a high-spin six-coordinate iron(II) derivative. The ΔE_q for low-spin pseudooctahedral [Fe(*ms*-CRH)(NCS)$_2$] (0.67 mm/sec) is typical of low-spin iron(II) derivatives,[21,23] the low ΔE_q value resulting from the spherically symmetric filled t_{2g} (O_h) orbitals. For the high-spin iron(III) derivatives [Fe(*ms*-CRH)X$_2$]BF$_4$ the ΔE_q values are typically small[21,23] because of the spherical symmetry of the half-filled 3d shell.

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Registry No. [Fe(*ms*-CRH)Cl]Cl, 31122-39-1; [Fe(*ms*-CRH)Br]Br, 31122-40-4; [Fe(*ms*-CRH)I]I, 31122-41-5; [Fe(*ms*-CRH)Cl]PF$_6$, 53537-54-5; [Fe(*ms*-CRH)Br]PF$_6$, 53537-56-7; [Fe(*ms*-CRH)I]PF$_6$, 53537-58-9; [Fe(*ms*-CRH)(N$_3$)$_2$], 53432-27-2; [Fe(*ms*-CRH)OAc]PF$_6$, 53432-29-4; [Fe(*ms*-CRH)(NCS)$_2$], 53432-30-7; [Fe(*ms*-CRH)Cl$_2$]ClO$_4$, 53466-54-9; [Fe(*ms*-CRH)Cl$_2$]BF$_4$, 53466-55-0; [Fe(*ms*-CRH)Br$_2$]ClO$_4$, 53466-57-2; [Fe(*ms*-CRH)Br$_2$]BF$_4$, 53466-58-3; [Ni(*ms*-CRH)](ClO$_4$)$_2$, 53537-60-3.

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Interaction of Ethylenediaminetetraacetatocobaltate(II) with Ferricyanide and Monosubstituted Ferricyanide Ions. I. $Fe(CN)_6^{3-}$ and $Fe(CN)_5P(C_6H_5)_3^{2-}$

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A deep purple cyanide-bridged intermediate is formed between Co^{II}EDTA and either $Fe(CN)_6^{3-}$ or $Fe(CN)_5P(C_6H_5)_3^{2-}$. The equilibrium and rate constants for the formation of the intermediate and the rate constant for the decomposition of the intermediate at 30°, pH 6.00 (EDTA–NaOH), and $I = 0.26\ M$ (EDTA–NaClO$_4$) are 201 M^{-1}, $3.8 \times 10^4\ M^{-1}\ \text{sec}^{-1}$, and $1.74 \times 10^{-2}\ \text{sec}^{-1}$ for $Fe(CN)_6^{3-}$ and 1,490 M^{-1}, $2.0 \times 10^4\ M^{-1}\ \text{sec}^{-1}$, and $2.10 \times 10^{-3}\ \text{sec}^{-1}$ for $Fe(CN)_5P(C_6H_5)_3^{2-}$. Activation parameters and thermodynamic data are also reported. The resultes indicate that the charge and size of the substituent group and the net driving force all influence the stability and rate of formation of the intermediates in these reactions.

The first example of the inner-sphere reaction of a cobalt(II)–chelate complex was reported by Adamson and Gonick[1] in 1963. A purple intermediate was observed in the oxidation of ethylenediaminetetraacetatocobaltate(II), Co^{II}EDTA, with hexacyanoferrate(III), $Fe(CN)_6^{3-}$. On the basis of magnetic and spectrophotometric measurements, it was concluded that the intermediate was the bridged-binuclear successor complex, *viz.*, a Co^{III}–NC–Fe^{II} species. This intermediate was shown to decompose slowly to the products of the reaction, Co^{III}EDTA and $Fe(CN)_6^{4-}$.

Huchital and Wilkins[2] later reported results for the formation of the intermediate in this reaction using the more sophisticated stopped-flow and T-jump techniques. These workers found that a second intermediate could form *via* the oxidation of the first intermediate by excess $Fe(CN)_6^{3-}$, producing a Co^{III}–NC–Fe^{III} species. The rate of formation of this intermediate was about 50–100 times slower than for the first intermediate. More recently Huchital and coworkers[3] extended these studies to other cobalt(II)–chelate systems. Rate and equilibria data were discussed with regard to the stereochemisty of the chelate and the effets of substitution on the chelate ring on the stability of the intermediate.

In order to understand more fully the factors at play in these redox reactions, we have investigated the oxidation reactions of Co^{II}EDTA in which the oxidants are a monosubstituted ferricyanide ion, $Fe(CN)_5X^{2-}$. The cases in which X is NH$_3$, H$_2$O, and P(C$_6$H$_5$)$_3$ have been examined. Of primary interest here are the effects of the charge and size of the substituent group and the number of cyano groups available for bridge formation. We report here on the oxidation of Co^{II}EDTA by $Fe(CN)_5P(C_6H_5)_3^{2-}$ at $I = 0.26\ M$ and pH 6.00. Results are also presented for the Co^{II}EDTA reaction with ferricyanide ion, reexamined under the above solution conditions.

Experimental Section

Materials. NaClO$_4$ (BDH Chemicals), K$_3$Fe(CN)$_6$ and Co(NO$_3$)$_2$·6H$_2$O (Baker and Adamson), NaOH (Corco Chemicals), and Na$_2$H$_2$EDTA·2H$_2$O (Fisher) were all reagent grade chemicals and were used without further purification. Na$_2$Fe(CN)$_5$P(C$_6$H$_5$)$_3$ was prepared as the dihydrate by the method of Nast and Krieger.[4] The results of the atomic absorption analysis for iron content and the

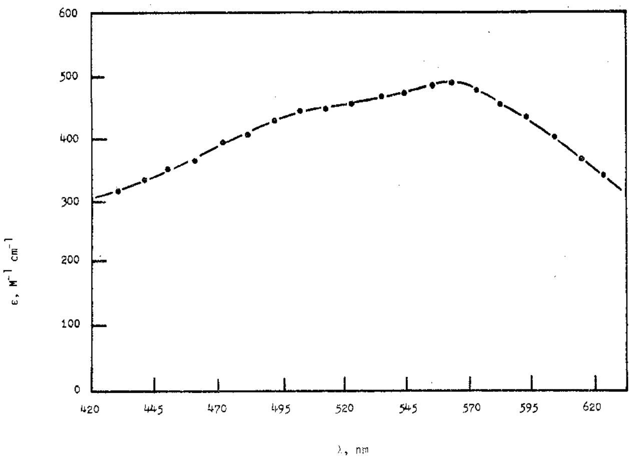

Figure 1. The absorption spectrum of $(EDTA)Co^{III}$-NC-$Fe^{II}(CN)_4$-$P(C_6H_5)_3$.

elemental analysis are as follows. *Anal.* Calcd for $Na_2Fe(CN)_5P(C_6H_5)_3 \cdot 2H_2O$: Fe, 10.5; C, 52.1; H, 3.58; N. 13.2. Found: Fe, 10.6; C, 53.3; H, 3.53; N, 12.6.

The ir and uv spectra of the prepared material agreed with those in the literature.[4,5] Redistilled, deionized water was used in the preparation of all solutions.

Solution Preparation. Stock solutions were prepared by weight except for the cobaltous nitrate solution which was standardized by titration with standard EDTA. $Co^{II}EDTA$ was prepared *in situ* in each run, using a 10% excess of EDTA. All sample solutions were prepared so that every kinetic run was at $I = 0.26$ M and pH 6.00 (EDTA–NaOH–$NaClO_4$). $K_3Fe(CN)_6$ was converted to the sodium salt by ion-exchange methods, thus eliminating the interference of specific cation effects which were observed in preliminary studies. Aqueous solutions of the oxidants were used in the slow decomposition reactions, but for the rapid reactions, the oxidant solutions were brought to pH 6.00 and $I = 0.26$ M with $NaClO_4$, NaOH, and 0.01 M EDTA.

Apparatus. Kinetic measurements were performed with a Cary 15 spectrophotometer (slow reactions) and an Aminco-Morrow stopped-flow apparatus. Spectra were obtained with a Beckman DK-2 spectrophotometer. All instruments were thermostated and the temperature uncertainty was so maintained within ±0.07° in all cases.

Kinetic Measurements. All reactions were carried out under pseudo-first-order conditions with $Co^{II}EDTA$ in large excess over the oxidants. Reactions were observed at either 420 or 590 nm for the ferricyanide reactions and either 625 or 585 nm for the phosphine reactions (phosphine = $Fe(CN)_5P(C_6H_5)_3{}^{2-}$). Results agreed within experimental error for the two wavelengths used for each oxidant. Rate constants were determined as the linear regression slopes of plots of ln $(A_t - A_\infty)$ *vs.* time, where A_t is the absorbance at time t and A_∞ is the final absorbance reading after about 10–12 half-lives. Values of A_∞ were estimated for each run by the Mangelsdorf method,[6] and these values agreed well with the experimental readings. All solutions used for the slow reactions involving the phosphine oxidant were thoroughly flushed with argon and anaerobic syringe techniques employed in order to eliminate the interferences of air oxidation of the reaction products.

Spectrophotometry. The intermediate formed in the $Co^{II}EDTA$–phosphine reaction was found to be stable enough that its spectrum was readily obtainable. The cell compartment of the Beckman DK-2 was thermostated at 17.5° and 0.282 M $Co^{II}EDTA$ was placed in the sample and reference cells. Enough oxidant stock solution was injected into the sample cell (equal volume of water injected into the reference cell) to result in a phosphine concentration of 2.0×10^{-4} M. Under these conditions, 99% of the oxidant is complexed in the intermediate. The spectrum was repetitively recorded and logarithmically extrapolated to zero time at 20 wavelengths. Since all other absorbing species are either blanked out or outside the wavelength range of interest, the extrapolated values of the absorbance comprise the spectrum of the intermediate, shown in Figure 1. The absorption coefficient is 480 M^{-1} cm^{-1} at the maximum wavelength of 558 nm, in good agreement with a preliminary value of 490 M^{-1} cm^{-1} at 560 nm reported by Stasiw.[5]

Table I. Apparent Rate Constants for the Decomposition of $[(EDTA)Co^{III}\text{-}NC\text{-}Fe^{II}(CN)_5]^{5-}$ to Products[a]

$[Co^{II}EDTA]_0$, mM	10^3k_{3app},[b] sec^{-1}	$[Co^{II}EDTA]_0$, mM	10^3k_{3app},[b] sec^{-1}
	20.03°		30.03°
4.71	3.04 ± 0.01	4.70	8.55 ± 0.02
5.65	3.30 ± 0.01	5.64	9.13 ± 0.03
7.06	3.45 ± 0.02	7.05	10.1 ± 0.1
9.42	3.82 ± 0.02	9.40	11.2 ± 0.1
14.1	3.99 ± 0.01	14.1	13.0 ± 0.1
28.3	4.37 ± 0.03	28.2	14.9 ± 0.1
	25.04°		35.02°
4.70	5.38 ± 0.02	2.81	8.62 ± 0.04
5.64	5.81 ± 0.03	3.52	9.98 ± 0.02
7.06	6.29 ± 0.02	4.69	12.2 ± 0.1
9.41	6.85 ± 0.06	6.10	14.7 ± 0.1
14.1	7.68 ± 0.02	9.38	17.5 ± 0.1
28.2	8.41 ± 0.07		

[a] $I = 0.26$ M, pH 6.00, $[Fe(CN)_6{}^{3-}]_0 = 1.00 \times 10^{-4}$ M. [b] Observed pseudo-first-order rate constants, λ_0 420 nm.

Results

$Co^{II}EDTA + Fe(CN)_6{}^{3-}$. Previous investigations[1-3] of this reaction were carried out at pH 5.00 and $I = 0.66$ M (sodium acetate–acetic acid). These conditions were deemed too stringent for studies involving $Fe(CN)_5X^{2-}$ complexes, due to the high substitution lability of the X group. Many electrolytes and most common buffers are known to attack these complexes to some degree.[5] For this reason, we have chosen the milder conditions of pH 6.00 and $I = 0.26$ M ($NaClO_4$–NaOH–EDTA) for the present investigations of the $Co^{II}EDTA$–$Fe(CN)_5X^{2-}$ reactions. The reaction between $Fe(CN)_6{}^{3-}$ and $Co^{II}EDTA$ is considered the reference reaction and is therefore reexamined here for the purposes of comparison under the same conditions.

Plots of ln $(A_t - A_\infty)$ *vs.* time for the slow decomposition phase of this reaction were linear for at least 4 half-lives. Values of the observed pseudo-first-order rate constants, $k_{3_{app}}$, determined as the slopes of these plots for various concentrations of $Co^{II}EDTA$ and four temperatures, are presented in Table I.

Huchital and Wilkins[2] reported eq 1–3 for this reaction. The

$$Co^{II}EDTA^{2-} + Fe(CN)_6{}^{3-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{I_1}{[(EDTA)Co^{III}\text{-}NC\text{-}Fe^{II}(CN)_5]^{5-}} \quad (1)$$

$$[(EDTA)Co^{III}\text{-}NC\text{-}Fe^{II}(CN)_5]^{5-} + Fe(CN)_6{}^{3-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{I_2}{[(EDTA)Co^{III}\text{-}NC\text{-}Fe^{III}(CN)_5]^{4-}} + Fe(CN)_6{}^{4-} \quad (2)$$

$$[(EDTA)Co^{III}\text{-}NC\text{-}Fe^{II}(CN)_5]^{5-} \xrightarrow{k_3} Co^{III}EDTA^- + Fe(CN)_6{}^{4-} \quad (3)$$

first step is the inner-sphere formation of the first intermediate, I_1. This is the successor complex, so called because the electron has already been transferred from the reductant to the oxidant. The bridged-binuclear precursor complex Co^{II}–NC–Fe^{III} has never been detected.[2] The second step is the outer-sphere formation of I_2, containing the prosthetic group Co^{III}–NC–Fe^{III}, formed by oxidation of I_1 with excess ferricyanide. This reaction can be ignored in the present work because I_2 forms about 2 orders of magnitude slower than I_1 and because the concentration of I_2 is never more than a few per cent of the total iron concentration. The last step is the first-order breakup of I_1. Investigations of the slow reaction involve this decomposition and the first step. The observed pseudo-first-order rate constant for these two processes can be expressed as

$$k_{3_{app}} = \frac{k_3K_1[Co^{II}EDTA]}{1 + K_1[Co^{II}EDTA]} \quad (4)$$

Table II. Parameters Derived from the Decomposition of $[(EDTA)Co^{III}\text{-}NC\text{-}Fe^{II}(CN)_5]^{5-}$

Temp, °C	10^3k_3, sec^{-1}	K_1, M^{-1}	Temp, °C	10^3k_3, sec^{-1}	K_1, M^{-1}
20.03	4.79 ± 0.08	376 ± 26	30.03	17.4 ± 0.4	201 ± 11
25.04	9.56 ± 0.08	273 ± 7	35.02	32.9 ± 1.8	126 ± 11

Table III. Kinetics of Formation of I_1 from $Co^{II}EDTA + Fe(CN)_6^{3-}$ [a]

Temp, °C	$[Co^{II}EDTA]$, mM	$[Fe(CN)_6^{3-}]$, mM	k_{1app},[b] sec^{-1}
2.30	2.63	0.176	98 ± 6
	3.42	0.176	123 ± 9
	5.26	0.176	183 ± 13
	7.89	0.176	270 ± 1
	10.5	0.176	350 ± 50
5.75	2.63	0.249	109 ± 2
	3.42	0.249	137 ± 2
	5.26	0.249	203 ± 5
	7.89	0.249	286 ± 5
	10.5	0.249	373 ± 35
9.20	5.26	0.390	212 ± 5
	10.5	0.390	407 ± 12
	15.8	0.390	565 ± 17
	19.7	0.390	701 ± 64
12.66	3.42	0.390	169 ± 4
	5.26	0.390	232 ± 2
	7.89	0.390	338 ± 14
	10.5	0.390	418 ± 6

[a] $I = 0.26\ M$, pH 6.00, λ_0 420 or 590 nm. [b] Observed pseudo-first-order rate constants.

Table IV. Reaction Parameters for the Formation of I_1 from $Co^{II}EDTA$ and $Fe(CN)_6^{3-}$

Temp, °C	$10^{-4}k_1$, M^{-1} sec^{-1}	k_{-1}, sec^{-1}	Temp, °C	$10^{-4}k_1$, M^{-1} sec^{-1}	k_{-1}, sec^{-1}
2.30	3.21 ± 0.04	13	9.20	3.36 ± 0.09	43
5.75	3.36 ± 0.04	24	12.65	3.56 ± 0.13	48

The reciprocal expression is

$$\frac{1}{k_{3\text{app}}} = \frac{1}{k_3} + \frac{1}{k_3 K_1 [Co^{II}EDTA]} \tag{5}$$

Double-reciprocal plots of $k_{3_{app}}^{-1}$ vs. $[Co^{II}EDTA]^{-1}$ for this reaction, as shown in Figure 2, are linear at all four temperatures. Values of k_3 and K_1, evaluated from the linear regression slopes and intercepts of these plots according to eq 5, are presented in Table II. A linear regression fit of values of k_3 to the Eyring equation yields the activation parameters $\Delta H_3^\ddagger = +22.3 \pm 0.3$ kcal/mol and $\Delta S_3^\ddagger = +7.1 \pm 0.3$ cal/(mol deg). A linearly regressed plot of the temperature variation of K_1 yields the value $\Delta H_1° = -13 \pm 1$ kcal/mol. First-order rate plots for the formation of I_1 were again linear for at least 4 half-lives. Values of the observed rate constants, $k_{1_{app}}$, determined at several concentrations of $Co^{II}EDTA$ and four temperatures, are given in Table III. For step 1 of the reaction scheme, the apparent rate constant is given by

$$k_{1\text{app}} = k_{-1} + k_1 [Co^{II}EDTA] \tag{6}$$

Thus, plots of $k_{1_{app}}$ vs. $[Co^{II}EDTA]$ should be linear with slope equal to k_1 and intercept equal to k_{-1}. As displayed in Figure 3, the plots are indeed linear, though the lines are closely grouped for the four temperatures and the intercepts are small and relatively uncertain. Values of k_1 and k_{-1} for this reaction are presented in Table IV. Results of the linearly regressed Eyring plot are $\Delta H_1^\ddagger = +0.9 \pm 0.4$ kcal/mol and $\Delta S_1^\ddagger = -35 \pm 4$ cal/(mol deg).

Table V. Apparent Rate Constants for the Decomposition of $[(EDTA)Co^{III}\text{-}NC\text{-}Fe^{II}(CN)_4P(C_6H_5)_3]^{4-}$ to Products[a]

$[Co^{II}EDTA]_0$, mM	10^3k_{3app},[b] sec^{-1}	$[Co^{II}EDTA]_0$, mM	10^3k_{3app},[b] sec^{-1}
	30.01°		40.02°
4.70	1.84 ± 0.02	4.68	6.53 ± 0.02
5.64	1.87 ± 0.01	5.62	6.67 ± 0.06
7.05	1.92 ± 0.02	7.02	6.94 ± 0.03
9.40	1.95 ± 0.01	9.36	7.30 ± 0.03
14.1	2.00 ± 0.01	14.0	7.39 ± 0.03
28.2	2.05 ± 0.01	28.1	7.86 ± 0.04
	35.02°		45.02°
2.81	3.06 ± 0.03	4.67	10.0 ± 0.1
3.52	3.19 ± 0.02	5.61	10.2 ± 0.1
6.10	3.47 ± 0.02	7.01	10.7 ± 0.1
9.38	3.65 ± 0.03	9.34	11.6 ± 0.1
28.1	3.88 ± 0.03	14.0	11.9 ± 0.1

[a] $I = 0.26\ M$, pH 6.00, $[Fe(CN)_5P(C_6H_5)_3^{2-}]_0 = (2.44\text{–}2.83) \times 10^{-4}\ M$. [b] Observed pseudo-first-order rate constants, λ_0 625 or 535 nm.

Table VI. Parameters Derived from the Decomposition of $[(EDTA)Co^{III}\text{-}NC\text{-}Fe^{II}(CN)_4P(C_6H_5)_3]^{4-}$

Temp, °C	10^3k_3, sec^{-1}	K_1, M^{-1}	Temp, °C	10^3k_3, sec^{-1}	K_1, M^{-1}
30.01	2.10 ± 0.01	1490 ± 26	40.02	8.13 ± 0.09	850 ± 68
35.02	4.00 ± 0.01	1110 ± 16	45.02	13.3 ± 0.4	620 ± 87

Table VII. Kinetics of Formation of I_1 from $Co^{II}EDTA + Fe(CN)_5P(C_6H_5)_3^{2-}$ [a]

Temp, °C	$[Co^{II}EDTA]$, mM	$[Fe(CN)_5P(C_6H_5)_3^{2-}]$, m$M$	k_{1app},[b] sec^{-1}
2.30	2.63	0.283	31.6 ± 0.2
	3.42	0.283	40.0 ± 0.2
	5.26	0.283	69 ± 1
	7.89	0.287	99 ± 3
5.75	2.63	0.309	33.2 ± 0.8
	3.42	0.339	42.3 ± 0.7
	5.26	0.287	70 ± 5
	7.89	0.287	103 ± 3
	10.5	0.298	139 ± 9
9.20	2.63	0.279	40.1 ± 0.5
	3.42	0.279	50.0 ± 0.5
	5.26	0.279	73 ± 1
	10.5	0.279	153 ± 9
	15.8	0.279	228 ± 14
	19.7	0.279	278 ± 8
12.65	3.42	0.280	57 ± 4
	5.26	0.280	88 ± 3
	7.89	0.280	125 ± 5
	10.5	0.280	169 ± 2

[a] $I = 0.26\ M$, pH 6.00, λ_0 625 or 585 nm. [b] Observed pseudo-first-order rate constants.

Table VIII. Reaction Parameters for the Formation of I_1 from $Co^{II}EDTA$ and $Fe(CN)_5P(C_6H_5)_3^{2-}$

Temp, °C	$10^{-4}k_1$, M^{-1} sec^{-1}	k_{-1}, sec^{-1}	Temp, °C	$10^{-4}k_1$, M^{-1}, sec^{-1}	k_{-1}, sec^{-1}
2.30	1.22 ± 0.05	0.65	9.20	1.41 ± 0.02	1.9
5.75	1.34 ± 0.02		12.65	1.56 ± 0.04	4.3

$Co^{II}EDTA + Fe(CN)_5P(C_6H_5)_3^{2-}$. Pseudo-first-order rate plots for the very slow decomposition of I_1 formed in this reaction were linear for at least 3 half-lives. Values of $k_{3_{app}}$ obtained as the slopes of the linear regression lines at various concentrations of $Co^{II}EDTA$ and four temperatures are given in Table V. Double-reciprocal plots of this data, linear at all four temperatures, are shown in Figure 4. The linear regression analysis of these lines results in the values of k_3 and K_1 for each of the four temperatures, and these are presented in Table VI. Least-squares analysis of the temperature variations of these constants resulted in the parameters $\Delta H_3^\ddagger = +23 \pm 1$ kcal/mol, $\Delta S_3^\ddagger = +6.4 \pm 0.4$ cal/(mol deg), and $\Delta H_1° = -11.1 \pm 0.3$ kcal/mol. The rapid formation of I_1 in this reaction was generally followed at 625 nm, but results obtained at 585 nm agreed within experimental error. The

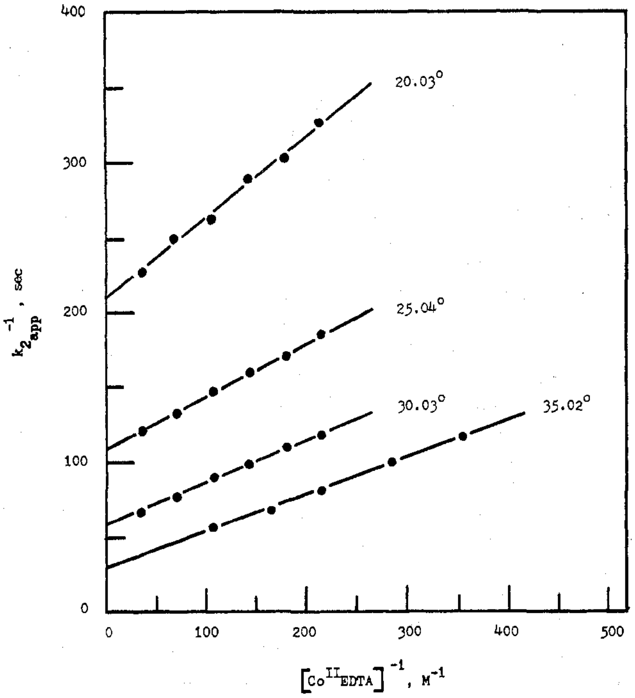

Figure 2. Double-reciprocal plot for the decomposition of I_1 to products for the ferricyanide reaction.

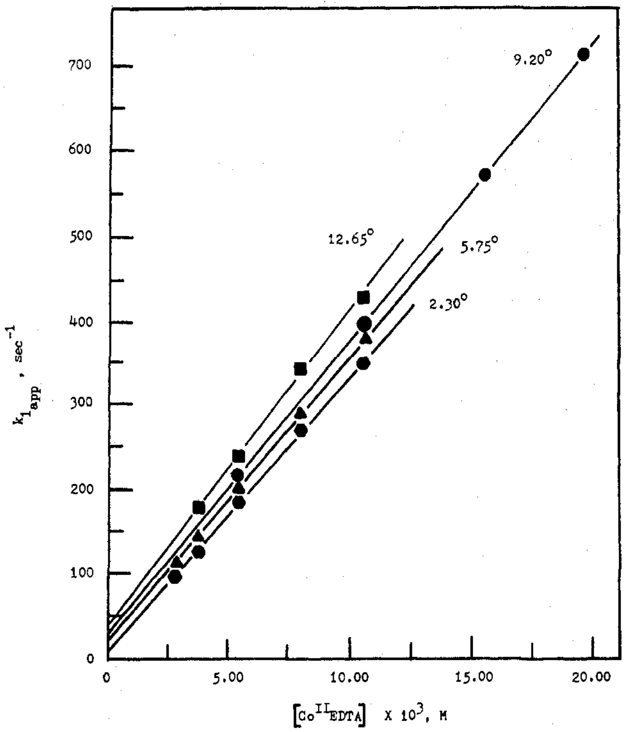

Figure 3. Dependence of $k_{1\text{app}}$ on [Co^{II}EDTA] for the formation of I_1 *in the ferricyanide reaction.*

rate plots were linear for more than 92% reaction in all cases. Values of $k_{1_{app}}$ are given in Table VII and are plotted according to eq 6 in Figure 5. The slopes and intercepts of these linearly regressed lines yield the values of k_1 and k_{-1}, respectively, and these results are presented in Table VIII. From the temperature variation of k_1, the following activation parameters are obtained: $\Delta H_1^{\ddagger} = +3.0 \pm 0.3$ kcal/mol and $\Delta S_1^{\ddagger} = -29 \pm 2$ cal/(mol deg). Very small intercepts and the resultant scatter in the values of k_{-1} precluded the determination of the activation parameters for the breakdown of I_1 to reactants for these reactions. This is not entirely unexpected, since inspection of eq 6 shows that k_{-1} is the very small difference between the large values of $k_{1_{app}}$ and k_1[Co^{II}EDTA].

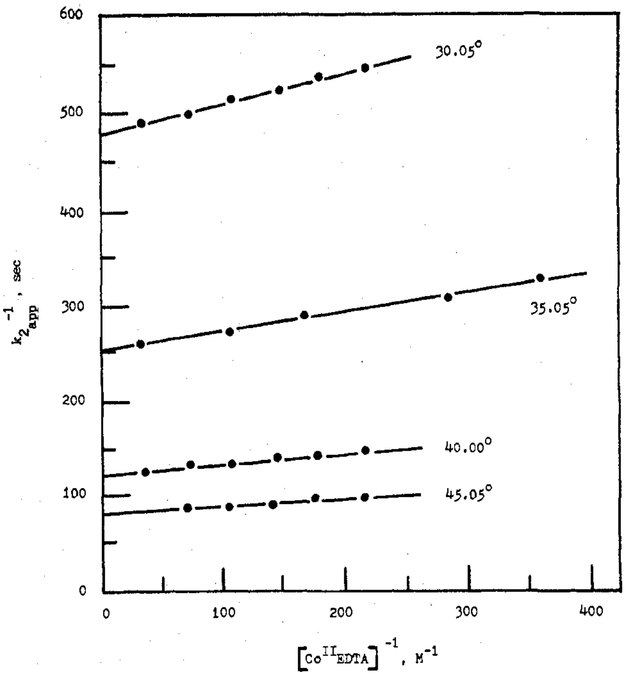

Figure 4. Double-reciprocal plot for the decomposition of I_1 to products for the phosphine reaction.

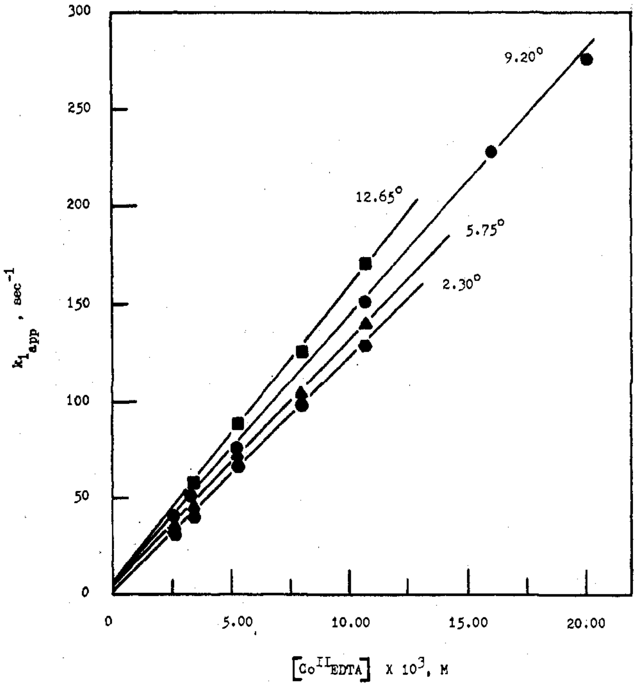

Figure 5. Dependence of $k_{1\text{app}}$ on [Co^{II}EDTA] for the formation of I_1 in the phosphine reaction.

Discussion

Spectrum of I_1. The specrum of the phosphine intermediate obtained here is similar to spectra obtained for other such intermediates.[1-3] All reported spectra are similar to, but greater than, the sum of the spectra of Co^{III}EDTA and Fe^{II}(CN)$_5$X, with λ_{max} 560 nm and ϵ_{max} 710 for CoEDTA–Fe(CN)$_6$, λ_{max} 540 nm and ϵ_{max} 685 for CoCyDTA–Fe(CN)$_6$, and λ_{max} 558 nm and ϵ_{max} 480 for CoEDTA–Fe(CN)$_5$P(C$_6$H$_5$)$_3$. It should be noted that because of the likelihood of hydrolysis of the reduced phosphine complex during the time of the analysis, this reagent was not added to the sample cell to depress the possible formation of I_2 in the present work. This procedure was followed in the determinations of the other spectra. However, since the formation of I_2 was observed during this work to consume only a few per cent of the total iron concentration, the error is deemed negligible in this case. The decreased absorption coefficient for the phosphine intermediate is somewhat expected, since the phosphine complex is much less symmetrical than ferricyanide. It is believed that the loss of symmetry on formation of I_1 is the cause of the increased coefficients of the ferricyanide intermediates relative to the reaction products. Since the iron nucleus of the phosphine intermediate is less symmetrical than the hexacyanides, then the lower value of the phosphine I_1 absorption coefficients is logical. Essentially, the main loss of symmetry on formation of I_1(phosphine) occurs at the cobalt nucleus.

Formation of I. Values of k_1, the rate constant for formation of the intermediate, are uniformly higher for the ferricyanide reaction than for the phosphine reaction, in spite of the greater driving force and lower formal charge of the phosphine oxidant. This is not entirely unexpected, since there are only five cyano groups available for bridging on the phosphine oxidant. However, this cannot be the only factor influencing the rate, for the phosphine reaction proceeds more slowly than five-sixths of the ferricyanide rate. Preliminary studies of $Co^{II}EDTA$ oxidation by $Fe(CN)_5SCN^{3-}$ and $Fe(CN)_5NH_3^{2-}$ have yielded estimates of k_1 in the range of $(1.2–1.4) \times 10^4$ M^{-1} sec^{-1} at 2.30°. These values are also lower than those for the ferricyanide reaction and lower than expected from consideration of the number of bridging groups alone.

The latter effect has been observed for other inner-sphere reactions presented in the literature. For example, Haim[7] has reported that the rate constants for the hexaaquoferrate(II) reduction of *trans*-$Co(NH_3)_4(N_3)_2^+$ and $Co(NH_3)_5N_3^{2+}$ are 4.4 and 0.53 M^{-1} sec^{-1}, respectively. After consideration of the effects of the difference in charge on the oxidant complexes, we note that the rate of electron transfer is decreased by a factor of 4–6 times when the number of bridging azido groups is halved. A similar effect was observed in the hexaaquoferrate(II) reductions of the chloro, thiocyanato, aquo, and ammine derivatives of chlorobis(ethylenediamine)cobalt(III).[8] The rate constants are 1.6×10^{-3} M^{-1} sec^{-1} for *cis*-$Co(en)_2Cl_2^+$, 1.7×10^{-4} M^{-1} sec^{-1} for *cis*-$Co(en)_2(NCS)Cl^+$, 1.8×10^{-5} M^{-1} sec^{-1} for *cis*-$Co(en)_2(NH_3)Cl^{2+}$, and 4.5×10^{-4} M^{-1} sec^{-1} for *cis*-$Co(en)_2(H_2O)Cl^{2+}$. We find that the dichloro complex reacts about 6–9 times faster than the chloro–thiocyanato complex and about 70–90 times faster than the chloro–ammine complex. As in several other reactions,[9] the aquo complex is out of line and reacts somewhat more rapidly than expected, though about 2–3 times slower than the dichloro complex. These examples illustrate that the inner-sphere reactions cited proceed more slowly by significantly more than a factor of 2 when the number of bridging ligands on the oxidant complex is cut in half. This effect is probably due to the decrease in reactive surface area when one of the bridging ligands is removed. Collisions between the reductant and the faces and edges of the oxidant molecule near the nonbridging ligand should be inefficient for bridge formation and may account for decreases in rate of 25% or more. In other words, if collisions occurred *only* at the bridging ligands, then a complex with $N - 1$ bridging ligands should logically react only $(N - 1)/N$ times as rapidly as a complex containing N of the same bridging ligand, all other things being equal. Since collisions occur at sites other than directly at the bridging ligands, then the reactive surface area effect must be considered.

A further decrease in rate is expected for the phosphine reaction, based on the steric interference of four of the five cyano groups resident on the oxidant complex. Molecular models indicate that the rather large triphenylphosphine group impedes the bridge-forming ability of the four cyano groups on the same side of the oxidant complex by about 20–40%. Only when the three phenyl groups are rotated into a relatively rigid "propeller-like" arrangement, are the cyano groups able to engage fully in bridge formation. Therefore, the phosphine complex is expected to react by an inner-sphere mechanism much more slowly than ferricyanide, based on the combined effects of a steric interference by triphenylphosphine and an overall decrease in the reactive surface area compared to the hexacyanide complex. On the other hand, the driving force and oxidant charge are expected to favor the phosphine oxidant. The oxidizing ability of $Fe(CN)_5P(C_6H_5)_3^{2-}$ (standard electrode potential = +0.54 V)[5] is much greater than that for $Fe(CN)_6^{3-}$ (= +0.40 V),[10,11] indicating a much lower barrier to electron transfer to the iron in the phosphine complex. Likewise, the less negative charge on the phosphine complex relative to that on the cyanide complex should lead to a greater collision frequency in the reaction with $Co^{II}EDTA^{2-}$, based on simple electrostatic arguments. It is obvious from the relatively small difference between values of k_1 for the ferricyanide and phosphine reactions that the aforementioned factors, *viz.*, the decreased number of cyano groups and the steric effect and the driving force and charge effects, nearly cancel for the phosphine reaction. The smaller value of k_1(phosphine) indicates that perhaps the lower number of cyano groups and the steric effect predominate for this reaction.

The activation parameters for the two reactions lend support to this interpretation. The enthalpy for the phosphine reaction is larger by about 2 kcal, while the entropies are the same within experimental error. Since the difference in the electrostatic contribution[12] to the enthalpy is less than 0.5 kcal for 3–,2– and 2–,2– interactions, we propose that the larger enthalpy for the phosphine reaction is due to the rotational barrier which the phosphine complex must surmount in order to bring a cyano group into alignment with the active position of $CoEDTA^{2-}$. On the other hand, the difference in the electrostatic contribution[12] to the entropy for the two reactions is about 6–10 cal/(mol deg). Since the entropies are very nearly the same for the two reactions, this range must be a measure of the steric contribution in the phosphine reaction. It seems likely that the phosphine reaction would proceed about 2–3 times more slowly were it not for the lower charge on the oxidant.

Over the temperature range studied, K_1(phosphine) is about 8 times larger than K_1(ferricyanide). This increased degree of formation of I_1(phosphine) is effected *via* the much smaller values of k_{-1}, the rate constants for the decomposition of I_1 back to reactants. In order to understand these differences, we must recall that I_1 is the successor complex in which cyanide bridge formation and electron transfer have both taken place. Thus for I_1 to decompose to the reactants, these processes must be reversed; *i.e.*, an electron must be transferred from Fe^{II} to Co^{III} *via* the cyanide bridge, and the pendant, in-plane acetate group of CoEDTA must then displace the bridging cyano group. Two factors, important with respect to these processes, are the electrode potential and overall charge of the oxidant complexes.

The potentials indicate that the reduced phosphine complex is a poorer reducing agent than ferrocyanide. In other words, there is a larger barrier to electron transfer to $Co^{III}EDTA$ from the reduced phosphine-bridged complex than from the ferrocyanide-bridged complex. Furthermore, once the electron is transferred back to the cobalt nucleus, there is less electrostatic repulsion effected between the 2– charged phosphine complex and $CoEDTA^{2-}$ than for the 3– charged ferricyanide complex and $CoEDTA^{2-}$. Both of these factors lead to increased stabilization of I_1(phosphine) with respect to reactants, decreased values of k_{-1}, and thus increased values of K_1 relative to the ferricyanide case.

Dissociation of I_1. In the decomposition step, I_1(phosphine) decomposes to the final products about 7–8 times more slowly than I_1(ferricyanide). This process does not involve electron transfer but only the substitution process in which the pendant acetate group displaces the cyano bridge in an S_N2 process.[13] In both reactions, the entering group and leaving groups are the same, and the main difference is the charge associated with the iron nucleus in the respective intermediates. The lower charge on the phosphine nucleus should result in a lesser electrostatic repulsion between it and the cobalt nucleus, a somewhat shorter Co–NC bond length, and consequently a slower rate of decomposition, as observed. Unfortunately, little corroboration is available from the activation parameters, since the enthalpy and entropy values for the two reactions are approximately the same within experimental error. One could expect that the enthalpy would be slightly more positive and the entropy slightly more negative for the phosphine reaction relative to the ferricyanide reaction based on the above arguments, and, though the results tend to follow this direction, little more can be extracted from these values at this time.

Outer-Sphere Pathways. The oxidation of Co^{II}EDTA and similar cobalt(II)–chelate complexes by ferricyanide ion has been successfully treated in terms of the inner-sphere pathway outlined herein. Recently,[14] however, Haim has suggested an alternate mechanism involving a direct outer-sphere electron-transfer path between Co^{II}EDTA and $Fe(CN)_6^{3-}$, *viz.*

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

The value of k_{os}, the rate constant for the outer-sphere redox process, can be determined from the data if one assumes that the bridged binuclear Co^{III}–Fe^{II} complex is a "dead end" as far as production of the final mononuclear species is concerned. If this approach is applied to the ferricyanide and phosphine oxidants in this work, the values of k_{os} obtained are 3.50 and 3.13 M^{-1} sec^{-1}, respectively. We have extended these studies to substituted ammine and aquo oxidants ($Fe(CN)_5NH_3^{2-}$ and $Fe(CN)_5OH_2^{2-}$).[15] Preliminary values of k_{os} are *ca.* 1 M^{-1} sec^{-1} for the ammine oxidant and *ca.* 16 M^{-1} sec^{-1} for the aquo oxidant.

Using these four oxidants, comparisons can now be made using the Marcus relationships.[16] Values for the exchange rate constants are not very reliable, but it seems reasonable from literature and other reports[5,10] that the values for substituted iron complexes are greater than or equal to the $Fe(CN)_6^{4-}$–$Fe(CN)_6^{3-}$ rate constant (*ca.* 5 × 10^3)^2. For the oxidation of a single reductant by different oxidants the Marcus relationship reduces to

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

where k_{12} and k_{13} are the cross reaction rate constants and K_{12} and K_{13} are the thermodynamic equilibrium constants (obtained from reduction potentials) for the same cross reactions. Ratios of k_{13}/k_{12} have been calculated and are listed in Table IX. Agreement is good for the ammine and aquo systems but poor for the phosphine system. It is interesting to note that the cross reaction rate constants (k_{12}) calculated from the original Marcus equation are 0.06 and 1.0 M^{-1} sec^{-1} for the $Fe(CN)_6^{3-}$ and $Fe(CN)_5P(C_6H_5)_3^{2-}$ oxidants.

Table IX. Rate and Equilibrium Data for the Outer-Sphere Pathway in the Co^{II}EDTA–$Fe(CN)_5$ Reaction

Oxidant	$E°$,[a] V	K_{12},[b] M^{-1} sec^{-1}	k_{ox}/k_{CN}	k_{os},[c] M^{-1} sec^{-1}
$Fe(CN)_6^{3-}$	+0.40[d]	3.21	1	3.50
$Fe(CN)_5(C_6H_5)_3P$	+0.54	746	15.2	3.13
$Fe(CN)_5CH_2^{2-}$	+0.48	72.3	4.75	16.2
$Fe(CN)_5NH_3^{2-}$	+0.33	0.211	0.26	0.97

[a] Reduction potentials; $E°$ for $CoEDTA^-$–$CoEDTA^{2-}$ is +0.37 V. [b] Equilibrium constant for the cross reaction $CoEDTA^{2-}$ + $Fe(CN)_5X^{n-} \rightleftharpoons CoEDTA^- + Fe(CN)_5X^{(n+1)-}$. [c] Calculated from slopes of double-reciprocal plots. See ref 14 for details. [d] Reduction potential values from ref 17 and R. G. Wilkins and R. E. Yelin, *J. Amer. Chem. Soc.*, **92**, 1191 (1970).

We therefore propose the following interpretation for these reactions. The binuclear intermediate (I_1) is not a "dead end" to the production of $CoEDTA^-$ and $Fe(CN)_6^{3-}$, but rather both mechanisms are operative. In systems where K_1 is small, the outer-sphere pathway predominates, while when K_1 is large, the dissociation path is important.[17] Research is continuing in our laboratory on the outer-sphere reduction of Co^{III}EDTA by substituted ferrocyanides in an effort to test these hypotheses further.

Registry No. Co^{II}EDTA, 14931-83-0; $Fe(CN)_6^{3-}$, 13408-62-3; $Fe(CN)_5P(C_6H_5)_3^{2-}$, 22548-72-7; $Fe(CN)_5OH_2^{2-}$, 19413-97-9; $Fe(CN)_5NH_3^{2-}$, 19413-98-0; [(EDTA)Co^{III}–NC–Fe^{II}(CN)$_5$]$^{5-}$, 38531-79-2; [(EDTA)Co^{III}–NC–Fe^{II}(CN)$_4$P(C$_6$H$_5$)$_3$]$^{4-}$, 53385-19-6.

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(15) Several aspects of this work are being restudied concerning possible involvement of mononuclear and binuclear forms of the iron(III) oxidants. The values reported here for k_{os}, thus, are preliminary numbers.
(16) See for example R. G. Linck, *MTP (Med. Tech. Publ. Co.) Int. Rev. Sci.: Inorg. Chem., Ser. One*, 303 (1972).
(17) From the rate constants for dissociation (k_d) and outer-sphere redox (k_{os}) and the value of K_1, *rates* of the two competing processes can be calculated. We have done this for the system (and conditions) under which the reverse reaction has been studied.[14] The values of k_{os} used were 0.06 (Marcus equation value) and 0.67 ($=K_1k_r$ = 3.21 × 0.21). The results show that the dissociation process is 5–50 times faster than the outer-sphere process for this system. Extension to the phosphine system studied here indicates that the rates are competitive. However, this assumes a value of k_d which is essentially a maximum rate constant (derived to fit). Thus, it is reasonable that for the phosphine system the mononuclear products *are* produced by an outer-sphere pathway.