Carbonylation of Pentacyanocobaltate(II)

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Abstract: It is shown that over a wide range of conditions, carbon monoxide reacts with aqueous solutions of pentacyanocobaltate(II) in accord with the stoichiometry $2Co(CN)_5{}^{3-} + 2CO \rightarrow Co(CN)_6{}^{3-} + Co(CN)_3(CO)_2{}^{2-} + CN^-$. The kinetics of the reaction were found to conform to the rate law $d[Co(CN)_3(CO)_2{}^{2-}]/dt = k[Co(CN)_5{}^{3-}]^2 \cdot [CO][CN^-]^{-1}$, with k (25°, $\mu = 0.5\ M$) $= 2.7 \times 10^{-2}\ M^{-1}\ sec^{-1}$, $\Delta H^{\ddagger} = (14.4 \pm 0.4)$ kcal/mol, $\Delta S^{\ddagger} = -(18 \pm 2)$ eu. The probable structure of $Co(CN)_3(CO)_2{}^{2-}$ and the mechanism of its formation are discussed.

Despite extensive recent interest in various aspects of the chemistry of $Co(CN)_5{}^{3-}$,[1] the study of substituted low-valent cobalt cyanide complexes has received little attention. Some work has been done on mixed amine–cyanide cobalt(II) complexes as homogeneous hydrogenation catalysts[2-4] but only a few such complexes and a few related mixed phosphine–cyanide complexes appear to have been reasonably well characterized.[5,6] In this paper we describe the carbonylation of aqueous solutions of pentacyanocobaltate(II) to form the complex $Co(CN)_3(CO)_2{}^{2-}$ according to eq 1, and report the results of a study of the kinetics of this reaction.

$$2Co(CN)_5{}^{3-} + 2CO \longrightarrow Co(CN)_6{}^{3-} + Co(CN)_3(CO)_2{}^{2-} + CN^- \quad (1)$$

Several earlier investigations of the carbonylation of aqueous solutions of cobalt(II) cyanide have yielded highly discordant results. The earliest such study by Manchot[7] in 1926 resulted in the isolation of a product, claimed to be a salt of a mixed-ligand cobalt(II) complex, $K_3[Co(CN)_5CO]$, but subsequently revealed to be a mixture of $K_3[Co(CN)_6]$ and $K[Co(CO)_4]$.[8] Several subsequent studies of the carbonylation of aqueous cobalt(II) cyanide have all been described in terms of reduction of the cobalt(II) to various products of lower oxidation state including $Co(CN)_3CO^{2-}$ and $Co(CO)_4{}^-$.[9,10] The occurrence of the particular reaction described by eq 1 (which, over a wide range of conditions, appears to be the primary reaction between CO and $Co(CN)_5{}^{3-}$ in aqueous solution) and the existence of the mixed-ligand cobalt(I) complex, $Co(CN)_3(CO)_2{}^{2-}$, do not appear to have been previously recognized.

Experimental Section

Materials. Solutions of the desired composition were prepared by dissolving analytical reagent grade cobalt(II) chloride, sodium cyanide, sodium hydroxide, and sodium chloride (used to adjust the ionic strength) in distilled water with rigorous exclusion of oxygen (achieved by purging with nitrogen which had been passed twice through acidified chromium(II) perchlorate solutions in contact with amalgamated zinc). Carbon monoxide was Matheson CP grade.

Stoichiometry Measurements. In addition to the spectral measurements to be described, the stoichiometry of the reaction was confirmed by direct determination of the uptake of CO and the release of CN^-. The volume of CO taken up at constant pressure was followed using the gas-buret apparatus and procedure described previously.[11] The increase in free CN^- as the reaction proceeded was measured by periodic sampling of the solution and titration of the free CN^- with a standard solution of Co^{2+} to an end point (corresponding to quantitative formation of $Co(CN)_5{}^{3-}$) marked by the first appearance of a precipitate of $Co(CN)_2$. The validity of this procedure was confirmed using solutions of known composition. Infrared spectral measurements on the reaction solutions to monitor the bands at 2080, 2120, and 1960 cm^{-1} due to $Co(CN)_5{}^{3-}$, $Co(CN)_6{}^{3-}$, and $Co(CN)_3(CO)_2{}^{2-}$, respectively, were made with a Beckman IR10 spectrophotometer using a cell with CaF_2 windows separated by a 0.015-mm spacer.

Kinetic Measurements. Apart from a few kinetic experiments made at atmospheric pressure in order to follow the rate of CO uptake, the kinetic experiments were generally performed under high CO pressures (typically 20 atm) in a glass-lined Parr Series 4500 stirred autoclave pressurized to the desired constant partial pressure of CO and thermostated to ±0.2°. Samples of the solution were withdrawn periodically for spectrophotometric analysis in a Cary 14 recording spectrophotometer. The reaction was most conveniently followed by monitoring the 970-nm (ϵ 290 $M^{-1}\ cm^{-1}$) band of $Co(CN)_5{}^{3-}$, all other species present being transparent in this region. Carbon monoxide concentrations were computed from the measured partial pressures using literature solubility data.[12]

Results and Discussion

Stoichiometry and Products. Over a wide range of solution compositions and carbon monoxide pressures, the uptake of CO by aqueous solutions of $Co(CN)_5{}^{3-}$ resulted in the disappearance of the characteristic spectrum of $Co(CN)_5{}^{3-}$ and the consistent quantitative formation of a new species, identified as $Co(CN)_3(CO)_2{}^{2-}$, whose spectrum is depicted in Figure 1. The evidence for the identification of this species and for its formation in accord with the stoichiometric reaction described by eq 1 is as follows. (1) Good agreement was obtained between the rate of disappearance of $Co(CN)_5{}^{3-}$ (monitored at 970 nm) and the rate of formation of the new species, monitored near its absorption shoulder at 250 nm (where the absorption of $Co(CN)_5{}^{3-}$ passes through a minimum), indicating the absence of appreciable accumulation of intermediates. (2) In several experiments in which the CO uptake was measured, the rate of consumption of CO was found to agree with the spectrophotometrically determined rate of disappearance of $Co(CN)_5{}^{3-}$, ($d[CO]/d[Co(CN)_5{}^{3-}] = 1.0 \pm 0.1$). (3) The amount of CN^- liberated, determined by

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titration as described earlier, was found to be consistent with the spectrophotometrically determined consumption of $Co(CN)_5^{3-}$ ($-d[CN^-]/d[Co(CN)_5^{3-}] = 0.5 \pm 0.1$). (4) The formulation of the products (whose overall empirical composition is established by the above observations) as an equimolar mixture of cobalt(III) and cobalt(I) is consistent with the determination (using the Evans method)[13] that the final solution is diamagnetic and with the kinetic behavior to be described (notably the second-order dependence of the rate on the $Co(CN)_5^{3-}$ concentration). (5) During the stages of reaction described above there was no formation of carbonate in the solution (as determined by testing with barium chloride), indicating the absence of any oxidation of carbon monoxide and hence, presumably, of any *net* reduction of the cobalt. (6) Quantitative infrared measurements on the solutions as reaction proceeded revealed the disappearance of the 2080-cm^{-1} band of $Co(CN)_5^{3-}$ to be accompanied by the growths of (i) the characteristic 2120-cm^{-1} band of $Co(CN)_6^{3-}$ and (ii) a prominent new band at 1960 cm^{-1} along with a smaller band at 2000 cm^{-1} consistent with the formation of the proposed carbonyl product; the simultaneous intensity changes associated with the calibrated bands of $Co(CN)_5^{3-}$ and $Co(CN)_6^{3-}$ were consistent with eq 1. (7) A product having the same spectrum as that attributed to $Co(CN)_3(CO)_2^{2-}$ (curve D, Figure 1) was obtained *in the expected spectral yield* from the reaction of CO with an aqueous solution of $Co(CN)_5H^{3-}$ in accord with eq 2.

$$Co(CN)_5H^{3-} + 2CO + OH^- \longrightarrow Co(CN)_3(CO)_2^{2-} + 2CN^- + H_2O \quad (2)$$

The stoichiometry of the latter reaction was confirmed by measurement of the CO taken up and of the CN^- released.[14] While the kinetics of this reaction have not yet been fully examined, the dependence of the rate on the OH^- concentration suggests a mechanism involving reaction of CO with $Co(CN)_5^{4-}$ formed in the preequilibrium step, $Co(CN)_5H^{3-} + OH^- \rightleftharpoons Co(CN)_5^{4-} + H_2O$.[15] A detailed kinetic study of reaction 2 is in progress.

Aqueous solutions of the product ion $Co(CN)_3(CO)_2^{2-}$, prepared by either reaction 1 or 2, were fairly stable, at *low* CN^- concentrations ($<10^{-2}$ *M*) under either nitrogen or hydrogen atmospheres, *e.g.*, for several hours under 10 atm of H_2. Higher CN^- concentrations induced slow further (apparently disproportionative) decomposition, with formation of more $Co(CN)_6^{3-}$. Under high pressures of carbon monoxide (>10 atm) the product also underwent a very slow further reaction (even at low CN^- concentrations) which, over a period of *several days*, resulted in the formation of detectable amounts of carbonate and presumably in the formation of cobalt carbonyl complexes of lower oxidation states such as those obtained by earlier workers.[8-10] None of these secondary reactions was sufficiently rapid to interfere with our kinetic measurements on reaction 1, and we did not pursue their further examination in any detail.

Attempts to obtain the product $Co(CN)_3(CO)_2^{2-}$ ion as a pure salt by the addition of cations such as Cs^+, Ca^{2+}, Ba^{2+}, and $N(C_4H_9)_4^+$ and/or the admixture of solvents such as ethanol, acetone, and 1,4-dioxane were invariably unsuccessful. All such treatments resulted in apparent decomposition and in the formation of precipitates severely contaminated with salts of $Co(CN)_6^{3-}$.

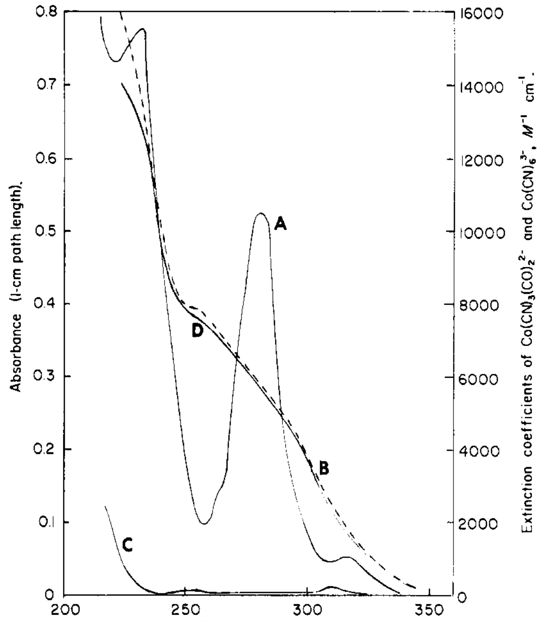

Figure 1. Spectral change accompanying reaction of 1.0×10^{-4} *M* $Co(CN)_5^{3-}$ with CO: (A) initial absorption spectrum (1.0×10^{-4} *M* $Co(CN)_5^{3-}$), (B) final absorption spectrum (5.0×10^{-5} *M* $Co(CN)_3(CO)_2^{2-}$ + 5.0×10^{-5} *M* $Co(CN)_6^{3-}$, (C) 5.0×10^{-5} *M* $Co(CN)_6^{3-}$; (D) 5.0×10^{-5} *M* $Co(CN)_3(CO)_2^{2-}$ (obtained by subtracting curve C from curve B).

Kinetic Measurements. Kinetic measurements on reaction 1 were made over a wide range of CO partial pressures (2.7–27 atm), as well as of other pertinent variables (2.5×10^{-3}–1.0×10^{-2} *M* initial $Co(CN)_5^{3-}$, 2.5×10^{-2}–2.5×10^{-1} *M* CN^-, 1.5×10^{-3}–1.5×10^{-2} *M* OH^-, 0.08–1.0 *M* ionic strength, 0.6° to 35.0°). The resulting observed kinetic behavior conformed accurately to the rate law described by

$$d[Co(CN)_3(CO)_2^{2-}]/dt \; (= -{}^1/_2 d[Co(CN)_5^{3-}]/dt) = k[Co(CN)_5^{3-}]^2[CO][CN^-]^{-1} \quad (3)$$

Since the concentration of CN^- (initially always in at least tenfold excess over $Co(CN)_5^{3-}$) and of CO remained substantially constant during each experiment, the observed kinetics were pseudo-second order, corresponding to the integrated rate law

$$[Co(CN)_5^{3-}]^{-1} - [Co(CN)_5^{3-}]^{-1}_{\text{initial}} = 2k[CO][CN^-]^{-1}t = k_{\text{obsd}}t \quad (4)$$

Typical linear plots of $[Co(CN)_5^{3-}]^{-1}$ *vs.* *t*, in accord with eq 4, are depicted in Figure 2. Values of *k*, determined from the slopes of such plots ($=2k \cdot [CO][CN^-]^{-1}$), are listed in Table I and are seen to be substantially independent of the initial concentrations of $Co(CN)_5^{3-}$, of the CO partial pressure, and of the concentrations of CN^- and OH^- over the considerable ranges examined. Measurements of *k* over the temperature range 0.6–35° (Table I) yielded a good Arrhenius plot from which the following activation parameters (at $\mu = 0.5$ *M*) were determined: $\Delta H^{\ddagger} = 14.4 \pm 0.4$ kcal/mol, $\Delta S^{\ddagger} = -(18 \pm 2)$ eu.

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Table I. Kinetic Data

Temp, °C	CO partial pressure, atm	Initial solution composition, M^a: 10^3[CO]	$10^3[\mathrm{Co(CN)_5^{3-}}]$	$10^2[\mathrm{CN^-}]$	Ionic strength, M	10^2k_{obsd}, M^{-1} sec^{-1}	10^2k, M^{-1} sec^{-1}
25.0	20.4	19.6	2.5	10.0	0.50	1.07	2.73
25.0	20.4	19.6	5.0	10.0	0.50	1.04	2.66
25.0	20.4	19.6	10.0	10.0	0.50	1.03	2.63
25.0	20.4	19.6	2.5	2.5	0.50	4.16	2.66
25.0	20.4	19.6	5.0	5.0	0.50	2.03	2.59[b]
25.0	20.4	19.6	10.0	25.0	0.50	0.42	2.68
25.0	2.75	2.6	5.0	5.0	0.50	0.29	2.76
25.0	10.2	9.8	5.0	5.0	0.50	1.05	2.68
25.0	27.2	26.1	5.0	5.0	0.50	2.77	2.65
0.6	24.8	39.2	5.0	5.0	0.50	0.46	0.29
15.0	17.2	19.6	5.0	5.0	0.50	0.85	1.08
35.0	23.3	19.6	5.0	5.0	0.50	4.85	6.19
25.0	20.4	19.6	5.0	5.0	0.08	1.18	1.51
25.0	20.4	19.6	5.0	5.0	1.00	2.35	3.00

[a] $[\mathrm{OH^-}] = 1.5 \times 10^{-3}$ M unless otherwise noted. [b] Unaffected by increase of $[\mathrm{OH^-}]$ to 1.5×10^{-2} M and by the addition of 1×10^{-2} M $\mathrm{Co(CN)_6^{3-}}$.

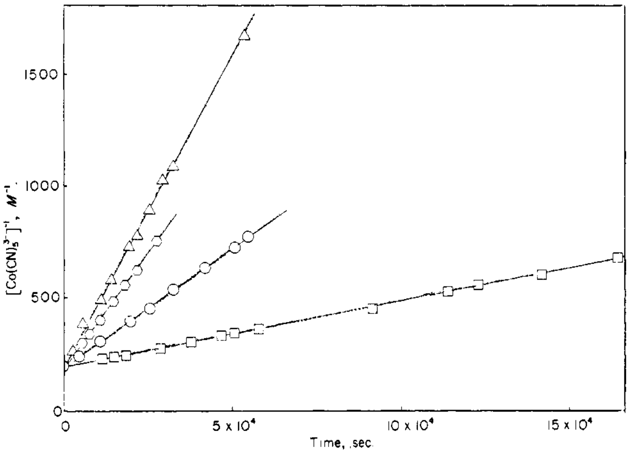

Figure 2. Representative pseudo-second-order rate plots according to eq 3. CO partial pressures (atm): □, 2.75; ○, 10.2; ⬡, 20.4; △, 27.2 (other conditions given in Table I).

Discussion

The product ion, $\mathrm{Co(CN)_3(CO)_2^{2-}}$, is isoelectronic with $\mathrm{Fe(CO)_5}$, $\mathrm{Mn(CO)_5^-}$, $\mathrm{Mn(CO)_4NO}$, $\mathrm{Ni(CN)_5^{3-}}$, $\mathrm{Co(CNCH_3)_5^+}$,[16] etc. With the exception of $\mathrm{Ni(CN)_5^{3-}}$ (which exists in a square-pyramidal as well as a distorted trigonal-bipyramidal modification),[17] these species are all believed to have trigonal-bipyramidal structures[18] and it is likely that this is the case also for $\mathrm{Co(CN)_3(CO)_2^{2-}}$. However, our data do not serve to establish this point. Attention is directed to several earlier reports of other carbonyl derivatives of cobalt(I) including the closely related five-coordinate complexes $\mathrm{Co(PPh_3)_2(CO)_2X}$ (X = I, Br, Cl, or CN),[19,20] $\mathrm{Co(PPh_3)(CO)_3X}$,[19] and $\mathrm{Co(PPh_3)_2(CO)_3^+}$,[19] as well as a four-coordinate cyanocarbonyl complex, $\mathrm{Co(CN)_3(CO)^{2-}}$, reportedly also formed by carbonylation of aqueous pentacyanocobaltate(II) under conditions somewhat different from ours.[9]

The rate law of reaction 1 (eq 3) serves to define the composition of the activated complex, namely $[\mathrm{Co_2(CN)_9(CO)^{5-}}]^{\ddagger}$. The measured activation parameters refer to the formation of this activated complex from $2\mathrm{Co(CN)_5^{3-}}$ and CO, *i.e.*, to the process described by eq 5. The moderately negative value for $\Delta S^{\ddagger}$ (−18 eu) and the small observed increase of k with ionic strength (Table I) seem reasonable for this process.

$$2\mathrm{Co(CN)_5^{3-}} + \mathrm{CO} \longrightarrow [\mathrm{Co_2(CN)_9CO^{5-}}]^{\ddagger} + \mathrm{CN^-} \qquad (5)$$

The available kinetic information does not discriminate among several plausible alternative detailed mechanisms for the reaction. One such mechanism, depicted by eq 6–8, assumes the formation of $\mathrm{Co(CN)_4CO^{2-}}$ in a preequilibrium step, followed by a rate-determining inner-sphere $\mathrm{CN^-}$-bridged electron transfer from $\mathrm{Co(CN)_5^{3-}}$.[21] According to this, the experimental rate constant $k = K_6k_7$.

$$\mathrm{Co(CN)_5^{3-}} + \mathrm{CO} \overset{K_6}{\rightleftarrows} \mathrm{Co(CN)_4CO^{2-}} + \mathrm{CN^-} \quad \text{(pre-equilibrium)} \qquad (6)$$

$$\mathrm{Co(CN)_4CO^{2-}} + \mathrm{Co(CN)_5^{3-}} \xrightarrow{k_7} [\mathrm{(CO)(CN)_3Co\text{-}CN\text{-}Co(CN)_5^{5-}}]^{\ddagger} \longrightarrow \mathrm{Co(CN)_3(CO)^{2-}} + \mathrm{Co(CN)_6^{3-}} \quad \text{(rate determining)} \qquad (7)$$

$$\mathrm{Co(CN)_3(CO)^{2-}} + \mathrm{CO} \longrightarrow \mathrm{Co(CN)_3(CO)_2^{2-}} \quad \text{(fast)} \qquad (8)$$

It is possible that the preequilibrium 6 is itself a composite process, such as that depicted by eq 9, involving the species $\mathrm{Co(CN)_4^{2-}}$, which has been postulated as coexisting in equilibrium with $\mathrm{Co(CN)_5^{3-}}$ in aqueous solution[22,23] and as a reaction intermediate, *e.g.*, in the acid decomposition of $\mathrm{Co(CN)_5^{3-}}$.[24]

$$\mathrm{Co(CN)_5^{3-}} \overset{-\mathrm{CN^-}}{\rightleftarrows} \mathrm{Co(CN)_4^{2-}} \overset{\mathrm{CO}}{\rightleftarrows} \mathrm{Co(CN)_4(CO)^{2-}} \qquad (9)$$

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