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The Pentacyano Complexes of Cobalt(III).¹ II. The Competition of Thiocyanate Ion and Water for the Transient Intermediate Generated in the Acid-Catalyzed Aquation of $\text{Co}(\text{CN})_5\text{N}_3^{-3}$

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Received November 10, 1961

The pseudo-first-order rate constant for the acid-catalyzed aquation of $\text{Co}(\text{CN})_5\text{N}_3^{-3}$ conforms to the equation $k = k_a K(\text{H}^+)/[1 + K(\text{H}^+)]$. At 40° and ionic strength 1.0, $k_a = 3.2 \times 10^{-3} \text{ sec.}^{-1}$ and $K = 4.7$. In the absence of added thiocyanate ions, the products of the reaction are $\text{Co}(\text{CN})_5\text{OH}_2^{-2}$ and HN_3 . The presence of 0.40 to 0.90 *M* thiocyanate ions does not affect the rate of the acid-catalyzed aquation, but as the thiocyanate ion concentration is increased, $\text{Co}(\text{CN})_5\text{NCS}^{-3}$ becomes an increasingly important product. This change in stoichiometry without a corresponding change in rate yields strong support for an $\text{S}_{\text{N}}1$ mechanism involving the pentacoordinated intermediate $\text{Co}(\text{CN})_5^{-2}$.

Introduction

Competition studies in which various nucleophiles compete for a reactive intermediate may be very valuable in elucidating the mechanisms of substitution reactions.^{2,3} In the present paper we report the results of such competition studies in the acid-catalyzed aquation of $\text{Co}(\text{CN})_5\text{N}_3^{-3}$. The rates of disappearance of $\text{Co}(\text{CN})_5\text{N}_3^{-3}$ and of appearance of $\text{Co}(\text{CN})_5\text{NCS}^{-3}$ and $\text{Co}(\text{CN})_5\text{OH}_2^{-2}$ have been measured at various acidities, in the absence and presence of thiocyanate ions. The results obtained provide strong evidence for an $\text{S}_{\text{N}}1$ mechanism involving the pentacoordinated intermediate $\text{Co}(\text{CN})_5^{-2}$.

Experimental

The reagents and the preparation of the complexes have been described previously.⁴

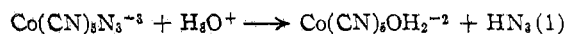
All kinetic experiments were carried out at 40° and unit ionic strength. In a given experiment the solution containing all of the reagents except the $\text{K}_3[\text{Co}(\text{CN})_5\text{N}_3]$ was prepared in a volumetric flask and brought to temperature equilibrium in a thermostat. The desired amount of solid $\text{K}_3[\text{Co}(\text{CN})_5\text{N}_3^{-3}]$ then was added and rapidly dissolved by vigorous shaking of the volumetric flask. In all experiments the solution of the solid was complete in a time less than 40 sec. Zero time was taken as the time at which the solid was added to the volumetric flask. At appropriate time intervals aliquots of the solution were removed for optical analysis in rapid-delivery pipets. Before carrying out the optical analysis the reaction was

quenched by discharging the contents of the pipet into an alkaline solution in order to neutralize both the perchloric acid and the $\text{Co}(\text{CN})_5\text{OH}_2^{-2}$ ions, the latter species being converted to the kinetically inert conjugate base $\text{Co}(\text{CN})_5\text{OH}^{-3}$. The time of quenching was taken as the time at which half of the liquid had been delivered from a pipet with a total delivery time of 7 sec. Neutralization of $\text{Co}(\text{CN})_5\text{OH}_2^{-2}$ ($\text{p}K = 9.7$) was essentially complete, since the alkali concentration after neutralization was approximately 0.1 *M*.

The optical analysis of the alkaline solutions was carried out using a Beckman DU quartz spectrophotometer at 278 and 380 $\text{m}\mu$. At 278 $\text{m}\mu$ the molar absorptivity indexes of $\text{Co}(\text{CN})_5\text{N}_3^{-3}$, $\text{Co}(\text{CN})_5\text{NCS}^{-3}$, and $\text{Co}(\text{CN})_5\text{OH}^{-3}$ are 7300, 7300, and 219, respectively. At 380 $\text{m}\mu$ the corresponding values are 666, 226, and 226.

Results

In the absence of added thiocyanate ion, the stoichiometry of the acid-catalyzed aquation was found to be that given by eq. 1.



Values of the pseudo-first-order rate constant k for reaction 1 were obtained at various acidities from the slopes of the linear plots of $\log(D - D_\infty)$ vs. time, with D and D_∞ being the absorbancies of the solution at time t and after more than seven half-lives, respectively. Maximum accuracy was achieved by carrying out the optical analysis at 278 $\text{m}\mu$, but quite satisfactory results could have been obtained at 380 $\text{m}\mu$, the wave length employed in the measurement of the comparable rate constant k_{380} to be discussed below. An inspection of the numerical values of k presented in column 2 of Table I indicates that reaction 1 is less than first order in hydrogen ion concentration. The sig-

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

(2) See, for example, L. C. Bateman, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 974 (1940).

(3) C. G. Swain, C. B. Scott, and K. H. Lohman, *J. Am. Chem. Soc.*, **75**, 136 (1953).

(4) A. Haim and W. K. Wilmarth, *Inorg. Chem.*, **1**, 573 (1962).

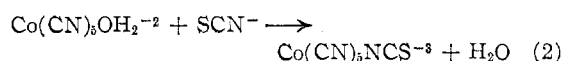
TABLE I
ACID-CATALYZED AQUATION OF $\text{Co}(\text{CN})_5\text{N}_3^{-3}$ AT 40° ,
 $\mu = 1.0$

(H ⁺)	$10^5 k$, sec. ⁻¹	$10^5 k$, sec. ⁻¹ , calcd. ^a
0.0042	5.90	6.15
.0084	12.1	12.1
.0168	23.5	23.5
.0336	43.2	43.6
.0364	47.2	47.0
.0505	64	61
.091	94	95
.166	132	140

^a Calculated using eq. 5.

nificance of this observation will be considered in the Discussion section.

Results next were obtained using solutions containing added thiocyanate ions. It was found that the presence of the thiocyanate ions did not influence the rate of disappearance of $\text{Co}(\text{CN})_5\text{N}_3^{-3}$. However, the stoichiometry of the reaction was found to be no longer that given by eq. 1, since both $\text{Co}(\text{CN})_5\text{OH}_2^{-2}$ and $\text{Co}(\text{CN})_5\text{NCS}^{-3}$ were produced even in the initial stages of the reaction⁵ before there was a significant formation of $\text{Co}(\text{CN})_5\text{NCS}^{-3}$ by reaction 2.



Let us first consider the data showing that the rate of disappearance of $\text{Co}(\text{CN})_5\text{N}_3^{-3}$ is independent of the thiocyanate ion concentration. To obtain the pseudo-first-order rate constants k_{380} which represent the rate of disappearance of $\text{Co}(\text{CN})_5\text{N}_3^{-3}$ it was necessary to carry out the optical analysis at $380 \text{ m}\mu$, where $\text{Co}(\text{CN})_5\text{OH}_2^{-2}$ and $\text{Co}(\text{CN})_5\text{NCS}^{-3}$ have identical molar absorptivity indexes. By choosing this wave length it was possible to obtain linear plots of $\log(D - D_\infty)$ vs. time, despite the initial production of both $\text{Co}(\text{CN})_5\text{NCS}^{-3}$ and $\text{Co}(\text{CN})_5\text{OH}_2^{-2}$ and the ultimate conversion of all of the $\text{Co}(\text{CN})_5\text{OH}_2^{-2}$ to $\text{Co}(\text{CN})_5\text{NCS}^{-3}$ by reaction 2. The numerical values of k_{380} obtained from the slope of the linear plots mentioned above are presented in column 3 of Table II. The rate constants obtained in the absence of thiocyanate ion but under otherwise comparable conditions are listed as the last entries in column 2 of Table I. A comparison of the pertinent rate constants leads to the conclusion that the rate of disappearance of $\text{Co}(\text{CN})_5\text{N}_3^{-3}$

(5) A kinetic study of reaction 2 is reported in paper I of this series.

TABLE II
ACID-CATALYZED AQUATION OF $\text{Co}(\text{CN})_5\text{N}_3^{-3}$ AT 40° ,
 $\mu = 1.0$, IN THE PRESENCE OF SCN^-

(H ⁺)	(SCN ⁻)	$10^5 k_{380}$, sec. ⁻¹	$10^5 k_{278}$, sec. ⁻¹	$10^5 k_{278}$, sec. ⁻¹ , calcd. ^a
0.019	0	...	94	...
.092	0.50	96	83 ± 3	85
.091	.70	94	80 ± 3	76
.091	.90	91	66 ± 4	69
.166	0	133	132	...
.166	0.40	132	121 ± 5	116
.166	.80	133	104 ± 4	104

^a Calculated according to eq. 9.

is independent of the thiocyanate concentration.

The change in stoichiometry caused by the presence of thiocyanate ions was most conveniently studied by following the appearance of $\text{Co}(\text{CN})_5\text{OH}_2^{-2}$ at $278 \text{ m}\mu$, where $\text{Co}(\text{CN})_5\text{N}_3^{-3}$ and $\text{Co}(\text{CN})_5\text{NCS}^{-3}$ have equal molar absorptivity indexes. A pseudo-first-order rate constant k_{278} was obtained from the initial slope of the line defined by the points in a plot of $\log(D - D_\infty')$ vs. time, where D_∞' is the absorbance calculated for the solution assuming all of the Co(III) is in the form of $\text{Co}(\text{CN})_5\text{OH}_2^{-2}$.⁶ In such plots the curve deviates from linearity after 25–35% reaction because of the disappearance of the initially formed $\text{Co}(\text{CN})_5\text{OH}_2^{-2}$ in reaction 2. However, complications caused by reaction 2 may be avoided by using D_∞' , as defined above, for the absorbance at infinite time and by evaluating the rate constant from the quite accurately defined limiting slope at zero time.

The procedure involved in obtaining k_{278} and k_{380} may be illustrated by a graphical presentation of the data obtained in experiment 4 of Table II and carried out at 0.90 M thiocyanate ion and 0.091 M acidity. The ordinate values of the points on the lower straight line in Fig. 1 represent values of $\log(D - D_\infty)$, where the absorbance was measured at $380 \text{ m}\mu$. The rate constant $k_{380} = 91 \times 10^{-5} \text{ sec.}^{-1}$ characterizing the disappearance of $\text{Co}(\text{CN})_5\text{N}_3^{-3}$ is clearly obtained with good accuracy, since the experimental points show very little scatter. The points on the upper curve are based on values of $\log(D - D_\infty')$ measured at $278 \text{ m}\mu$. The dotted line, which indicates our evaluation of the initial slope, corresponds to a value of $k_{278} = 66 \times 10^{-5} \text{ sec.}^{-1}$. The solid line was obtained by calculating the absorbance using the known molar absorptivity

(6) In the alkaline solution where optical analysis is carried out, the neutralization of $\text{Co}(\text{CN})_5\text{OH}_2^{-2}$ will be essentially quantitative.

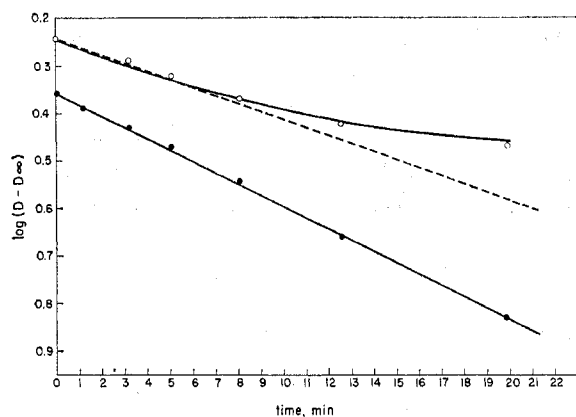
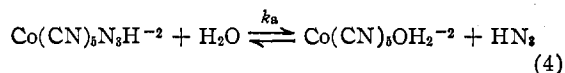
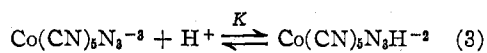


Fig. 1.—A typical experiment illustrating the change in stoichiometry in the presence of thiocyanate ion; ● and ○ represent measurements at 380 and 278 $m\mu$, respectively. The dotted line represents our evaluation of the initial slope.

indexes of the various $\text{Co}(\text{III})$ species and eq. 10, 11, and 12.

Discussion

In the absence of added thiocyanate ion the acid-catalyzed aquation of $\text{Co}(\text{CN})_5\text{N}_3^{-3}$ is adequately described by the mechanism given by eq. 3 and 4.



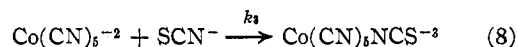
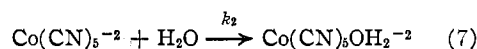
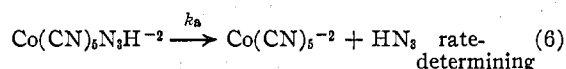
As we shall show below, reaction 4 does not occur in a single step, but this complication may be ignored for the moment. If the assumptions are made that reaction 3 is rapidly reversible and that reaction 4 is rate-determining, then it may readily be shown that the expected dependence of k upon hydrogen ion concentration is given by eq. 5.

$$k = \frac{k_a K (\text{H}^+)}{1 + K (\text{H}^+)} \quad (5)$$

In eq. 5, K and k_a are the equilibrium constant and first-order rate constant for reactions 3 and 4, respectively. The constants k_a and K may be evaluated by using eq. 5 and the data given in columns 1 and 2 of Table I. The procedure involves obtaining $1/k_a$ and K from the intercept and the ratio of intercept to slope in the linear plot of $1/k$ vs. $1/(\text{H}^+)$ and leads to the results $k_a = 3.2 \times 10^{-3} \text{ sec.}^{-1}$ and $K = 4.7$. The excellent agreement between theory and experiment may be seen by comparing the experimental and calculated values of k given in Table I, the calcu-

lated values being obtained from eq. 5 and the values of k_a and K listed above.

Let us now consider the experiments carried out with solutions containing thiocyanate ion. It first should be noted that there can be no important $\text{S}_\text{N}2$ path for reaction of thiocyanate ion with $\text{Co}(\text{CN})_5\text{N}_3^{-3}$ or $\text{Co}(\text{CN})_5\text{N}_3\text{H}^{-2}$, since the rate of disappearance of these latter species is zero order in thiocyanate ion. Consequently, the decrease in rate of formation of $\text{Co}(\text{CN})_5\text{OH}_2^{-2}$ in the presence of thiocyanate ion must be caused by capture of a reactive intermediate generated in reaction 4. A mechanism compatible with all of our observations is given by eq. 6, 7, and 8.



In this reformulation of the mechanism, reaction 4 is replaced by reactions 6 and 7, and the formation of some $\text{Co}(\text{CN})_5\text{NCS}^{-3}$ even in the initial stages of the reaction is to be attributed to reaction 8, a process which competes with reaction 7 for the $\text{Co}(\text{CN})_5^{-2}$ intermediate.

In the Appendix it is shown that the above mechanism requires that the dependence of k_{278} be given by eq. 9.

$$k_{278} = \frac{k_2 k_3}{(\text{SCN}^-) + k_2/k_3} \quad (9)$$

The value $k_2/k_3 = 2.95$ used in calculating the values of k_{278} given in column 5 of Table II was obtained from the previous study of the substitution of water in $\text{Co}(\text{CN})_5\text{OH}_2^{-2}$ by thiocyanate ion.⁴ The excellent agreement between experimental and calculated values of k_{278} given in Table II provides strong support for an $\text{S}_\text{N}1$ mechanism, both for reaction 4 and for the substitution of water in $\text{Co}(\text{CN})_5\text{OH}_2$ by thiocyanate ion.

The acid-catalyzed aquation of ligands which are conjugate bases of weak acids has been observed in a number of other systems,⁷ but previous studies frequently provide a value only for the product $k_a K$. The numerical values of k_a and K are therefore of some inherent interest. Both $\text{Co}(\text{CN})_5\text{N}_3\text{H}^{-2}$ and $\text{Co}(\text{CN})_5\text{N}_3^{-3}$ appear to undergo solvolysis by an $\text{S}_\text{N}1$ mechanism. The large increase in lability caused by addition of the

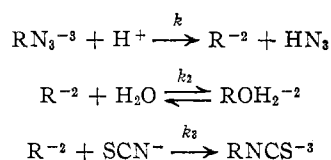
(7) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 152.

proton to the azide⁸ ligand is given by the ratio $k_6/k_4 = 5800$.

It is of interest to compare the acidity constant of $\text{Co}(\text{CN})_5\text{N}_3\text{H}^{-2}$ with that of HN_3 . The addition of $\text{Co}(\text{CN})_5^{-2}$ to the latter species increases the acidity constant by a factor of approximately 5×10^3 . The acidity constant of $\text{Co}(\text{CN})_5\text{OH}_2^{-2}$ is larger than that of H_2O by a factor⁹ of 2×10^5 . The somewhat different behavior of the two pairs of acids is not particularly surprising, since the structures of H_2O and HN_3 are quite different.

Appendix

Let us consider the mechanism



The symbol R^{-2} has been used to represent $\text{Co}(\text{CN})_5^{-2}$, and k has been defined by eq. 4. The rate equations may be obtained by making only the usual steady-state approximation

$$\begin{aligned} -\frac{d}{dt} [(\text{RN}_3^{-3}) + (\text{RN}_3\text{H}^{-2})] &= \\ k[(\text{RN}_3^{-3}) + (\text{RN}_3\text{H}^{-2})] &= k(\Sigma \text{RN}_3^{-3}) \\ \frac{d(\text{ROH}_2^{-2})}{dt} &= \frac{k(k_2/k_3)(\Sigma \text{RN}_3^{-3}) - k_1(\text{ROH}_2^{-2})(\text{SCN}^-)}{(\text{SCN}^-) + k_2/k_3} \\ \frac{d(\text{ROH}_2^{-2})}{dt} &= nk(\Sigma \text{RN}_3^{-3}) - k_{\text{SCN}}(\text{ROH}_2^{-2}) \\ \frac{d(\text{RNCS}^{-3})}{dt} &= \frac{k(\Sigma \text{RN}_3^{-3})(\text{SCN}^-) + k_1(\text{ROH}_2^{-2})(\text{SCN}^-)}{(\text{SCN}^-) + k_2/k_3} \\ \frac{d(\text{RNCS}^{-3})}{dt} &= mk(\Sigma \text{RN}_3^{-3}) + k_{\text{SCN}}(\text{ROH}_2^{-2}) \end{aligned}$$

(8) The value of $k_4 = 5.5 \times 10^{-7} \text{ sec}^{-1}$ is taken from paper I of this series, the reference being given in footnote 4.

(9) In this comparison it is assumed that the usual ionization constant of water should be divided by 55 to make a formal correction for the concentration of the water.

The symbol $(\Sigma \text{RN}_3^{-3})$ is used to indicate the sum of the concentration of RN_3^{-3} and RN_3H^{-2} . The quantities m , n , and k_{SCN} are defined in terms of the above equations. Integration yields expressions which predict the concentrations of the various $\text{Co}(\text{III})$ species as a function of time.

$$(\Sigma \text{RN}_3^{-3}) = C_0 e^{-kt} \quad (10)$$

$$(\text{ROH}_2^{-2}) = C_0 \frac{nk}{k - k_{\text{SCN}}} e^{-k_{\text{SCN}}t} - e^{-kt} \quad (11)$$

$$(\text{RNCS}^{-3}) = C_0 \left(1 - \frac{nk}{k - k_{\text{SCN}}} e^{-k_{\text{SCN}}t} + \frac{k_{\text{SCN}} - mk}{k - k_{\text{SCN}}} e^{-kt} \right) \quad (12)$$

C_0 is the total concentration of cobalt(III) in the solution. By subtracting (ROH_2^{-2}) from C_0 , taking natural logarithms, and differentiating with respect to time, we obtained eq. 13.

$$-\frac{d \ln [C_0 - (\text{ROH}_2^{-2})]}{dt} = \frac{(ke^{-kt} - k_{\text{SCN}} e^{-k_{\text{SCN}}t})nk/(k - k_{\text{SCN}})}{1 - [(e^{-k_{\text{SCN}}t} - e^{-kt})nk/(k - k_{\text{SCN}})]} \quad (13)$$

Since it can be shown that $(D_t - D_{\infty'})$ is proportional to $[C_0 - (\text{ROH}_2^{-2})]$, the predicted value of the initial slope in the plot of $\log (D_t - D_{\infty'})$ vs. time is given by the limit of eq. 13 as time goes to zero.

$$k_{278} = -\lim_{t \rightarrow 0} \frac{d \ln (D_t - D_{\infty'})}{dt} = nk = \frac{kk_2/k_3}{(\text{SCN}^-) + k_2/k_3}$$

The quantity $[C_0 - (\text{ROH}_2^{-2})]$ corresponds to the sum of the concentrations of $\text{Co}(\text{CN})_5\text{NCS}^{-3}$, $\text{Co}(\text{CN})_5\text{N}_3^{-3}$, and $\text{Co}(\text{CN})_5\text{N}_3\text{H}^{-2}$. The rate of change of total concentration of these species with time obviously represents the rate of generation of $\text{Co}(\text{CN})_5\text{OH}_2^{-2}$ in the solution.