coordination certainly becomes less favorable for the addition of a third phosphine molecule. Therefore stronger bonds are required in order to increase the stability of the complexes $Co(PR_3)_3X_2$. These are probably the factors which demand the presence of a good anionic ligand (either in σ or π, or in the $\sigma + \pi$ sense) in the five-coordinated compounds. However it appears that once the ligand field requirements are satisfied, the tendency to five-coordination becomes the ruling factor, and coordination of three phosphorus atoms can be achieved, with the rather unusual stoichiometry reported here, even with ditertiary phosphines.

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A Kinetic Study of the Decomposition of Pentacyanocobaltate(II) Ion in Perchloric Acid Solution[1]

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Solutions of cobalt(II) containing cyanide ion are known to contain the species $Co(CN)_5^{3-}$, provided the ratio CN/Co, R, is ≥ 5. The structure, reactions, and optical and esr spectra of this ion have been subjects of a large number of studies[2-10] which have recently been reviewed.[11,12] Structural evidence based largely on esr data[9,10] established that the complex has a square-pyramidal configuration with C_{4v} symmetry. The complex has been suggested[10] to be a six-coordinate species $Co(CN)_5OH_2^{3-}$ largely on the similarity of its spectrum with those of CoL_5OH_2 with L = CH_3NC and C_6H_5NC. Aside from this evidence, all of the reactions of the complex are most easily formulated as belonging to a five-coordinate $Co(CN)_5^{3-}$ ion.[2,4-6] This reactive species may be the predominant species, or a coordinated water molecule may be removed prior to reaction. We shall represent the ion as $Co(CN)_5^{3-}$, intending no comment on the question of five- or six-coordination.

Our particular interest in this ion arose in the course of kinetic studies on the mechanism of reduction of substituted cobalt(III) complexes $Co(CN)_5X^{3-}$ by V^{2+} in strongly acidic solution,[13] where it appeared that $Co(CN)_5^{3-}$ was generated as an intermediate. In acid solution, such an intermediate would presumably decompose to Co_{aq}^{2+} and HCN (eq 1). To the best of

$$Co(CN)_5^{3-} + 5H^+ = Co_{aq}^{2+} + 5HCN \qquad (1)$$

our knowledge, the complex has not been examined previously under such conditions.

We have carried out kinetic studies on the decomposition of the known complex $Co(CN)_5^{3-}$ in perchloric acid.

Experimental Section

Materials.—Reagent grade materials, cobalt(II) perchlorate, sodium and potassium cyanide, and perchloric acid, were used without further purification. Lithium perchlorate, used to maintain ionic strength, was prepared from the carbonate and was recrystallized twice before use. Stock solutions were analyzed by standard volumetric or spectrophotometric methods. All solutions were prepared in conductance water, obtained by a double redistillation of laboratory-distilled water from alkaline permanganate in a tin-lined Barnstead still.

Solutions of pentacyanocobaltate(II) ion were prepared by mixing solutions of cobalt(II) perchlorate and sodium or potassium cyanide, often containing added lithium perchlorate. The complex was prepared with $R \geq 5.2$. These solutions were prepared and handled under an inert atmosphere. Our early work used nitrogen which had been purified of traces of oxygen by passage through two to four scrubbing solutions of acidified chromium(II) perchlorate in contact with amalgamated zinc. Most kinetic runs were, however, carried out under high-purity argon to avoid the reaction of the complex with the traces of hydrogen (eq 2) possibly generated from the reaction of zinc with perchloric acid. Presumably the hydrido complex decomposes rapidly in acid solution (eq 3), although this point was not checked. No

$$Co(CN)_5^{3-} + 0.5H_2 = Co(CN)_5H^{3-} \qquad (2)$$

$$Co(CN)_5H^{3-} + H^+ + H_2O = Co(CN)_5OH_2^{2-} + H_2 \quad (3)$$

rate differences were noted between runs in nitrogen or argon atmospheres.

Rate Procedures.—The rate of reaction 1 was studied by stopped-flow spectrophotometry using the apparatus previously described.[14] Most studies were carried out at wavelengths in the ultraviolet region using as the light source either a conventional Beckman deuterium lamp or a quartz iodide lamp (General Electric 1959), the latter powered by a Sorenson supply (QRC 40-8A) operated at 28-V dc.

Results and Interpretation

Reaction Kinetics.—The visible and ultraviolet spectra of solutions of pentacyanocobaltate(II) prepared with careful exclusion of oxygen and hydrogen were in essential agreement with published results.[3] Addition of perchloric acid to dilute solutions, $\leq 10^{-3}$ M, again with careful exclusion of oxygen, produced Co_{aq}^{2+} in quantitative yield in accord with eq 1.[15] The

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[1] Work performed in the Ames Laboratory under the auspices of the U. S. Atomic Energy Commission.

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[15] The yield of Co^{2+} was verified by spectrophotometric analysis as the thiocyanate complex in 50 vol % acetone. Were a cobalt(III) species such as $Co(CN)_5OH_2^{2-}$ also formed, the analysis for Co^{2+} would have been low.

spectrum of the reaction products was essentially that of cobalt(II) perchlorate. It was also shown that the spectrum of Co^{2+} in excess perchloric acid was unaffected by addition of sodium cyanide.

The rate of disappearance of $Co(CN)_5^{3-}$ followed a pseudo-first-order equation (eq 4). Values of k'

$$-d[Co(CN)_5^{3-}]/dt = k'[Co(CN)_5^{3-}] \qquad (4)$$

were evaluated, using the method of Guggenheim,[16] from the deflection-time readings taken from the oscillograms. The values of k' were independent of $[Co(CN)_5^{3-}]_0$, of the wavelength chosen to study the reaction, and of the concentration of cyanide ion in the solution of the complex, as summarized in Table I.

TABLE I

RATE CONSTANTS FOR THE REACTION OF $Co(CN)_5^{3-}$ WITH H^+ AS A FUNCTION OF $[Co(CN)_5^{3-}]_0$ AND OF $[CN^-]$[a]

$10^4[Co(CN)_5^{3-}]_0$, M	λ, Å	R	k', sec^{-1} [b]
2.0	2800–2900	5.2	0.258 ± 0.006 (6)
6.0	2800	5.2	0.258 ± 0 (2)
6.0	3100	5.2	0.252 ± 0.012 (6)
6.0	3160	5.2	0.262 ± 0.010 (10)
6.0	3300	5.2	0.252 ± 0.008 (7)
6.0	3500	5.2	0.245 ± 0.009 (6)
2.0	2870	50	0.267 ± 0.003 (3)
2.0	2870	100	0.260 ± 0.003 (4)
2.0	2870	150	0.260 ± 0.015 (5)

[a] Conditions: $[H^+] = 0.500\ M$, $T = 25.0°$, $\mu = 1.00\ M$. [b] Uncertainties represent the average deviation from the mean of the individual runs, the number performed under the given conditions being listed in parentheses.

Two difficulties were encountered when attempts were made to extend the starting concentration of $Co(CN)_5^{3-}$ above *ca.* 0.001 M. Such solutions were unstable as the rate of the second-order reaction with solvent (eq 5) becomes appreciable, presumably both

$$2Co(CN)_5^{3-} + H_2O = Co(CN)_5H^{3-} + Co(CN)_5OH^- \quad (5)$$

species so formed being converted to $Co(CN)_5OH_2^{2-}$ in acid. When freshly prepared solutions with $[Co(CN)_5^{3-}]_0 \geq 0.004\ M$ were acidified, a fine cream-colored precipitate was formed. The solid contained cobalt and cyanide, but alkali metal cations were absent. It was formed regardless of the use of potassium or sodium cyanide, or whether lithium perchlorate was added; it formed as well when perchlorate was completely replaced by chloride ion. The material has not been identified completely although it might be $Co^{II}[Co^{III}(CN)_5H_2O]$.[17,18] Its identity was incidental to the main purpose of this work and kinetic studies were restricted to starting concentrations $\leq 6 \times 10^{-4}\ M$ $Co(CN)_5^{3-}$.

Hydrogen Ion Dependence.—On the basis of the kinetic results cited above, most subsequent experiments were performed at a single initial Co(II) concentration, $2 \times 10^{-4}\ M$, at λ 2870 Å, with $R = 5.2$. The rate was studied as a function of hydrogen ion concentrations, covering the range $0.01 \leq [H^+] \leq 0.800\ M$ at $\mu = 1.00\ M$. In all experiments the reaction followed pseudo-first-order kinetics quite closely, but the value of the rate constant k' in eq 4 depended upon $[H^+]$, as shown in Table II.

TABLE II

HYDROGEN ION DEPENDENCE

$[H^+]$, M	k', sec^{-1} Obsd	k', sec^{-1} Calcd[a]
0.01	0.070 ± 0.004 (4)	0.0686
0.040	0.084 ± 0.003 (4)	0.0836
0.100	0.112 ± 0.001 (4)	0.112
0.200	0.149 ± 0.004 (7)	0.154
0.300	0.186 ± 0.003 (4)	0.192
0.400	0.238 ± 0.008 (8)	0.225
0.500	0.257 ± 0.009 (49)	0.255
0.600	0.280 ± 0.012 (8)	0.282
0.650	0.291 ± 0.008 (4)	0.295
0.750	0.313 ± 0.013 (4)	0.318
0.800	0.332 ± 0.010 (8)	0.329

[a] From the best values of the three parameters, given in the text, according to eq 6.

A plot of log k' *vs.* log $[H^+]$ is presented in Figure 1; the slopes of this plot represent the apparent order with respect to $[H^+]$ at a particular $[H^+]$ and suggest the following functional dependence of k' upon $[H^+]$

$$k' = \frac{a + b[H^+]}{c + [H^+]} \qquad (6)$$

The individual rate constants that constituted the averages given in Table II were fitted to the three-parameter relation in eq 6 using a nonlinear, least-squares computer program. The resulting rate parameters are $a = 0.091 \pm 0.013\ M\ sec^{-1}$, $b = 0.80 \pm 0.07\ sec^{-1}$, and $c = 1.43 \pm 0.19\ M$, where the uncertainties given represent one standard deviation.

Reaction Mechanism.—The form of the rate equation suggests that two independent transition states are important and that a labile protolytic equilibrium causes the form of the predominant cobalt(II) species to vary with $[H^+]$. Consider an equilibrium reaction (eq 7) that is followed by one or more parallel rate-

$$Co(CN)_4(CNH)^{2-} \rightleftharpoons Co(CN)_5^{3-} + H^+ \quad \text{(rapid, } K\text{)} \qquad (7)$$

determining steps (eq 8–10) that yield lower cyano-

$$Co(CN)_5^{3-} \xrightarrow{k_1} \qquad (8)$$

$$Co(CN)_5^{3-} + H^+ \xrightarrow{k_2} \qquad (9)$$

$$Co(CN)_4(CNH)^{2-} \xrightarrow{k_3} \qquad (10)$$

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[16] E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926).

[17] The infrared spectrum (KBr pellet) showed a strong cyanide absorption at 2160 cm^{-1} with a possible shoulder on the low-frequency side. Water bands were present for air-dried samples at 70° and for a sample dried over P_2O_5. The solid dissolved in base but not in perchloric acid unless SCN^- and acetone were present; the latter reaction formed the typical blue color of cobalt(II) thiocyanate complexes.

[18] Pratt and Williams[10] have observed that even "freshly prepared" solutions of $Co(CN)_5^{3-}$ may be partly decomposed, presumably owing to the acceleration of reaction 5 by the heat evolved upon mixing cobalt(II) and cyanide. Addition of cobalt(II) perchlorate to a solution of $Co(CN)_5OH_2^{2-}$ in perchloric acid yields a precipitate of very similar appearance. No further clue to the identity of this material was sought. It is definitely not cobalt(II) cyanide, but it might consist of a cobalt(II) cation and a lower cyanocobaltate(II) anion.

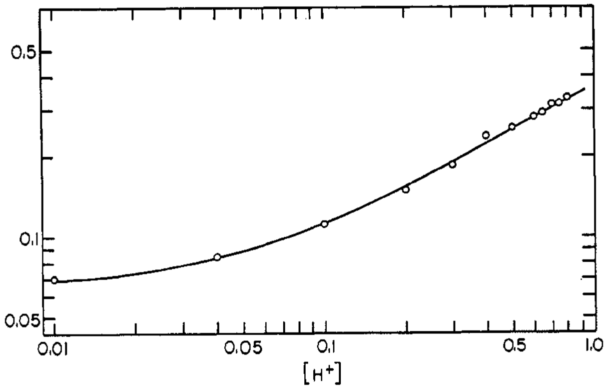

Figure 1.—Dependence of rate upon [H$^+$], illustrated by a plot of k' vs. [H$^+$], each on a logarithmic scale. The line shown is that corresponding to a least-squares fit of the data to eq 6.

cobalt(II) species which are converted to the final products rapidly compared to these three processes. The distinction intended between reactions 9 and 10 is the question of whether the role H^+ plays in the mechanism of decomposition is the same as it plays in stabilizing $Co(CN)_5^{3-}$ in solutions of relatively high hydrogen ion concentration. The kinetic data cannot distinguish the alternatives.

The rate equation associated with this mechanism is

$$\frac{-\mathrm{d}\ln[\mathrm{Co(CN)}_5^{3-}]}{\mathrm{d}t} = k' = \frac{k_1K + (k_2K + k_3)[\mathrm{H}^+]}{K + [\mathrm{H}^+]} \qquad (11)$$

Comparing this expression to eq 6, it is apparent that the empirical parameters are $a = k_1K$, $b = k_2K + k_3$, and $c = K$. The rate parameter b represents the composite contributions of reactions 9 and 10; these cannot be further sorted out from the information available since the transition states along either path have the same composition.

The simplest interpretation of the kinetic data and of the lack of dependence upon [CN$^-$] is that loss of the first cyanide comprises the rate-determining step. Subsequent reactions in which cyanide is presumably replaced by water in a stepwise fashion must occur relatively rapidly. An alternative proposal is that one or more cyanide ions be lost rapidly and, in effect, irreversibly owing to the high hydrogen ion concentration. We cannot rule out this eventuality, although it was rendered less likely by our failure to detect changes in absorption intensity in $Co(CN)_5^{3-}$ (in CN$^-$ solution) compared to the species present at the start of a decomposition run at low [H$^+$].

The question concerning the stage at which the spin change accompanying reaction 1 occurs cannot be answered. It is interesting to note, however, that the abnormally low rate of cobalt(II) substitution (*cf.* the rate[19] of Co_{aq}^{2+}–H_2O exchange, $k_{ex} = 10^6\ M^{-1}\ sec^{-1}$) undoubtedly originates in the low-spin $t_{2g}^6\ e_g^1$ configuration of the Co(II) complex.

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The Mass Spectrum of Methyldifluorosilyltetracarbonylcobalt[1a]

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The existence of methyldifluorosilyltetracarbonylcobalt, $CH_3SiF_2Co(CO)_4$, was mentioned recently in a brief publication.[2] This compound was prepared by allowing $CH_3SiH_2Co(CO)_4$ to react with excess PF_5. The products of this reaction—$CH_3SiF_2Co(CO)_4$, CH_3SiF_2H, $HCo(CO)_3(PF_3)$, $HCo(CO)_2(PF_3)_2$, and $HCo(CO)(PF_3)_3$—were separated by vacuum distillation and vapor-phase chromatography. The detailed information concerning the preparation and separation will be reported elsewhere.[3] The purpose of this report is to furnish the mass spectral data for $CH_3SiF_2Co(CO)_4$, from which the heat of formation of $CH_3SiF_2Co(CO)_4$ and the CH_3F_2Si–$Co(CO)_4$ bond dissociation energy have been derived.

Experimental Section

The mass spectral data reported here were obtained on a modified[4] Bendix Model 12-107 time-of-flight (TOF) mass spectrometer. The TOF mass spectrometer was employed in this study because its relatively cool ion source (35 ± 5°) reduced the possibility of thermal decomposition of the compound and also permitted fragmentation patterns and appearance potential data to be obtained rapidly.[4] A fresh sample of $CH_3SiF_2Co(CO)_4$ was introduced into the mass spectrometer for each measurement. Winters and Kiser have reported[5] that some metal carbonyls decompose in the mass spectrometer causing a contamination problem; thus, as a precautionary measure, the ion source and electron multiplier were disassembled and cleaned every 4 hr throughout this investigation. In these cleaning procedures we were unable to detect any evidence for the thermal decomposition of $CH_3SiF_2Co(CO)_4$ in our mass spectrometer. The intense ion currents for the Co^+ and CO^+ ions suggest that some decomposition may have taken place; however, it was impossible to substantiate this suspicion by inspection of the ion source and electron multiplier components. Measurements taken before and after the cleaning procedure agreed within the limits quoted.

Results and Discussion

The monoisotopic fragmentation pattern of $CH_3SiF_2Co(CO)_4$, corrected for residual background in the mass spectrometer, is shown in Table I. Ions of minor abundance (<0.05) are not reported. These very

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(1) (a) Part of this report is based on a portion of the thesis to be submitted by S. K. Gondal to the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy. This study was supported in part by the Advanced Research Projects Agency, Office of the Secretary of Defense. (b) Naval Research Laboratory. (c) University of Pennsylvania.

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