous solution.[14] Exploratory spectrophotometric studies have not detected the presence of such a complex, but more refined studies will be required before any final conclusion can be drawn. Fortunately, the inclusion of such a complex in the above mechanism would not alter the physical significance or numerical values of the kinetic parameters under discussion. Second, there is the possibility that reaction 15 is a trimolecular process, with the I_2 and I^- reactants adding to $Co(CN)_5^{2-}$ at separate stages of the reaction

$$Co(CN)_5^{2-} + I_2 + I^- \underset{k_6}{\overset{k_5'}{\rightleftharpoons}} Co(CN)_5I^{3-} + I_2 \qquad (15)$$
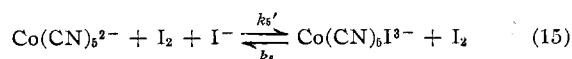
This formulation, which is kinetically indistinguishable from reaction 12, would require that the numerical value of 0.279 be assigned to the quantity k_3K/k_5', where K is the dissociation quotient for I_3^-. Third,

it should be emphasized that nothing is known about the geometry of the activated complex generated by either reaction 12 or 15. To be more specific, the I_2 may be bonded to I^-, to a cyanide ligand, or to the t_{2g} electrons of the $Co(III)$ ion.

The data for the displacement of X^- in $Co(CN)_5X^{3-}$ by H_2O will be considered next. In terms of the mechanism under consideration, this process must proceed stepwise by the reverse of reactions 10 and 9. The analyses of the aquation data for $Co(CN)_5Cl^{3-}$ and $Co(CN)_5Br^{3-}$ require no particular comment, since the aquation was quantitative and proceeded by a conventional first-order process. Under these conditions the reverse of reaction 10 is the rate-determining step, and the first-order rate constant k may be identified as the kinetic parameter k_4.

In the $Co(CN)_5I^{3-}$ system aquation was not quantitative in the absence of added alkali, the experimental conditions employed in the first two experiments of Table II. The treatment of this data has been discussed in the Experimental Section. In the presence of added OH^- and I^-, the experimental conditions employed in the last two experiments of Table II, it can be shown that the pseudo-first-order rate constant k is related to k_4, the desired rate constant, by

$$k = k_4\left[1 + \frac{KK_w[I^-]}{K_a[OH^-]}\right] \qquad (16)$$

Use of eq 16 and the numerical values of $k = 0.73 \times 10^{-5}$ and 0.74×10^{-5} sec^{-1}, the values observed in the last two experiments of Table II, leads to values of $k_4 = 0.75 \times 10^{-5}$ and 0.76×10^{-5} sec^{-1}, results which are in good agreement with the value of 0.76×10^{-5} sec^{-1} obtained in the first experiment of the table.[15] In these experiments the zero-order dependence of k_4 upon the OH^- concentration indicates that direct displacement of I^- in $Co(CN)_5I^{3-}$ by OH^- in an S_N2 mechanism is not an important reaction path, a characteristic feature of an S_N1 reaction mechanism.

It is possible to test the internal consistency of the equilibrium quotient and kinetic parameters by comparing the experimental value of K with that calculated from the relationship $K = k_1k_3/k_2k_4$, a restriction imposed by microscopic reversibility considerations. In the I^- system the value of $k_1k_3/k_2k_4 = 42$ may be compared with the measured equilibrium quotient of 36. The Br^- experiments yield a value of $k_1k_3/k_2k_4 = 0.99$, a result to be compared with an average value of the equilibrium quotient of 0.88. In the Cl^- system, k_1k_3/k_2k_4 has the value 0.36 while the measured value for the formation quotient of $Co(CN)_5Cl^{3-}$ was found in a single exploratory experiment to have the value 0.25.

In the Br^- system, a comparison of the calculated and experimental values of k presented in columns 4 and 5 of Table IV indicates that the data are entirely compatible with the proposed mechanism. However,

(14) Recent studies of the alkyl iodide complexes include those by J. E. Brujake, Jr., and R. M. Noyes, *J. Am. Chem. Soc.*, **83**, 1555 (1961); L. I. Katzin and R. L. McBeck, *J. Phys. Chem.*, **62**, 253 (1958).

(15) The numerical values used in the calculation are $K = 36$, $K_a = 2 \times 10^{-10}$, and $K_w = 5 \times 10^{-14}$. The latter value, which is that reported for 1.0 M NaCl at 40°, has been used because comparable data for NaClO₄ solutions do not appear to be available.

it should be noted that the data could also be represented to within the limit of error by the equation $k = k'[X] + k''$. When k_2/k_3 is large compared with the maximum change in the X^- concentration, as it is for the Br^- system, it becomes impossible to distinguish between the two alternative forms of the rate law.[16] However, it seems plausible to assume that the Br^- anation proceeds by the reaction mechanism applicable to I^-, I_3^-, and other more reactive nucleophiles.[3,4]

Calculations indicated that it should be possible to distinguish between the two alternative forms of the rate law for the Br^- anation at an ionic strength of 5.0. However, even under these conditions only a linear dependence of k upon Br^- concentration was observed. If it is assumed that the SN1 mechanism is applicable to the Br^- system, then it must be concluded that medium effects cannot be neglected at this rather extreme ionic strength.

In summary, it can be concluded that the present studies are consistent with and add some additional support to the SN1 substitution mechanism suggested in our earlier papers. However, the mechanism should probably be regarded as tentative until studies of the exchange of $Co(CN)_5OH_2{}^{2-}$ with O^{18}-labeled H_2O have been completed. A comparison of the value of k_1 obtained from the labeling experiments with that obtained from the study of other nucleophiles should provide a most compelling test of the validity of the mechanism.

The order of reactivity and stability $I^- > Br^- > Cl^-$ observed in the present work indicates that in these pentacyano complexes the Co(III) ion is behaving as a class b metal or, using a more recent terminology, as a soft acid.[17–19] Many factors contribute to the relative stability and lability[20] of complex ions, and the importance of any one factor is difficult to assess. However, it seems plausible that metal to ligand π bonding plays an important role in these electron-rich cyano complexes, with the π bonding decreasing throughout the series $I^- > Br^- > Cl^-$. π bonding may also contribute to the remarkable reactivity of I_3^-, a nucleophile more than three times as reactive as I^-. However, as we have pointed out above, the geometry of the activated complex in the I_3^- reaction is not known, and it may be that the reactivity arises from the action of I_2 as a Lewis acid. In this connection, it is of interest to note that $Co(CN)_5I^{3-}$ reacts with aqueous Br_2 to form $Co(CN)_5Br^{3-}$ in the time of mixing,[21] a behavior analogous to that observed in the reaction of $Co(NH_3)_5I^{2+}$ and Br_2. The extremely efficient catalysis[8] of the exchange of H_2O in $Co(CN)_5$-$OH_2{}^{2-}$ by Ag^+ is presumably another example of Lewis acid catalysis in these pentacyano complexes.

The mechanism presented above for the I_3^- anation reaction implies that I_2 should be a catalyst for the aquation of $Co(CN)_5I^{3-}$. Catalysis of the aquation has been observed in exploratory experiments, but more data must be obtained before the quantitative predictions of the reaction rate can be tested. It is of interest to note that I_2 is also a catalyst for the aquation[22] of $Cr(OH_2)_5I^{2+}$.

(16) This situation exists when $k_2/k_3 \gg [X^-]$ and the value of the denominator of eq 11 is insensitive to variation of the X^- concentration.

(17) For a review of the relative affinity of ligand atoms, see S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.* (London), **12**, 265 (1958).

(18) A general discussion of the stability of complex ions may be found in F. J. C. Rossotti, "Modern Coordination Chemistry," Interscience Publishers, Inc., New York, N. Y., 1960, Chapter I.

(19) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).

(20) J. O. Edwards and R. G. Pearson, *ibid.*, **84**, 16 (1962), have recently discussed factors determining nucleophilic reactivity.

(21) A. Haim and H. Taube, *ibid.*, **85**, 3108 (1963).

(22) J. H. Espenson, *Inorg. Chem.*, **4**, 1334 (1965).