does not make a geometric adjustment to accommodate the extra electron. Slight changes in geometry brought about by differences in amino acid composition could alter the relative energies of the reduced form of the proteins and thus also provide an explanation for the differences in redox potential of, for example, spinach ferredoxin ($E_0' = -0.430$) and putidaredoxin ($E_0' = -0.235$ V).[4a] Certain features of the proposed explanation which are subject to experimental testing are currently being investigated.

Summary

The main findings of this work may be summarized as follows. (1) There exists a series of binuclear complexes $[Co(S_2CSR)_2(SR)]_2$ analogous to those of iron(III). These can be prepared by the thermal elimination of carbon disulfide from $Co(S_2CSR)_3$. The reaction is first order in monomer, with the rate-determining step being cleavage of the CoS_2C–SR bond. (2) The solid state structure of $[Co(S_2CSC_2H_5)_2(SC_2H_5)]_2$ contains bridging ethyl mercaptide groups in the anti configuration, four terminal thioxanthate ligands, and no metal–metal bond. The differences between this structure (II) and that of the iron complex of identical composition (I) are a consequence of their different electronic structures (Figure 1). (3) In solution, the cobalt dimers have structure II, as determined by pmr studies. Paramagnetic anisotropy effects are shown to be of the correct order of magnitude to account for the large upfield shifts of the methylenic protons attached to bridging sulfur atoms. (4) The monomeric complexes $Co(S_2CSR)_3$ exhibit reversible one-electron reduction waves, extending the number of known compounds containing only four-membered chelate rings that show reversible electrochemical behavior. (5) The electrochemical behavior of sulfur-bridged dimers may be influenced by the geometric constraints on, and metal–metal bonding within, the M_2S_2 moiety. Such an argument has been introduced to rationalize the low redox potentials of the Fe_2S_2 non-heme iron proteins.

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and W. R. Dunham, *Struct. Bonding* (*Berlin*), **8**, 1 (1970), for one possible orbital representation of this state.

Carbonylation of Hydridopentacyanocobaltate(III)

Giovanni Guastalla, Jack Halpern,* and Marijan Pribanić

Contribution from the Department of Chemistry, The University of Chicago, Chicago, Illinois 60637. *Received July 10, 1971*

Abstract: Carbon monoxide was found to react with hydridopentacyanocobaltate(III) in aqueous solution according to the stoichiometry: $Co(CN)_5H^{3-} + 2CO + OH^- \rightarrow Co(CN)_3(CO)_2{}^{2-} + 2CN^- + H_2O$. Kinetic measurements yielded the rate law, $-d[Co(CN)_5H^{3-}]/dt = k[Co(CN)_5H^{3-}][OH^-]$ where $k = 6.3 \times 10^{-3}\ M^{-1}\ sec^{-1}$ at 23° and 1 M ionic strength. The results are interpreted in terms of the mechanistic sequence, $Co(CN)_5H^{3-} + OH^- \rightleftarrows Co(CN)_5{}^{4-} + H_2O$ (k_5, k_{-5}); $Co(CN)_5{}^{4-} \rightarrow Co(CN)_4{}^{3-} + CN^-$ (k_6); $Co(CN)_4{}^{3-} + 2CO \rightarrow Co(CN)_3(CO)_2{}^{2-} + CN^-$ (fast). In combination with previously determined values of k_5 and k_{-5}, the present kinetic measurements yield $k_6 = 4.5 \times 10^3\ sec^{-1}$.

Extending our earlier studies on the carbonylation of pentacyanocobaltate(II),[1] we have found that, in the presence of excess base, carbon monoxide reacts with hydridopentacyanocobaltate(III) in aqueous solution in accord with the stoichiometry described by eq 1. In this paper we describe a study of the kinetics of this reaction and discuss its mechanism. The results of these studies are also of some interest in relation to several other reactions of $Co(CN)_5H^{3-}$, studies of which have recently been reported.[2–4]

$$Co(CN)_5H^{3-} + 2CO + OH^- \longrightarrow Co(CN)_3(CO)_2{}^{2-} + 2CN^- + H_2O \quad (1)$$

Experimental Section

Materials. Solutions of $Co(CN)_5{}^{3-}$ 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) chloride solution). Solutions of $Co(CN)_5H^{3-}$ (typically *ca.* 0.03 M) were prepared by hydrogenation of corresponding solutions of $Co(CN)_5{}^{3-}$ according to eq 2 in a glass-lined Parr Series 4500 stirred autoclave, pressurized with approximately 20 atm of H_2 as previously described.[5] Under these conditions the equilibrium of reaction 2 lies sufficiently far to the right (and the reverse reaction following release of the hydrogen pressure is sufficiently slow) that interference from reaction of residual $Co(CN)_5{}^{3-}$ was negligible. The $Co(CH)_5H^{3-}$ concentration was determined spectrophotometrically using the 305-nm absorption band (ϵ 610). Carbon monoxide and hydrogen gases were Matheson CP grade.

$$2Co(CN)_5{}^{3-} + H_2 \rightleftarrows 2Co(CN)_5H^{3-} \quad (2)$$

Stoichiometry Measurements. In addition to the spectrophotometric 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

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[1] J. Halpern and M. Pribanić, *J. Amer. Chem. Soc.*, **93**, 96 (1971).
[2] J. Hanzlik and A. A. Vlček, *Inorg. Chem.*, **8**, 669 (1969).
[3] H. S. Lim and F. C. Anson, *ibid.*, **10**, 103 (1971).
[4] J. Halpern and M. Pribanić, *ibid.*, in press.
[5] (a) J. Halpern and L. Y. Wong, *J. Amer. Chem. Soc.*, **90**, 6665 (1968); (b) J. Halpern and M. Pribanić, *Inorg. Chem.*, **9**, 2616 (1970).

pressure as the reaction proceeded was measured using the gas-buret apparatus and the procedure described previously.[7] The corresponding increase in free CN^- was measured by spectral titration with Co^{2+} at 970 nm to an end point corresponding to quantitative formation of $Co(CN)_5{}^{3-}$.

Kinetic Measurements. The kinetics of the reaction were determined by two independent methods, namely (1) measuring the uptake of CO at constant pressure using the gas-buret apparatus and the procedure described previously,[6] and (2) monitoring the formation of $Co(CN)_3(CO)_2{}^{2-}$ spectrophotometrically at 250 nm where $Co(CN)_3(CO)_2{}^{2-}$ has a shoulder (ϵ 8 × 10^3) and the other species are virtually transparent. In the CO uptake experiments the initial $Co(CN)_5H^{3-}$ concentration was typically *ca.* 5 × 10^{-3} *M* and in the spectrophotometric experiments *ca.* 1 × 10^{-4} *M*. The initial concentration (corresponding to saturation with 1 atm of CO) in the latter experiments was *ca.* 10^{-3} *M*. The spectrophotometric experiments were performed in a Cary 14 spectrophotometer equipped with a thermostatted (±0.2°) cell compartment. The reactions were initiated by injecting, with a microsyringe, a calibrated small volume of a standard solution of $Co(CN)_5H^{3-}$ (typically 0.020 ml of 0.030 *M* $Co(CN)_5H^{3-}$) into a serum-capped spectrophotometer cell filled with a solution containing the desired concentrations of all the other reaction components and thermally equilibrated to the reaction temperature. The reactions were sufficiently rapid so that they could be followed essentially to completion.

Results and Discussion

Stoichiometry. The following observations served to confirm the stoichiometry of the reaction described by eq 1. (1) In each case the final spectrum of the product solution was in quantitative agreement with the spectrum of $Co(CN)_3(CO)_2{}^{2-}$ previously characterized as one of the products of the reaction of CO with $Co(CN)_5{}^{3-}$.[5b] (2) Gas uptake measurements, made as described earlier, yielded values of 1.8 ± 0.1 for the ratio of the number of moles of CO taken up to the number of moles of $Co(CN)_5H^{3-}$ originally present. (3) The ratio of the CN^- liberated during the reaction to the initial $Co(CN)_5H^{3-}$ concentration was determined, as described earlier, to be 2.0 ± 0.1, in accord with eq 1. (4) While attempts to isolate pure salts of $Co(CN)_3(CO)_2{}^{2-}$ were invariably unsuccessful because of accompanying decomposition and disproportionation, other pure cobalt(I) derivatives of the type $Co(CN)(CO)_2(PR_3)_2$ and $K[Co(CN)_2(CO)(PR_3)_2]$ (where $PR_3 = P(C_2H_5)_3$, $P(C_6H_5)_3$, etc.), formed by the addition of the corresponding phosphines to the product solutions, could readily be isolated in pure form and fully characterized. A number of such new compounds have now been prepared and their chemistry is being investigated.[7]

Kinetics. Kinetic measurements were performed over the temperature range 13.0–33.2° and over a wide range of solution compositions encompassing the following initial concentration ranges: 9 × 10^{-5}–5 × 10^{-3} *M* $Co(CN)_5H^{3-}$, 0.20–1.0 *M* OH^-, 4.7 × 10^{-4}–1.2 × 10^{-3} *M* CO (0.50–1.2 atm), and 9 × 10^{-5}–0.25 *M* CN^-. The ionic strength, adjusted with NaCl, was held constant at 1.0 *M*.

The kinetic results conformed to the rate law described by eq 3. Under the conditions of our measurements, with CO in excess over $Co(CN)_5H^{3-}$ and with the OH^- concentration sufficiently high to remain virtually constant throughout each experiment, the observed kinetic behavior was always pseudo first order (over at least 3 half-lives) in accord with eq 4, where $k_{obsd} = k[OH^-]$.

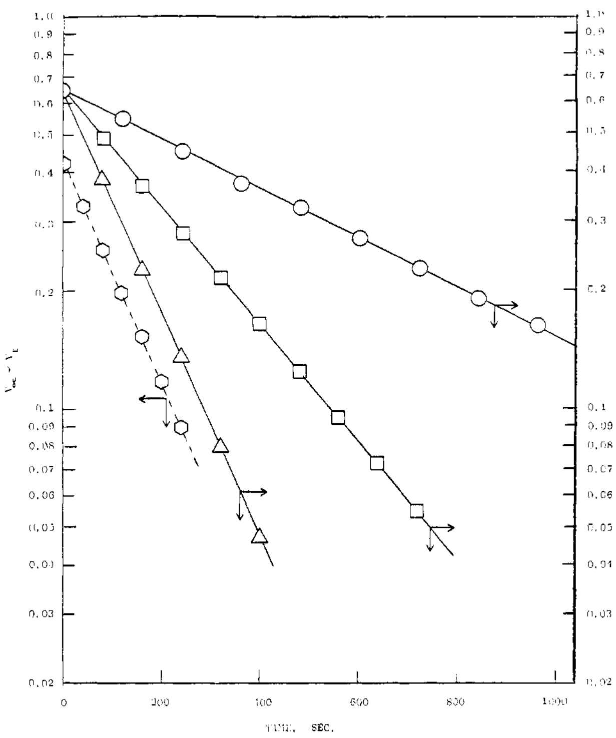

Figure 1. Typical pseudo-first-order plots depicting the dependence of the rate on the OH^- concentration and the agreement between the spectral and gas uptake kinetic measurements. Spectral runs: ○, 0.20 *M* OH^-; □, 0.60 *M* OH^-; △, 1.00 *M* OH^-. Gas uptake run: ⬡, 0.97 *M* OH^-. Other conditions are in Table I and text. A_∞ and A_t are the final value and the value at time *t* of the absorbance at 250 nm. V_∞ and V_t are the corresponding values (in arbitrary units) of the volumes of CO taken up.

$$-d[Co(CN)_5H^{3-}]/dt = k[Co(CN)_5H^{3-}][OH^-] \quad (3)$$

$$-d \ln [Co(CN)_5H^{3-}]/dt = k_{obsd} \quad (4)$$

Typical pseudo-first-order rate plots, derived from experiments in which the reactions were followed both spectrally and by CO uptake, are depicted in Figure 1. The results of the kinetic measurements are summarized in Table I where the value of *k* at constant temperature [(6.3 ± 0.5) × 10^{-3} M^{-1} sec^{-1} at 23°] is seen to be virtually independent of the concentration of $Co(CN)_5H^{3-}$, OH^-, and CO and unaffected by added CN^-. Measurement of the temperature dependence of *k* yielded the activation parameters, $\Delta H^{\ddagger} = 16 \pm 1$ kcal/mol and $\Delta S^{\ddagger} = -17 \pm 4$ eu.

Mechanism. The rate law represented by eq 3 is similar in form to the rate laws found for several other reactions of $Co(CN)_5H^{3-}$, including the reaction with $Fe(CN)_6{}^{3-}$,[4] as well as the limiting form of the rate law for the reaction with $Hg(CN)_2$.[3] Both of these reactions have been interpreted in terms of mechanisms involving the rate-determining step depicted by eq 5, followed by subsequent fast reactions of the $Co(CN)_5{}^{4-}$ ion formed in this step with the substrate, *i.e.*, with $Fe(CN)_6{}^{3-}$ or $Hg(CN)_2$.

$$Co(CN)_5H^{3-} + OH^- \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} Co(CN)_5{}^{4-} + H_2O \quad (5)$$

However, this simple mechanistic scheme cannot be extended to the present reaction with CO since the value

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[6] A. J. Chalk and J. Halpern, *J. Amer. Chem. Soc.*, 81, 5846 (1959).

[7] J. Bercaw, G. Guastalla, and J. Halpern, *Chem. Commun.*, 1594 (1970).

Table I. Summary of Kinetic Data[a]

[OH⁻], M	Temp, °C	Method[b]	$10^3 k_{obsd}$, sec^{-1}	$10^3 k$, M^{-1} sec^{-1}
0.20	23.0	sp	1.4	7.0
0.29	23.0	Gas	2.0	6.9
0.40	23.0	sp	2.4	6.0
0.39	23.0	Gas	3.0	7.6
0.50	23.0	sp	3.3	6.6[c]
0.58	23.0	sp	3.9	6.7
0.60	23.0	sp	3.6	6.0
0.68	23.0	sp	4.2	6.2
0.78	23.0	Gas	4.8	6.1
0.80	23.0	sp	4.8	6.0[d]
0.87	23.0	Gas	5.1	5.9
0.97	23.0	Gas	6.2	6.4
1.00	23.0	sp	6.6	6.6
0.97	13.0	Gas	2.1	2.2
0.97	33.2	Gas	13.4	13.8

[a] Initial $Co(CN)_5H^{3-}$ concentrations *ca.* 5 × 10^{-3} M in CO uptake experiments and *ca.* 9 × 10^{-5} M in spectral experiments; [CO] ~ 10^{-3} M (1 atm partial pressure) unless otherwise stated; ionic strength adjusted to 1.0 M with NaCl. [b] sp = spectral; gas = CO uptake. [c] Unaffected by variation of [CN⁻] from 9 × 10^{-5} to 0.25 M. [d] Unaffected by variation of [CO] from 4.7 × 10^{-4} to 1.2 × 10^{-3} M (0.5–1.2 atm).

of k for this reaction (*i.e.*, 6.3 × 10^{-3} M^{-1} sec^{-1} at 23°, μ = 1.0) is significantly lower than the corresponding value of k_5 (1.6 × 10^{-1} M^{-1} sec^{-1} at 25°, μ = 1.0)[4] for the reaction with $Fe(CN)_6^{3-}$ (or with $Hg(CN)_2$). The activation parameters are also significantly different. Hence, despite the similarity of the forms of their rate laws and the independence of the rate constants in each case of the substrate (*i.e.*, CO or $Fe(CN)_6^{3-}$) concentration, both reactions cannot proceed through mechanisms characterized by a common uniquely rate-determining step.

To explain this behavior we propose a mechanism for the reaction of $Co(CN)_5H^{3-}$ with CO (*i.e.*, eq 1) in which the reversible step 5 is followed by the following sequence of steps.[8]

$$Co(CN)_5^{4-} \xrightarrow{k_6} Co(CN)_4^{3-} + CN^- \tag{6}$$

$$Co(CN)_4^{3-} + CO \xrightarrow{\text{fast}} Co(CN)_4CO^{3-} \tag{7}$$

$$Co(CN)_4CO^{3-} + CO \xrightarrow{\text{fast}} Co(CN)_3(CO)_2^{2-} + CN^- \tag{8}$$

According to this interpretation, $k = k_5k_6/(k_{-5} + k_6)$. Combining the present value of k with the previously determined values of k_5 (1.6 × 10^{-1} M^{-1} sec^{-1})[4] and k_{-5} (1.1 × 10^5 sec^{-1})[9] yields $k_{-5}/k_6 = 25$ and $k_6 = 4.5 \times 10^3$ sec^{-1}.

The proposed mechanistic scheme, in addition to explaining the observed kinetic patterns, seems highly plausible on chemical grounds. The dissociation of $Co(CN)_5^{4-}$ seems reasonable in view of the known tendency of five-coordinate d^8 complexes such as $Ni(CN)_5^{3-}$ (with which $Co(CN)_5^{4-}$ is isoelectronic) to undergo such dissociation in aqueous solution. Since $Co(CN)_5^{4-}$ possesses an 18-electron valence shell, it also seems highly likely that the substitution of CN⁻ by CO to form $Co(CN)_4CO^{3-}$ will proceed through a dissociative mechanism (*i.e.*, eq 6 and 7) rather than an associative one.

Failure to observe any inhibition of the reaction by CN⁻ up to 0.25 M CN⁻ (compared to the much lower prevailing CO concentration of only 10^{-3} M) implies that the addition of CO to $Co(CN)_4^{3-}$ to form $Co(CN)_4CO^{3-}$ (eq 7) is much faster than the corresponding addition of CN⁻ to form $Co(CN)_5^{4-}$, *i.e.*, to the reverse of eq 6. This is not surprising since CO, being a better π acceptor than CN⁻, is expected to have a greater tendency to favor five-coordination relative to four-coordination for low-spin d^8 complexes. This difference is likely to be particularly pronounced in the case of a highly negatively charged complex such as $Co(CN)_4^{3-}$.

The occurrence of reaction 6, in competition with the reverse of reaction 5, has also been inferred recently by Lim and Anson[10] from observations on the electrochemical reductions of cobalt cyanide complexes.

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[8] It is likely that reaction 8 actually proceeds by a dissociative stepwise mechanism analogous to that depicted by eq 6 and 7, but our results provide no direct information about this.

[9] G. D. Venerable II and J. Halpern, *ibid.*, **93**, 2176 (1971).

[10] H. S. Lim and F. C. Anson, *J. Electroanal. Chem.*, **31**, 297 (1971).