syringe. The liberated CH_4 was sampled with a gastight syringe and detected by GLC. Infinity values were determined after acid hydrolysis of the reaction mixture.

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Registry No. $(CH_3)_2Co((1-)N_4)$, 33569-60-7; $[(CH_3)_2Co(N_4)]ClO_4$, 77310-45-3; Cd, 7440-43-9; Zn, 7440-66-6.

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Kinetics and Mechanism of the Reduction of Hexacyanoferrate(III) by (Ethylenediaminetetraacetato)hydroxocobaltate(II)

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The formation and disappearance of the binuclear cyanide-bridged complex between $Fe(CN)_6^{3-}$ and $CoEDTA^{2-}$ were investigated between pH 6.0 and 13.44. No change in the rate is observed until pH ~12, after which a drastic rise in the observed first-order rate constant is seen with increasing pH. Concurrently, the intensity of the deep purple binuclear complex decreases. These observations are attributed to the formation of the hydroxo complex $CoEDTA(OH)^{3-}$, which reduces $Fe(CN)_6^{3-}$ via an outer-sphere reaction without first reacting to form a binuclear (Fe^{II}–CN–Co^{III}) species. The failure of this species to form is taken as strong evidence of the outer-sphere mechanism in these reactions.

Introduction

The reduction of hexacyanoferrate(III) and substituted pentacyanoiron(III) complexes by (ethylenediaminetetraacetato)cobaltate(II) and related cobalt(II) chelates has been studied between pH 5 and 10 by several workers.[2–10] In each case the same pattern emerges: a rapid formation of a cyano-bridged binuclear complex followed by a slower formation of the final products, the mononuclear species $Fe^{II}(CN)_5X^{n-}$ and Co^{III}(chelate). The mechanism initially proposed[2,4,5,7] for these reactions involved the formation and subsequent dissociation of the cyano-bridged Fe^{II}–CN–Co^{III} entity as represented by reactions 1 and 2, with use of $Fe(CN)_6^{3-}$ and $CoEDTA^{2-}$ as examples.

$$CoEDTA^{2-} + Fe(CN)_6^{3-} \overset{K_1}{\rightleftharpoons} (EDTA)Co^{III}\text{–}NC\text{–}Fe^{II}(CN)_5^{5-} \quad (1)$$

$$(EDTA)Co^{III}\text{–}NC\text{–}Fe^{II}(CN)_5^{5-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CoEDTA^{-} + Fe(CN)_6^{4-} \quad (2)$$

An alternate mechanism, initially proposed by Haim and co-workers[6] and later substantiated by this research group,[8,9] attributes the slow formation of mononuclear products to an outer-sphere process. In this mechanism the binuclear complex is a "dead end" to product formation. Instead, reaction 3 is proposed to account for the product formation.

$$CoEDTA^{2-} + Fe(CN)_6^{3-} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} CoEDTA^{-} + Fe(CN)_6^{4-} \quad (3)$$

Recently,[10] evidence has been sought for the formation of a binuclear complex utilizing another bridging ligand, 4,4′-bipyridine. It was hoped that this species, which has served as an effective bridging ligand in earlier systems,[11,12] would act as a viable alternate to cyanide bridging, but this was not the case. In an effort to find such systems, we have continued our investigations using pentadentate cobalt(II) chelate complexes. Early work with (*N*-benzylethylenediaminetriacetato)cobaltate(II) and the parent iron complex $Fe(CN)_6^{3-}$ (performed as a model for cyanide-bridge formation) showed some interesting behavior above pH 10. The rate of production of products increased with pH, yet the apparent degree of formation of the binuclear complex decreased in this pH range. Similar results were obtained with (*N*-(hydroxyethyl)ethylenediaminetriacetato)cobaltate(II). To understand this effect more fully, the parent cobalt(II) complex, $CoEDTA^{2-}$, was investigated above pH 10. The results of this investigation are reported here.

Experimental Section

Materials. $Na_3Fe(CN)_6$ was purchased from Pfaltz & Bauer. Hydrated reagent $NaClO_4$ was purchased from G. F. Smith, and the disodium salt of ethylenediaminetetraacetic acid was purchased from Matheson Coleman and Bell. Cobalt(II) nitrate and a 50% standard NaOH solution were Fisher reagent-grade chemicals. Steam-distilled water was passed through a Barnstead Ultrapure mixed-bed ion exchanger and filtered before use.

Solution Preparation. Stock solutions of all chemicals were prepared by weight except for the $Co(NO_3)_2$ solutions, which were standardized by titration with standard EDTA and xylenol orange indicator.[13] Co^{II}EDTA solutions were prepared just prior to each run by using 10% excess Na_2H_2EDTA. Hexacyanoferrate(III) solutions were analyzed spectrophotometrically by using a molar absorptivity of 1023 M^{-1} cm^{-1} at 420 nm. Sample solutions were prepared so that kinetic runs were made at ionic strength 0.26 M and 25 °C. All pH adjustments were made with use of solutions prepared from carbonate-free standard 50% NaOH. No buffer was added. All pH measurements were made with a Fisher Accumet Model 520 pH meter equipped with a glass microprobe electrode. The electrode was placed in solutions for 30 s prior to measurement. Subsequent cleanings and standardization against pH 10 buffers were conducted between measurements.

Spectrophotometric and Kinetic Measurements. Kinetic measurements were obtained with a Cary 15 spectrometer equipped with a water-jacketed cell holder. Constant temperature in the cell compartment was maintained at 25 ± 0.01 °C by using a Lo-temptrol precision thermostatic bath. All solutions and the 2-cm absorbance cell were equilibrated to 25 °C before measurements were made. The

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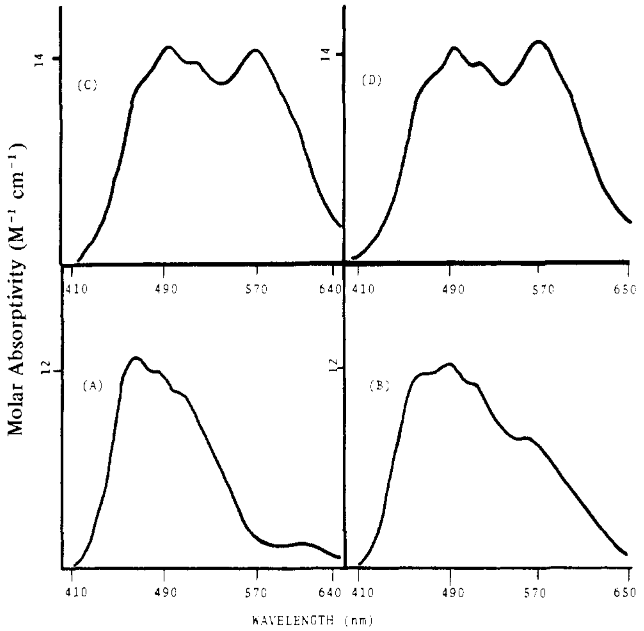

Figure 1. Spectra of 0.01 M solutions of (ethylenediaminetetraacetato)cobaltate(II) at 25 °C and $I = 0.26$ M: (A) pH 7.00; (B) pH 12.50; (C) pH 13.25; (D) pH 13.46.

pH was checked after the reaction was complete, and no changes were observed in this time period. Kinetic runs were carried out under pseudo-first-order conditions with Co^{II}EDTA in large excess over $Fe(CN)_6^{3-}$. The reaction was followed at 420 nm, the absorption maximum of the iron(III) reactant. First-order rate constants were obtained from linear regression slopes of plots of ln $(A_t - A_\infty)$ vs. time.

Spectrophotometric measurements to determine the spectral characteristics of the hydroxo complex of CoEDTA^{2-} were performed with the same Cary 15 spectrometer. The equilibrium formation of this hydroxo complex was monitored by following the increase in molar absorptivity as a function of pH at 490 nm, $I = 0.26$ M, and at 25 °C.

Results and Discussion

Equilibrium Measurements. The spectra of a 0.01 M solution of CoEDTA^{2-} as a function of pH are shown in Figure 1. In neutral media the absorption spectrum of CoEDTA^{2-} shows a maximum at 465 nm with two shoulders close by at 485 and 505 nm. The molar extinction coefficient at the maximum is 13.2 M^{-1} cm^{-1}. As the solution is made basic (eq 4) several spectral changes are observed that can be attributed

$$CoEDTA^{2-} + OH^- \underset{}{\overset{K_{OH}}{\rightleftharpoons}} CoEDTA(OH)^{3-} \qquad (4)$$

to the formation of the hydroxo complex. The hydroxo complex shows two maxima, at 490 nm ($\epsilon = 14.4$ M^{-1} cm^{-1}) and 568 nm ($\epsilon = 14.6$ M^{-1} cm^{-1}), and a shoulder at 514 nm ($\epsilon = 13.4$ M^{-1} cm^{-1}).

The equilibrium constant, K_{OH}, for reaction 4 was obtained by using the method of Bhat and Krishnamurthy.[14] The concentrations of the cobalt(II) species were calculated from a plot of the molar absorptivities vs. pH at 490 nm. The results are shown in Figure 2. All solutions were adjusted to an ionic strength of 0.26 M with $NaClO_4$. Above pH 13.46 no spectral changes are observed. Thus spectrum D in Figure 1 can be taken as the spectrum of the hydroxo complex. A corrected value for the ion product of water was determined to be $10^{-13.91}$. This value was obtained by calibration of the pH meter and glass electrode using standard solutions of NaOH adjusted to an ionic strength of 0.26 M at 25 °C. A plot of the calculated [OH$^-$] vs. measured [OH$^-$] was linear over the pH range 7–13.46. The value of $10^{-13.91}$ was obtained from the slope of this line. The value of K_{OH} was determined to be 6.98 ± 1.25 M^{-1}, which agrees very well with the value of 6.76 obtained by Bhat and Krishnamurthy[14] under variable ionic strength conditions of 0.01–0.1 M. The absorption spectra and molar absorptivities agree with the literature values except for that of CoEDTA(OH)$^{3-}$, which is slightly lower than previously reported (14.4 vs. ~16.3 M^{-1} cm^{-1}).

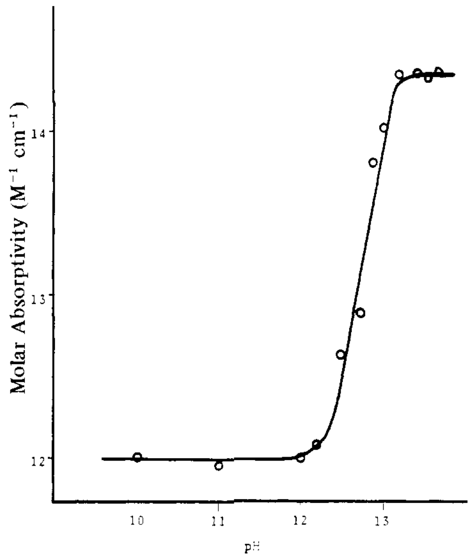

Figure 2. Plot of the change in molar absorptivity vs. pH for Co^{II}EDTA + OH$^-$ → Co^{II}EDTA(OH) at 490 nm ($I = 0.26$ M, 25 °C). Initial concentration of Co^{II}EDTA = 0.010 M.

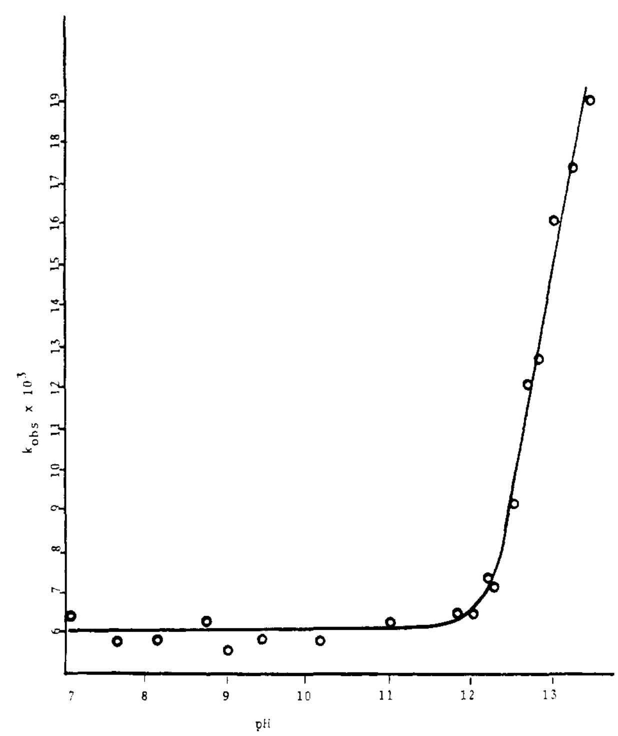

Figure 3. Plot of k_{obsd} vs. pH for the reaction of Co^{II}EDTA with Fe^{III}(CN)$_6$ at $I = 0.26$ M and 25 °C. [Co^{II}EDTA] = 0.010 M, [Fe^{III}(CN)$_6$] = 0.0010 M.

Kinetic Results. When excess CoEDTA^{2-} is mixed with $Fe(CN)_6^{3-}$ at pH <10, there is a rapid absorbance change (an increase in the region 460–650 nm and a decrease at 420 nm, the absorption maximum for $Fe(CN)_6^{3-}$) followed by a slower absorbance decrease at all wavelengths to form the final products CoEDTA$^-$ and $Fe(CN)_6^{4-}$. These changes were attributed to the formation of a binuclear redox product, EDTACo^{III}–NC–Fe^{II}(CN)$_5^{5-}$, and its subsequent disappear-

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[14] Bhat, T. R.; Krishnamurthy, M. *J. Inorg. Nucl. Chem.* **1963**, *25*, 1147.

ance via reaction 2 or via the reverse of (1) followed by (3).

The above kinetic measurements were extended to higher pHs. Reactions were carried out over the pH range 6.00–13.44 at $I = 0.26$ M. The absorbance data at 420 nm obeyed a first-order kinetic scheme as plots of ln $(A_t - A_\infty)$ vs. time were linear for several half-lives.[15] Linear regression analyses gave straight lines with correlation coefficients of 0.9993 or better. Figure 3 shows a plot of the observed first-order rate constant (k_{obsd}) vs. pH for the reaction.[16] Two observations are apparent: as the pH of the reaction mixture was increased, the observed rate constant increased while the intensity of the violet color of the binuclear complex that formed upon mixing became less and less pronounced. These observations can be explained by inclusion of another pathway for high-pH experiments, viz., outer-sphere redox reaction 5.

$$\mathrm{CoEDTA(OH)^{3-} + Fe(CN)_6^{3-} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} CoEDTA(OH)^{2-} + Fe(CN)_6^{4-}} \quad (5)$$

At low pHs, reactions 1 and 3 account for the formation of products. For this mechanism, the value of k_{obsd} is given by eq 6. At higher pH values reaction 5 becomes increasingly

$$k_{obsd} = k_3[\mathrm{CoEDTA^{2-}}]/(1 + K_1[\mathrm{CoEDTA^{2-}}]) \quad (6)$$

important so that in this region reactions 1, 3, and 5 represent the operative mechanism and k_{obsd} is given by eq 7. Using

$$k_{obsd} = \frac{k_3[\mathrm{CoEDTA^{2-}}] + k_4[\mathrm{CoEDTA(OH)^{3-}}]}{1 + K_1[\mathrm{CoEDTA^{2-}}]} \quad (7)$$

the equilibrium constant from reaction 4 and noting that $[\mathrm{Co^{II}}]_{tot} = [\mathrm{CoEDTA^{2-}}] + [\mathrm{CoEDTA(OH)^{3-}}]$, we can rearrange eq 7 to obtain eq 8. Taking the reciprocal of both sides,

$$k_{obsd} = \frac{(k_3 + k_4K_{OH}[\mathrm{OH^-}])[\mathrm{Co^{II}}]_{tot}}{1 + K_{OH}[\mathrm{OH^-}] + K_1[\mathrm{Co^{II}}]_{tot}} \quad (8)$$

we obtain eq 9.

$$\frac{1}{k_{obsd}} = \frac{1 + K_{OH}[\mathrm{OH^-}]}{(k_3 + k_4K_{OH}[\mathrm{OH^-}])[\mathrm{Co^{II}}]_{tot}} + \frac{K_1}{k_3 + k_4K_{OH}[\mathrm{OH^-}]} \quad (9)$$

When the experimental values of k_{obsd}^{-1} are plotted vs. $[\mathrm{Co^{II}}]_{tot}^{-1}$, linearity is observed at each of the three hydroxide ion concentrations used to perform this analysis. Linear regression plots of the data (Figure 4) yield slopes and intercepts that are a function of $[\mathrm{OH^-}]$. The slopes are 0.224, 0.222, and 0.297 M^{-1} s and the intercepts 46.7, 58.1, and 74.9 s for hydroxide concentrations of 0.095, 0.080, and 0.030 M, respectively. Values of k_4 were calculated from these slopes and intercepts as a "best fit" to the results. This was done by using the value $k_3 = 2.61$ M^{-1} s^{-1} obtained by Huchital and Lepore[8] at pH 6, $I = 0.26$ M, and 25 °C. From our average k_{obsd} of $(6.00 \pm 0.29) \times 10^{-3}$ s^{-1} in the pH 6–11 range, we were able to calculate an average value of $K_1 = 336 \pm 19$ M^{-1} using the rate law presented in the literature[6,8,10] for this pH range. The value calculated for k_4 is 6.84 ± 0.71 M^{-1} s^{-1}. The large error associated with k_4 is in part due to the difficulty of measurements of rate data at these high pHs and in part due to the associated errors in the other rate and equilibrium constants used in the calculations.

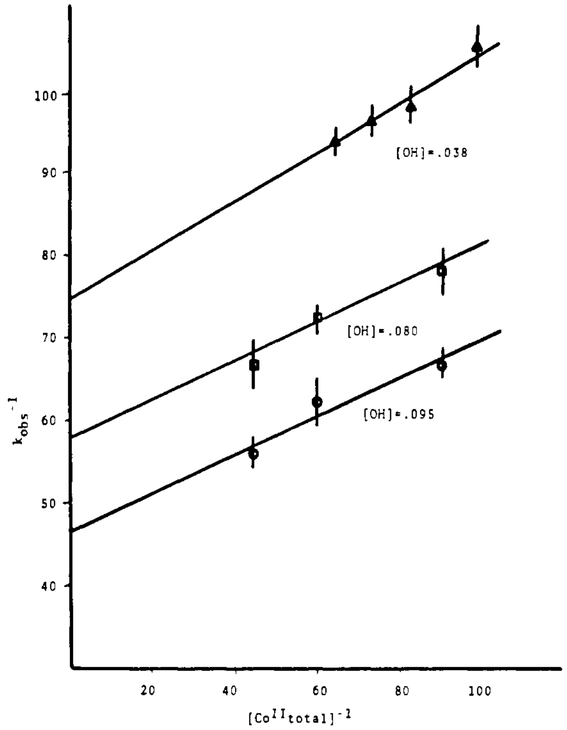

Figure 4. Plot of k_{obsd}^{-1} vs. $[\mathrm{Co^{II}}_{tot}]^{-1}$ at various $[\mathrm{OH^-}]$ concentrations. For each run $[\mathrm{Fe^{III}(CN)_6}] = 0.0010$ M.

The failure of an intermediate to form (similar to the binuclear species seen in all other systems[2–6,10]) can be considered additional evidence for an outer-sphere mechanism being operative in these reactions as originally proposed by Haim and co-workers.[6] An explanation of the relative values of k_3 (for the outer-sphere reduction of the parent EDTA complex) and k_4 (for the outer-sphere reduction of the hydroxo complex) can be obtained by using the Marcus theory for outer-sphere redox reactions. For two reductants reacting with a common oxidant, the Marcus relationship can be written in relative form as

$$k_{12}/k_{13} = (K_{12}/K_{13})^{1/2} \quad (10)$$

Here, k_{12} and k_{13} refer to the values of k_3 and k_4, respectively, while K_{12} and K_{13} are the equilibrium constants for the outer-sphere processes. Using the experimental values obtained here for k_3 and k_4 and a value of 3.21 M^{-1} for K_{12},[7] we calculate K_{13} to be 22.0 M^{-1}. Translated into reduction potentials, this increase can be attributed to a change in the reduction potential of the couple $\mathrm{CoEDTA(OH)^{2-/3-}}$ of 0.05 V compared to $\mathrm{CoEDTA^{-/2-}}$ (0.32 vs. 0.37 V).[17] Similar small changes in reduction potentials of CoEDTA(X) species have been observed by Grossman.[18]

Registry No. $\mathrm{Fe(CN)_6^{3-}}$, 13408-62-3; $\mathrm{CoEDTA^{2-}}$, 15136-66-0; $\mathrm{CoEDTA(OH)^{3-}}$, 15091-47-1.

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(15) At low $\mathrm{CoEDTA(OH)^{3-}}$ concentrations, care had to be taken in determining A_∞ because of a secondary slow reaction, $\mathrm{CoEDTA^- + OH^- \rightarrow CoEDTA(OH)^{2-}}$, which causes an increase in the absorbance at 420 nm. At high pH, where $[\mathrm{CoEDTA(OH)^{3-}}]$ becomes significant, this deviation disappeared.

(16) Values of k_{obsd} over the pH range 6–10 were in agreement with literature values.[5,7]

(17) It has been suggested that the difference between k_3 and k_4 might in part be due to a difference in the self-exchange rates of the respective Co(II/III) couples. Attempts to measure the $E°$ values using conventional Pt vs. SCE electrodes were unsuccessful due to the irreversibility of both of these couples (low self-exchange rates). The $\mathrm{Fe(CN)_6^{3-/4-}}$ couple can be measured by this method because of its greater reversibility (higher self-exchange rate). It was observed, however, that $\mathrm{CoEDTA(OH)^{3-}}$ is oxidized more readily by H_2O_2, which would be consistent with the hydroxo having a lower potential.

(18) Grossman, B. Ph.D. Thesis, State University of New York at Buffalo, 1969, p 43.