A Study of the Intermediates Formed in the Reaction of Ethylenediaminetetraacetatocobaltate(II) with Ferricyanide Ion

By DANIEL H. HUCHITAL and RALPH G. WILKINS

Rapid reaction techniques have been used to study the characteristics of the intermediates which arise in the redox reaction between $CoEDTA^{2-}$ and $Fe(CN)_6{}^{3-}$. The kinetics of formation and decomposition of the bridged cyanide intermediate (I_1) have been measured by temperature-jump and stopped-flow experiments: $CoEDTA^{2-} + Fe(CN)_6{}^{3-} \underset{k_r}{\overset{k_f}{\rightleftarrows}} [(EDTA)Co^{III}-NC-Fe^{II}(CN)_5]^{5-}$ (I_1), from which $k_f = 1.3 \times 10^5 \, M^{-1} \sec^{-1}$, $k_r = 86 \sec^{-1}$, and $K = 1.5 \times 10^3 \, M^{-1}$ at 25° (pH 5.0, $I = 0.6 \, M$ with acetate, acetic acid). The value for K is in excellent agreement with that obtained (1.6×10^3) from spectrophotometric measurements made on the system shortly after mixing the reactants and before slower decomposition of I_1 to the final products $CoEDTA^-$ and $Fe(CN)_6{}^{4-}$ occurs. Another intermediate (I_2) arises from the rapid reaction of I_1 with $Fe(CN)_6{}^{3-}$: $I_1 + Fe(CN)_6{}^{3-} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} [(EDTA)Co^{III}-NC-Fe^{III}(CN)_5]^{4-}$ (I_2) $+ Fe(CN)_6{}^{4-}$. At 25°, $k_2 = 2 \times 10^3$, $k_{-2} = 3 \times 10^4 \, M^{-1} \sec^{-1}$, and $K_2 = 0.07$ from stopped flow. The slight decrease in k_f with increasing temperatures indicates it is a composite value and the reason for this arising is discussed. The formation of I_1 may be controlled by the water release from the cobalt(II) complex, reacting as $Co(EDTA)(H_2O)^{2-}$.

Introduction

It has been clearly demonstrated that the formation of a bridged activated complex or intermediate is an important step in certain redox reactions, termed inner sphere.[1] The occurrence of a reaction intermediate may be indirectly deduced from the rate law or the nature of the products, or, in certain cases, it may clearly be seen during the progress of the reaction. Thus, dinuclear intermediates of vanadium(III), chromium(III), and iron(III) have been observed in several 1-equiv redox reactions of aquo ions.[2] In general these systems are characterized by rapid formation rates but slow decomposition to products. Espenson[2] has made a reasonable correlation of these slow decomposition rates with the substitution lability of the metal ion involved, e.g., V(III), etc. We feel it is also meaningful to correlate the formation of the intermediates with the water exchange rate of the labile metal ion reactant.[3] Thus the labile $Cr_{aq}{}^{2+}$ forms intermediates rapidly with U(VI),[4] V(IV),[2] and Ir(IV)[5] during the course of the redox reaction.[6] The present work then stems from our interest in the relation between metal ion lability and the rate of formation of such intermediates as well as the over-all redox reaction.

A reaction which we can use to examine some of the kinetic characteristics of intermediates in inner-sphere redox reactions involves the oxidation of ethylenediaminetetraacetatocobaltate(II) ion by ferricyanide. Adamson and Gonick[7] reported a rapid optical density change when these reactants were mixed, although the

final products, $CoEDTA^-$ and $Fe(CN)_6{}^{4-}$ were only slowly formed. Some preliminary experiments[8] showed that the rapid change could be measured by stopped-flow techniques and that the reversible formation of the intermediate was attended by strong relaxation effects when subjected to a temperature-jump experiment. We report here a detailed study of the system.

Experimental Section

Materials.—All chemicals used were reagent grade. Standard solutions were prepared by weight except that cobalt(II) nitrate solutions were standardized by titration with EDTA using murexide indicator.

Spectrophotometry.—Spectrophotometric studies were made on Cary Model 14 and 15 spectrophotometers. The spectrum of $[(EDTA)Co^{III}-NC-Fe^{II}(CN)_5]^{5-}$, I_1, see reaction 1, was obtained at 12° from a solution initially $2 \times 10^{-2} \, M$ in $CoEDTA^{2-}$ and $10^{-3} \, M$ in $Fe(CN)_6{}^{3-}$. With these conditions I_1 is produced in $\geqslant 99\%$ yield. The ion $[(EDTA)Co^{III}-NC-Fe^{III}(CN)_5]^{4-}$, I_2, see reaction 2, was prepared in more than 97% yield in solution at 3° by adding an equivalent amount of cerium(IV) to a solution initially $10^{-2} \, M$ in both $CoEDTA^{2-}$ and $Fe(CN)_6{}^{3-}$. The spectrum obtained was corrected for very slight side reactions of Ce(IV) with $CoEDTA^{2-}$ and $Fe(CN)_6{}^{4-}$. The spectrum of reactants, I_1, I_2, and the final products are reproduced in Figure 1. The spectrophotometric method for the determination of equilibrium constants involved the determination of optical densities at 420 and 560 mμ of solutions of known total [iron] and [cobalt], before reaction 3 (see below) became important to the readings. Using the known values for the extinction coefficients and the conservation equation, total [iron] $= [Fe(CN)_6{}^{3-}] + [I_1] + 2[I_2]$, the concentration of all species in solution could be determined and hence the values of K_1 and K_2 could be calculated.

Stopped-Flow Runs.—The glass–lucite stopped-flow apparatus used in this work has been described previously.[9] Reactions were followed at 420 or 560 mμ and in certain cases at intermediate wavelengths. The conditions used in nearly all of the flow and temperature-jump experiments were similar to those of previous workers,[7] i.e., pH 5 and $I = 0.60$–$0.65 \, M$, using appropriate amounts of sodium acetate and acetic acid.

Temperature-Jump Experiments.—The temperature-jump

(1) For a recent review see N. Sutin, *Ann. Rev. Phys. Chem.*, **17**, 119 (1966).

(2) J. H. Espenson, *Inorg. Chem.*, **4**, 1533 (1965), and cited references.

(3) M. Eigen and R. G. Wilkins, Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 55.

(4) T. W. Newton and F. B. Baker, *Inorg. Chem.*, **1**, 368 (1962).

(5) H. Taube and H. Myers, *J. Am. Chem. Soc.*, **76**, 2103 (1954).

(6) A dimer of vanadium(III), VOV^{4+}, is formed fairly slowly from V(II) and V(IV), thus reflecting the relative inertness of the latter two ions.[3]

(7) A. W. Adamson and E. Gonick, *Inorg. Chem.*, **2**, 129 (1963).

(8) R. G. Wilkins, unpublished work; cf. ref 3, p 73, and ref 7.

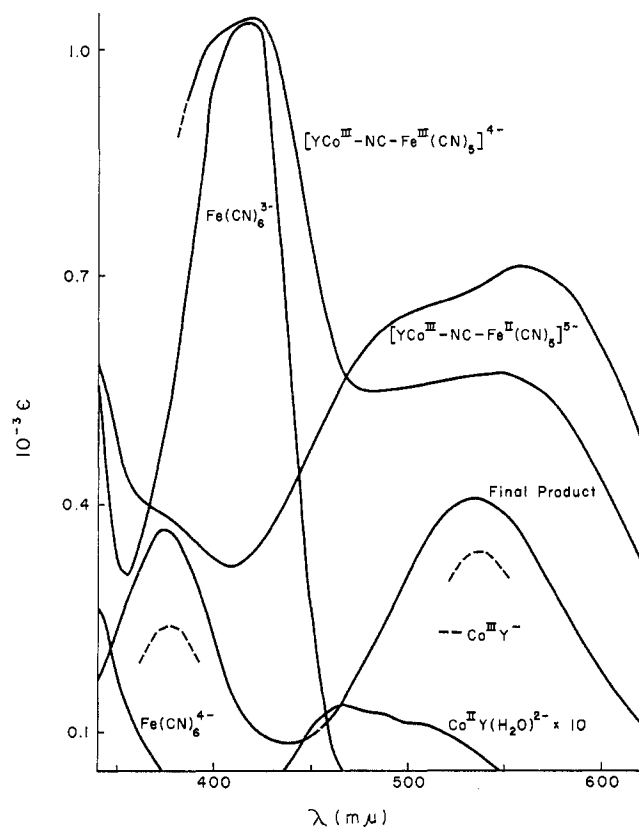(9) G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963).

Figure 1.—Spectra of reactants, intermediates, and products; Y = EDTA.

Figure 2.—Typical temperature-jump trace (λ 550 mμ). $[CoEDTA^{2-}]_0 = 1.0 \times 10^{-3} M$; $[Fe(CN)_6^{3-}]_0 = 2.0 \times 10^{-4} M$; temperature 12°; time scale = 5 msec/major division; increasing optical density upward.

model used in this work was purchased from Messanlagen Studiengesellschaft, Göttingen, West Germany. A jump of about 8° was obtained by discharging a 0.1-μf capacitor charged to 40 kv. The change of equilibrium in the sample cell was detected spectrally using a split-beam arrangement. The change was registered on a Tektronix 561-A oscilloscope with standard electronic arrangements.

A small volume of $Fe(CN)_6^{3-}$ solution (1 ml) was added to cobalt(II)-EDTA solution previously adjusted to the appropriate concentrations, pH, ionic strength, and temperature. The reaction mixture was then quickly transferred to the temperature-jump cell; the jump was made and the trace recorded as soon as feasible (usually a few minutes after mixing). Subsequent jumps made after the initial one showed small, but detectable, changes in the relaxation times. This arises because of the slow formation of the final products at the starting temperatures of the jump experiment (4, 9, and 17°) leading to disturbance of the rapid equilibria. Only one relaxation time (τ) was observed at several wavelengths (420, 465, and 550 mμ) and no very rapid optical density changes were observed. A typical oscilloscope trace is shown in Figure 2. The data could be treated as for a simple $A + B \rightleftharpoons I_1$ reaction, $\tau^{-1} = k_f(\bar{A} + \bar{B}) + k_r$. A plot of τ^{-1} vs. $(\bar{A} + \bar{B})$, i.e., $[CoEDTA^{2-} + Fe(CN)_6^{3-}]_{eq}$, was made. In the first instance the quantity in the brackets could be equated to $[CoEDTA^{2-}]$, this being usually in excess. The plot gave preliminary values of k_f (slope), k_r (intercept), and K_1 (slope/intercept). A more accurate assessment of $[A + B]_{eq}$ could now be made, and the plot was repeated. Further repetitions of this process gave constant values of k_f, k_r, and K_1 (usually after three to four plots). Although the system is complicated by the slower equilibrium (2), correction for this is within the error of the over-all analysis. Errors in the values of rate constants and equilibrium constants are ±10%. No relaxation effects were observed with mixtures of $CoEDTA^{2-}$ and $Fe(CN)_6^{4-}$.
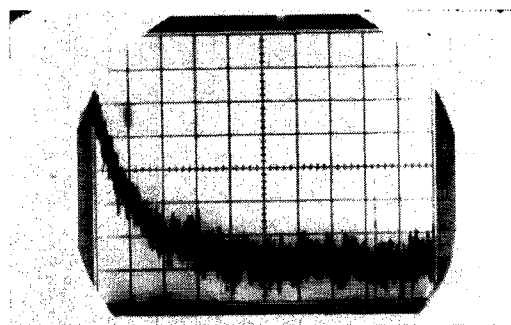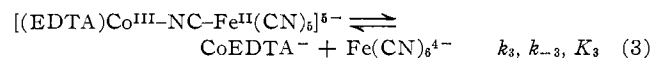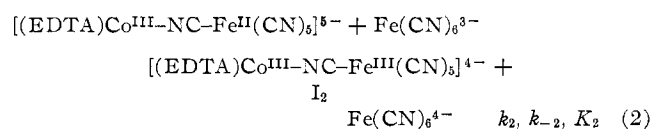
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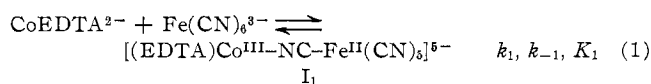
The results are reported in accordance with the following scheme. Except for the inclusion of (2) it is that suggested by Adamson and Gonick,[7] who showed that the intermediate produced in solution when 0.1 M reactants were mixed was diamagnetic. The data do

$$CoEDTA^{2-} + Fe(CN)_6^{3-} \rightleftharpoons$$
$$\underset{I_1}{[(EDTA)Co^{III}-NC-Fe^{II}(CN)_5]^{5-}} \qquad k_1, k_{-1}, K_1 \quad (1)$$

$$[(EDTA)Co^{III}-NC-Fe^{II}(CN)_5]^{5-} + Fe(CN)_6^{3-} \rightarrow$$
$$\underset{I_2}{[(EDTA)Co^{III}-NC-Fe^{III}(CN)_5]^{4-}} +$$
$$Fe(CN)_6^{4-} \qquad k_2, k_{-2}, K_2 \quad (2)$$

$$[(EDTA)Co^{III}-NC-Fe^{II}(CN)_5]^{5-} \rightleftharpoons$$
$$CoEDTA^- + Fe(CN)_6^{4-} \qquad k_3, k_{-3}, K_3 \quad (3)$$

not indicate whether I_2 is also undergoing independent decomposition, although it is usually present in much smaller amounts than I_1. We have confirmed that the final products are $Fe(CN)_6^{4-}$ and $CoEDTA^-$, in which the ligand is sexadentate. We cannot be certain however that the initial product of (3) is not at least some $Co(EDTA)(H_2O)^-$, in which the chelating ligand is quinquedentate, since this reverts to $CoEDTA^-$ with a similar rate constant (~ 0.1 min^{-1} at $I = 0.1 M$, pH 4–6, and a higher value at $I = 0.60$)[10] to that of k_3 (0.37 min^{-1})[7] at 25°.

Stopped-Flow Experiments.—When $2 \times 10^{-4} M$ solutions of reactants are mixed at 25° the decrease in optical density at 420 mμ with time is represented by the schematic trace shown in Figure 3. A rapid change which can be identified with reaction 1 is followed by a slower decrease, which is however much faster than the final decomposition (3) and can in fact be assigned to reaction 2. The equilibrium constants for (1) and for (2) can be determined from analysis of a series of flow traces as follows. At 420 mμ the only absorbing reactant is $Fe(CN)_6^{3-}$. As the concentration of $CoEDTA^{2-}$ is increased, maintaining a constant $[Fe(CN)_6^{3-}]$, the separation a, Figure 3, increases, asymptotically approaching a maximum value a_{max} obtained when $CoEDTA^{2-}$ is in sufficient excess to drive (1)
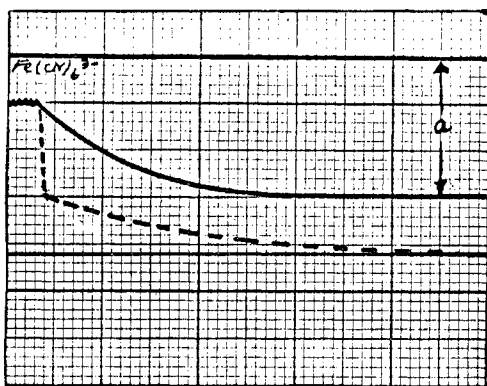
(10) I. A. W. Shimi and W. C. E. Higginson, *J. Chem. Soc.*, 260 (1958).

Figure 3.—Schematic flow trace. $[CoEDTA^{2-}] = 1.0 \times 10^{-4} M$; $[Fe(CN)_6^{3-}] = 1.0 \times 10^{-4} M$; $\mu = 0.6$; pH 5.0: upper curve, 10 msec/major division; lower curve, 500 msec/major division. H_2O base line is 22 major divisions below $Fe(CN)_6^{3-}$ line.

completely to I_1. With the conditions where $a = \frac{1}{2}a_{max}$

$$[Fe(CN)_6^{3-}]_e = [I_1]_e = \frac{1}{2}Fe[(CN)_6^{3-}]_0$$

$$[CoEDTA^{2-}]_e = [CoEDTA^{2-}]_0 - \frac{1}{2}[Fe(CN)_6^{3-}]_0 \quad (4)$$

the subscripts "0" and "e" representing initial and equilibrium concentrations. Thus

$$K_1 = [I_1]_e/[CoEDTA^{2-}]_e[Fe(CN)_6^{3-}]_e \quad (5)$$

$$K_1^{-1} = [CoEDTA^{2-}]_0 - \frac{1}{2}[Fe(CN)_6^{3-}]_0 \quad (6)$$

The value of K_2 was obtained by using the slower portion of the trace. The optical density at 420 mμ was determined from the trace before, $(OD)_1$, and after, $(OD)_2$, the slower reaction (2).

$$(OD)_1 = \epsilon_{Fe(CN)_6^{3-}}[Fe(CN)_6^{3-}]_1 + \epsilon_{I_1}[I_1]_1 \quad (7)$$

$$(OD)_2 = \epsilon_{Fe(CN)_6^{3-}}[Fe(CN)_6^{3-}]_2 + \epsilon_{I_1}[I_1]_2 + \epsilon_{I_2}[I_2]_2 \quad (8)$$

where the subscripts 1 and 2 refer to "equilibrium" concentrations at the end of reactions 1 and 2, respectively. Using the known value for K_1 and the conservation equation

$$[\text{iron}]_{\text{total}} = [Fe(CN)_6^{3-}] + [I_1] + 2[I_2] \quad (9)$$

enables the calculation of the concentrations of the species in reaction 2 and hence K_2.

Equal low concentrations of reactants were used in the kinetic study of the rapid reaction (1). For such a system, $A + B \rightleftharpoons I_1$ (k_f, k_r)[11]

$$k_f = \frac{[I_1]_e \ln\{2 - [I_1]_e^2/[Fe(CN)_6^{3-}]_0^2\}}{t_{1/2}([Fe(CN)_6^{3-}]_0^2 - [I_1]_e^2)} \quad (10)$$

where $t_{1/2}$ is the time for I_1 to form half its equilibrium concentration. All of the quantities in (10) can be determined. The results are shown in Table I. The dependence of the rate of the slower reaction on the concentrations of reactants is shown in Table II. Examination of the data shows that this reaction is associated with the intermediate I_1 reacting further with $Fe(CN)_6^{3-}$, i.e., reaction 2. In Table II, the conditions in runs 2–4 and, to a lesser extent, in run 1 are most suitable for kinetic analysis, the

(11) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1961, pp 186–188.

Table I
Flow Data for Reaction 1

T, °C	$10^4 a_0$,[a] M	$t_{1/2}$ (obsd), msec	K_1, M^{-1}	$10^{-5}k_f$, M^{-1} sec^{-1}
5.3	1.0	19	1.2×10^4	1.6
12.5	1.0	16.5	5.3×10^3	1.3
15.6	1.0	17	3.8×10^3	1.0
20.6	1.0	13	2.4×10^3	0.9
25.0	1.0	9	1.6×10^3	0.9
25.0	2.0	10	1.6×10^3	0.7
30.5	1.0	7.5	1.0×10^3	0.7

[a] $a_0 = [CoEDTA^{2-}] = [Fe(CN)_6^{3-}]$.

reactants are in equal concentration, and the equilibria established by reactions 1 and 2 are undisturbed during the further reaction of I_1 with $Fe(CN)_6^{3-}$. In these runs, it can be shown[11]

$$k_2 = \frac{[I_2]_e \ln\{3 - 2[I_2]_e/[I_1]_0\}}{2t_{1/2}[I_1]_0([I_1]_0 - [I_2]_e)} \quad (11)$$

where $t_{1/2}$ represents the time for $[I_2] = \frac{1}{2}[I_2]_e$. Because it is difficult to obtain very accurate data, reaction 2 was studied only at 25°.

Temperature-Jump Experiments.—Only one relaxation time is observed with (1). Normally, i.e., with the conditions shown in Table III, the relaxation times corresponding to (2) would be too long for observation by temperature jump. However, even when the concentrations of species were increased, one relaxation time only (corresponding still to (1)) persisted. This may be associated with a small ΔH for reaction 2. The data are given in Table III and all thermodynamic and kinetic parameters obtained in this study are collected in Table IV.

Discussion

The agreement between the values of K_1 and K_2 from direct spectrophotometry, temperature-jump measurements, and the flow experiments is excellent (Table IV). Reaction 2 was not considered by Adamson and Gonick and indeed is relatively unimportant in the majority of their experiments. It accounts, but only in part, for their lower reported K_1 (700 M^{-1} at 25°) than ours (1500 M^{-1} at 25°). It is difficult to understand all of the difference. We have confirmed the observation[7] that K_1 is larger at 5 than at 25°. The agreement in the values for ϵ_M for I_1 and I_2 at various wavelengths from the flow and the independent spectral measurements reassures us that we have identified the processes correctly.

Formation of I_1.—Our observations from the flow experiments that $-d/dt[Fe(CN)_6]^{3-} = d/dt[I_1]$ and that only one relaxation time is seen in the temperature jump agree with previous conclusions[7] that any intermediate arising in reaction 1 must be present in very low concentration in these studies. However the data, particularly from the flow experiments, suggest a slight decrease in the value for k_f with increasing temperature.[12] This is only reasonably accommodated if k_f is a composite value, and we can consider how this might

(12) This can be easily seen from the approximate form of expression 10, $k_f \approx 0.693K_1/t_{1/2}$. Since K_1 decreases proportionally more than $t_{1/2}$ with increasing temperature (Table I), the net effect is a decrease in k_f.

TABLE II

FLOW DATA FOR REACTION 2 AT 25°

Run no.	10^4[Co(II)]$_0$, M	10^4[Fe(III)]$_0$, M	10^4[Co-EDTA^{2-}]$_1$,[a] M	10^4[Fe-(CN)$_6^{3-}$]$_1$,[a] M	10^4[I$_1$]$_1$,[a] M	$t_{1/2}$, sec	k_2
1	10.0	2.0	8.9	0.8	1.2	0.80	$\sim$1.7 $\times$ 10^3
2	16.3	20.0	6.3	10.0	10.0	0.06	2.0 $\times$ 10^3
3	11.2	10.0	6.2	5.0	5.0	0.17	1.6 $\times$ 10^3
4	7.2	20.0	6.2	1.0	1.0	0.60	2.0 $\times$ 10^3
5	87	10.0	77	0.7	9.3	0.20	2.0 $\times$ 10^3 [b]
6	10.1	50.0	1.3	41	8.7	0.05	...

[a] Concentrations after reaction 1 and immediately prior to (2).   [b] Calculated for pseudo A $\xrightleftharpoons{k_2'}$ B + C reaction[11] with $k_2 = k_2'/$[I$_1$].

TABLE III

TEMPERATURE-JUMP RELAXATION TIMES[a]

T, °C	10^4[Co(II)]$_0$,[b] M	10^4[Fe(III)]$_0$[b] M	τ^{-1}, sec^{-1}
12	5.16	2.02	75, 77
12	7.22	2.02	109, 104, 125
12	2.06	7.00	94, 103
12	10.3	2.02	144, 136
12	2.06	10.0	143, 136, 149
12	15.5	2.02	196, 194
12	20.6	2.02	261 (2), 255 (2)
12	9.56	1.85	130, 141[c]
12	9.56	1.85	136, 141[d]
17	5.16	2.00	114, 102
17	8.26	2.00	167, 143
17	11.4	2.00	208, 213
17	17.5	2.00	290, 308
25	5.16	2.00	151, 157
25	8.26	2.00	190, 187
25	11.4	2.00	(282)
25	14.4	2.00	260, 266
25	9.8	2.00	206, 204

[a] All runs: [KNO$_3$] = 0.10 M; μ = 0.61–0.65; [EDTA]$_{excess}$ = 0.01 M; pH 5, unless otherwise noted.   [b] Initial concentrations.   [c] pH 4.25.   [d] pH 6.0.

by($\overline{\text{Co}}$ and $\overline{\text{Fe}}$ representing equilibrium concentrations of CoEDTA^{2-} and Fe(CN)$_6^{3-}$)

$$\tau_1^{-1} = k_{1a}(\overline{\text{Co}} + \overline{\text{Fe}}) + k_{-1a} + k_{1b} + k_{-1b} \qquad (12)$$

$$\tau_2^{-1} = \frac{(k_{1b} + k_{-1b})(k_{1a}[\overline{\text{Co}} + \overline{\text{Fe}}]) + k_{-1b}k_{-1a}}{k_{1a}(\overline{\text{Co}} + \overline{\text{Fe}}) + k_{-1a} + k_{1b} + k_{-1b}} \qquad (13)$$

Only one relaxation time (τ_2) is observed since τ_1 is associated with the relaxation of an intermediate in small concentration,[13] namely, [(EDTA)Co^{II}–NC–Fe^{III}(CN)$_5$]$^{5-}$.

Since $k_{-1a} > k_{1a}(\overline{\text{Co}} + \overline{\text{Fe}})$ and $k_{1b} > k_{-1b}$

$$\tau_2^{-1} = \frac{k_{1a}k_{1b}(\overline{\text{Co}} + \overline{\text{Fe}})}{k_{-1a} + k_{1b}} + \frac{k_{-1a}k_{-1b}}{k_{-1a} + k_{1b}} \qquad (14)$$

leading to the observed linearity (Figure 4) of a τ^{-1} vs. ($\overline{\text{Co}} + \overline{\text{Fe}}$) plot, slope k_f and intercept k_r. In the two limiting conditions

$k_{-1a} > k_{1b}$, $k_f = k_{1a}k_{1b}/k_{-1a}$, and $k_r = k_{-1b}$ (a)

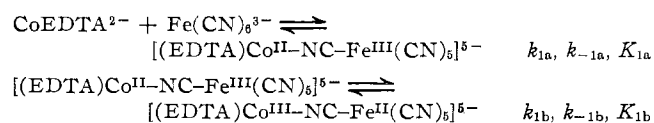$k_{-1a} < k_{1b}$, $k_f = k_{1a}$, and $k_r = k_{-1a}k_{-1b}/k_{1b}$ (b)

Kinetic treatment of the flow data gives similar relations. The agreement between k_f values from flow and

TABLE IV

THERMODYNAMIC AND KINETIC DATA FOR REACTIONS 1 AND 2

Reaction	T, °C	k_1, M^{-1} sec^{-1}	k_{-1}, sec^{-1}	E_1, kcal mole^{-1}	E_{-1}, kcal mole^{-1}	K_1, M^{-1}	ΔH_1, kcal mole^{-1}
1	12	1.2 $\times$ 10^5 [a] 1.3 $\times$ 10^5 [b]	24[a]	$\approx$0[a] or slightly negative[b]	16[a]	5.1 $\times$ 10^3 [a] 5.6 $\times$ 10^3 [b]	-15[a]
	17	1.6 $\times$ 10^5 [a] 1.0 $\times$ 10^5 [b]	39[a]			4.2 $\times$ 10^3 [a] 3.2 $\times$ 10^3 [c]	
	25	1.3 $\times$ 10^5 [a] 0.9 $\times$ 10^5 [b]	86[a]			1.5 $\times$ 10^3 [a] 1.6 $\times$ 10^3 [b] 1.6 $\times$ 10^3 [c]	
		k_2, M^{-1} sec^{-1}	k_{-2}, M^{-1} sec^{-1}			K_2	
2	25	2 $\times$ 10^3 [b]	3 $\times$ 10^4 [b]			0.07[b] 0.06[c]	

[a] Temperature jump.   [b] Stopped flow.   [c] Direct spectrophotometry.

arise. One possible mechanism for the formation of I$_1$ is[7]

CoEDTA^{2-} + Fe(CN)$_6^{3-}$ $\rightleftharpoons$
    [(EDTA)Co^{II}–NC–Fe^{III}(CN)$_5$]$^{5-}$ k_{1a}, k_{-1a}, K_{1a}

[(EDTA)Co^{II}–NC–Fe^{III}(CN)$_5$]$^{5-}$ $\rightleftharpoons$
    [(EDTA)Co^{III}–NC–Fe^{II}(CN)$_5$]$^{5-}$ k_{1b}, k_{-1b}, K_{1b}

For this scheme the two relaxation times are given[13,14]

temperature jump at 25° is good. Condition (a) is thus favored. The value for $k_{1a} \geq 10^5$ M^{-1} sec^{-1} is certainly compatible with the formation of the bridged cyanide complex of cobalt (II). This could occur either by replacement of water from the cobalt(II)–EDTA complex acting as Co(EDTA)(H$_2$O)$^{2-}$[15] or through breakage of a coordinated carboxylate of the EDTA

(13) G. W. Castellan, *Ber. Bunsenges. Physik. Chem.*, **67**, 898 (1963), and private communication.
(14) R. A. Alberty, G. Yagil, W. F. Diven, and M. Takahashi, *Acta Chem. Scand.*, **17**, 534 (1963).

(15) There is some evidence for EDTA acting as a quinquedentate ligand with bivalent metal ions, water completing the octahedron coordination shell; see W. C. E. Higginson, *J. Chem. Soc.*, 2761 (1962).
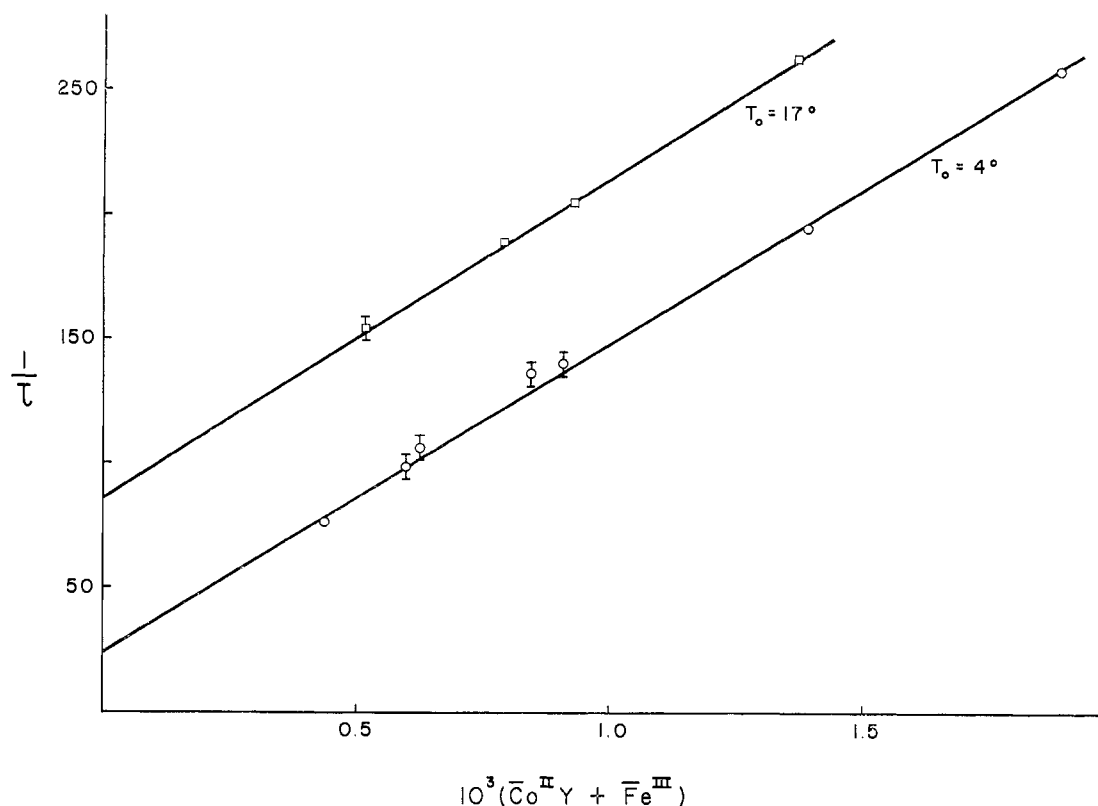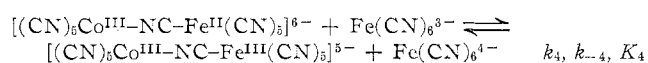
Figure 4.—Final plot of τ^{-1} against 10^3[CoEDTA^{2-} + Fe(CN)$_6{}^{3-}$]$_{\text{equilibrium}}$ for initial temperature-jump temperatures of 4 and 17°.

(less likely perhaps because of the independence of k_f from pH 6 to 4).[16]

The intermediate in (1) could however be an outer-sphere complex between the reactants which then rearranged to a cyanide bridge with concerted intramolecular electron transfer. Certainly a low formation constant would be expected for either type of intermediate in view of the value ($\sim$0.7)[17] for reaction of CoEDTA^{2-} with SCN$^-$. This value would be expected to be much reduced with a trinegative ion.

Formation of I₂.—Kinetic data for reaction 2 are forthcoming only from flow experiments since the process does not show up in the temperature-jump work. The results can be compared with those for an analogous reaction

[(CN)₅Co^{III}–NC–Fe^{II}(CN)₅]$^{6-}$ + Fe(CN)₆$^{3-}$ ⇌
    [(CN)₅Co^{III}–NC–Fe^{III}(CN)₅]$^{5-}$ + Fe(CN)₆$^{4-}$ k_4, k_{-4}, K_4

originally observed by Haim and Wilmarth[18] and since studied in our laboratories[19] in connection with the present work. We find (at 25°, I = 0.1) k_4 = 1.1 × 10^3, k_{-4} = 1.6 × 10^4, and K_4 = 0.07 ($\sim$0.1)[18] interestingly close to the values for k_3 (2 × 10^3), k_{-2} (3 × 10^4), and K_2 (0.07). The rate constants also resemble those[20] for the outer-sphere Fe(CN)₆$^{3-}$ oxidation of Fe-

(CN)₅NH₃$^{3-}$ and Fe(CN)₅P(C₂H₅)₃$^{3-}$, so that the bulkiness of the iron(II) cyanide complex appears to play a small role in the rate process.

The spectral characteristics of (EDTA)Co^{III}–NC–Fe^{II}(CN)₅$^{5-}$ compared with CoEDTA$^-$ and Fe(CN)₆$^{4-}$ have already been alluded to.[7] It is also interesting that the spectrum of (EDTA)Co^{III}–NC–Fe^{III}(CN)₅$^{4-}$ has the salient features of the constituent Co(III) and Fe(III) ions, but is over-all more intense. This situation resembles, for example, that of (H₂O)₅Cr^{III}–O–Np^V–O^{4+} compared with Cr(H₂O)₆$^{3+}$ and NpO₂$^+$ ions.[21]

Conclusions.—We can calculate a rate constant for an *outer-sphere* redox reaction between CoEDTA^{2-} and Fe(CN)₆$^{3-}$ on the basis of theoretical equations.[22] The value $\approx$ 1 M^{-1} sec^{-1} is much lower than that observed for k_f and shows strikingly the rate-accelerating action of an inner-sphere redox process. However, the over-all rate is much slower, dependent as it is on the breakdown of a rather stable cyanide bridge. The reaction of FeEDTA^{2-} with Fe(CN)₆$^{3-}$ is also rapid,[20] with an over-all second-order rate constant $\sim$2 × 10^5 M^{-1} sec^{-1}, but no intermediates were detected and it

(16) The rate constant for the reaction of CoCyDTA^{2-} (CyDTA^{4-} = cyclohexanediaminetetraacetate) with CN$^-$ is 1.6 × 10^6 M^{-1} sec^{-1} at 5°: D. W. Margerum, private communication.

(17) G. Schwarzenbach, *Helv. Chim. Acta*, **32**, 841 (1949).

(18) A. Haim and W. K. Wilmarth, *J. Am. Chem. Soc.*, **83**, 509 (1961).

(19) B. Grossman, unpublished work.

(20) R. Stasiw, unpublished work.

(21) J. C. Sullivan, *J. Am. Chem. Soc.*, **84**, 4257 (1962).

(22) R. A. Marcus, *Ann. Rev. Phys. Chem.*, **15**, 155 (1964). The rate constant for the cross-reaction (K_{12}) under discussion (k_{12}) is related to the isotopic exchange constant for CoEDTA^{2-}–CoEDTA$^-$, k_{11} = 2 × 10^{-7} M^{-1} sec^{-1}, and Fe(CN)₆$^{4-}$–Fe(CN)₆$^{3-}$, k_{22} $\simeq$ 10^5 M^{-1} sec^{-1},[23,24] by the expression k_{12} $\sim$ ($k_{11}k_{22}K_{12}$)$^{1/2}$. Since K_{12} $\sim$ 100^7, k_{12} $\sim$ 1 M^{-1} sec^{-1} at 25°.

(23) A. W. Adamson and K. S. Vorres, *J. Inorg. Nucl. Chem.*, **3**, 206 (1956); Y. A. Im and D. H. Busch, *J. Am. Chem. Soc.*, **83**, 3357 (1961).

(24) M. Shporer, G. Ron, A. Loewenstein, and G. Favon, *Inorg. Chem.*, **4**, 361 (1965), and references therein.

may very well be that an outer-sphere redox reaction is a major contribution here.

The Mechanism of Substitution Reactions of Pentaamminecobalt(III) Complexes. Product Distributions in the Induced Aquation of Some [Co(NH₃)₅X]²⁺ Ions in the Presence of Added Anions

BY D. A. BUCKINGHAM, I. I. OLSEN, A. M. SARGESON, AND H. SATRAPA

The competition ratios of added anions for the proposed intermediate $(NH_3)_5Co^{3+}$ have been measured or remeasured in aqueous solution. The intermediate was generated by the reaction of $(NH_3)_5CoN_3{}^{2+}$ or $(NH_3)_5CoOCONH_2{}^{2+}$ with NO^+ and $(NH_3)_5CoX^{2+}$ (X = Cl, Br, I) with Hg^{2+}; constant competition ratios were observed for each anion Y^- ($Y^- = Cl^-$, Br^-, NO_3^-, HSO_4^-, F^-) despite the fact that the leaving groups were widely different in each reaction. The common competition ratios do not agree, however, with those calculated for the spontaneous anation reaction of $(NH_3)_5CoOH_2{}^{3+}$ with the anions Cl^-, Br^-, and NO_3^- assuming the reaction takes place *via* the $(NH_3)_5Co^{3+}$ intermediate.

Introduction

For the elucidation of the mechanism of substitution reactions at the cobalt atom for cobalt(III) complexes it is important initially to establish the characteristics of two extremes for the process, one where bond making is the important act between substrate and reactant (SN2) leading to a seven-coordinate activated complex or intermediate and the other where bond breaking is important (SN1) and leads to a five-coordinate intermediate. In this paper we are concerned with the work devoted to characterizing the $Co(NH_3)_5{}^{3+}$ intermediate. Two principal methods have been used,[1,2] one by the evaluation of the H_2O^{18}/H_2O^{16} ratio in the common aquopentaammine product when the $[Co(NH_3)_6]^{3+}$ species is generated in water from a variety of sources, the other by competition of species other than H_2O for $Co(NH_3)_5{}^{3+}$. For example, the induced aquation of $[A_5CoX]^{2+}$ complexes by Hg^{2+} ion (A = NH_3; X = Cl, Br, I)

$$A_5CoX^{2+} + Hg_{aq}{}^{2+} \longrightarrow A_5CoOH_2{}^{3+} + HgX_{aq}{}^+ \quad (1)$$

gave a constant fractionation factor for H_2O^{18}/H_2O^{16} in the aquopentaammine products[1] which was interpreted as evidence for a common intermediate since the induced aquation of the halide ions by other metal ions such as Tl^{3+} and Ag^+ gave substantially different O^{18}/O^{16} fractionation factors in the common product from the different halide complexes. Also, Haim and Taube[2] obtained evidence for the same intermediate formed by the reaction of the $A_5CoN_3{}^{2+}$ ion

$$A_5CoN_3{}^{2+} + NO^+ \longrightarrow A_5Co^{3+} + N_2 + N_2O \quad (2)$$
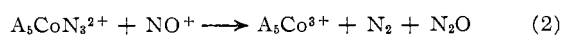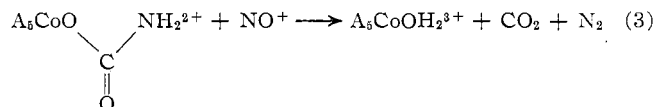
The rate law was of the form

$$R = k[\text{Co}][\text{HNO}_2][\text{H}^+] + k'[\text{Co}][\text{HNO}_2][\text{H}^+][\text{X}]$$
$$(\text{X} = Cl^-, Br^-, SCN^-, NO_3^-, SO_4{}^{2-})$$

and it was suggested that the intermediate $A_5Co-NNNNO^{3+}$ was formed which spontaneously decomposed to A_5Co^{3+} and N_2 and N_2O. Both of the gaseous products are excellent leaving groups conducive to the formation of the reactive cobalt(III) intermediate, which was characterized by allowing it to compete for other anions and solvent water molecules. The term in the rate law which is dependent on the anion concentration leads to an enhancement in the rate with an increase in $[X^-]$ but does not lead to a parallel increase in the formation of A_5CoX^{2+} as compared with $A_5CoOH_2{}^{3+}$. The product distributions for various anions were compared with the distributions expected if the direct anation reactions proceed *via* the same pentacoordinated intermediate and were found to agree. However, a later experiment by Pearson and Moore[3] showed that the nitrosation of the azido complex and the spontaneous aquation of the $A_5CoNO_3{}^+$ ion do not proceed by the same intermediate since the latter reaction gives first the aquo complex which then anates, so the apparent agreement is fortuitous.

More recently the carbamatopentaamminecobalt(III) ion was shown to react with NO^+ (eq 3) to give

$$A_5Co\overset{\displaystyle O}{\underset{\displaystyle \parallel}{\overset{\diagdown}{\underset{\diagup}{C}}}}NH_2{}^{2+} + NO^+ \longrightarrow A_5CoOH_2{}^{3+} + CO_2 + N_2 \quad (3)$$

80% Co–O bond rupture, and in this instance the leaving group is either CO_2 or $\overset{O}{\underset{O}{>}}CN{=}N$, both poor

(1) F. A. Posey and H. Taube, *J. Am. Chem. Soc.*, **79**, 255 (1957).
(2) A. Haim and H. Taube, *Inorg. Chem.*, **2**, 1199 (1963).
(3) R. G. Pearson and J. W. Moore, *ibid.*, **3**, 1334 (1964).