378. *Kinetic Studies of Oxidation–Reduction of Cobalt–Ethylenediaminetetra-acetic Acid Complexes. Part III.*[1] *The Reduction of Ethylenediaminetetra-acetatocobaltate*(III) *and Related Complexes by Ferrous Ion*

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The kinetics of oxidation of ferrous ion by various complexes of cobalt(III) with ethylenediaminetetra-acetic acid (edta) and hydroxyethylethylenediaminetriacetic acid (heta) have been studied in aqueous solution. The overall reaction occurs in two stages of which the first is formally an electron transfer giving the cobalt(II) complex and ferric ion. Except at high concentrations of hydrogen ion, the second stage is the reaction of these intermediate products to give cobaltous ion and the corresponding iron(III) complex. The rate of the overall reaction of the heta complexes is determined solely by the first stage, but the kinetics of the reaction of the edta complexes are more complicated. By comparing the reactivities of the various complexes in the first stage of the reaction, it is concluded that an inner-sphere type of mechanism is involved. The anomalous reactivity of the complex (ethylenediaminetriacetatoacetate)aquocobaltate(III) is interpreted as indicating the presence in solution in equilibrium with this complex of a small proportion of its isomer, hydroxo(ethylenediaminetriacetatoacetic acid)cobaltate(III), which is a much more active oxidant of the ferrous ion. Brief reference is made to erroneous conclusions reached earlier concerning the cobalt(III)-heta system.

We describe in this Paper a kinetic study of the oxidation of ferrous ion in aqueous solution by various edta and heta complexes of cobalt(III). [edta = H_4Y = ethylenediamine-NNN′N′-tetra-acetic acid; heta = H_3YOH = *N*-hydroxyethylethylenediamine-NN′N′-triacetic acid.] This work follows an investigation [2] of the oxidation of ferrous ion by the edta complex $Co(HY)Cl^-$ and its conjugate base $Co(Y)Cl^{2-}$.* During experiments with the heta-cobalt(III) system we found evidence for the existence of several different species and the relationships between them have already been discussed.[3] However, further work has now shown that these earlier conclusions about the existence of sexidentate heta complexes in geometrical isomeric forms are false. In consequence, we shall not deal in the present Paper with the reduction of heta complexes other than the aquoquinquedentate complex; our work with the latter appears to be unobjectionable. We defer the correction of our earlier Paper on the cobalt(III)-heta system until our new investigation has been completed, since at present we cannot give a complete account of the behaviour of this system. We now describe the kinetic behaviour of the individual complexes, concluding with a comparison of their reactivity. Reactions were followed by determining the concentration of the cobalt(III) complex spectrophotometrically, ferrous ion being in large excess. The medium was a mixture of dilute sodium and hydrogen perchlorates; except where stated otherwise, the ionic strength was 1·0M.

The Reaction between $Co(Y)^-$ *and Ferrous Ion.*—In preliminary experiments, the reduction of the sexidentate edta complex $Co(Y)^-$ by a large excess of ferrous ion was investigated at various hydrogen-ion concentrations between 0·1 and 3·0M in solutions of ionic strength *ca.* 3·2M. The reaction was of first order in the complex and at a given concentration of ferrous ion the velocity constant $k_{obs.} = -d \ln [Co(Y)^-]/dt$ increased linearly

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* Here and elsewhere in this Paper we have not indicated the oxidation state of cobalt(III) complexes by the use of a superscript III in their formulæ, but to avoid confusion we shall use a superscript II in the formulæ of all cobalt(II) complexes. Thus, for example, $Co(Y)H_2O^-$ refers to a cobalt(III) complex, $Co^{II}(Y)H_2O^{2-}$ to a cobalt(II) complex.

[1] Part II, Dyke and Higginson, *J.*, 1963, 2802.
[2] Pidcock and Higginson, *J.*, 1963, 2798.
[3] Wood and Higginson, *J.*, 1964, 1484.

with the hydrogen-ion concentration. At 25·0° with 0·050M-Fe^{2+} and *ca.* 2 × 10^{-3}M-$Co(Y)^-$ values of $10^4k_{obs.}$ were 8, 16, 36, and 110 $min.^{-1}$ at hydrogen-ion concentrations of 0·10, 0·30, 1·00, and 3·00M, respectively. The products of the reaction were cobaltous ion, ferric ion, and edta for hydrogen-ion concentrations above 1·0M, while at 0·10M-hydrogen ion the iron(III) was mainly in the form of its edta complex. Between 0·10 and 1·0M-hydrogen ion, the final solution contained appreciable amounts of both ferric ion and its edta complex. This change of product was evidently not connected with the change in $k_{obs.}$, for the latter showed the same dependence upon hydrogen-ion concentration in the region 0·10 to 1·0M as in the region 1·0 to 3·0M-hydrogen ion in which there was no change in products. We found that the increase in $k_{obs.}$ with hydrogen-ion concentration was mainly due to a side-reaction in which $Co(Y)^-$ reacts with hydrogen ions [4] to give $Co(HY)H_2O$ which then oxidises ferrous ion more rapidly than $Co(Y)^-$ itself. To make the contribution of this side-reaction small, we kept the hydrogen-ion concentration below 0·1M in experiments following the preliminary ones and thus it was possible to reduce the ionic strength to 1·0M in conformity with previous work.[2] Under these new conditions we showed that the rate of reaction was unaffected by the presence at the beginning of the reaction of ferric ions or the cobalt(II)-edta complex, both in concentrations similar to the initial $Co(Y)^-$ concentration, *ca.* 2 × 10^{-3}M. Also, the rate of reaction was not affected by the presence of 0·02M-chloride ion.

The experiments at ionic strength 1·0M showed that at the lower hydrogen-ion concentrations a second factor was contributing to the dependence of $k_{obs.}$ upon hydrogen-ion concentration. This effect arises from the occurrence of the overall reaction in two stages. The first is an oxidation-reduction giving ferric ion and a cobalt(II)-edta complex, and may occur directly or through $Co(HY)H_2O$. The cobalt(II)-edta complex is probably a quinquedentate monoaquo-complex [5] and we represent it by $Co^{II}(hY)H_2O$, the use of the small letter h in this formula implying a mixture of $Co^{II}(HY)H_2O^-$ and $Co^{II}(Y)H_2O^{2-}$ in proportions determined by the hydrogen-ion concentration of the solution through the equilibrium $Co^{II}(HY)H_2O^- \rightleftharpoons H^+ + Co^{II}(Y)H_2O^{2-}$. In solutions of hydrogen-ion concentration 0·2M or less, the second stage is the reaction of the $Co^{II}(hY)H_2O$ and ferric ion formed in the first stage to give cobaltous ion and $Fe^{III}(hY)H_2O$, the small letter h in the latter formula having the significance defined above. Owing to the instability of $Fe^{III}(hY)H_2O$ in solutions of hydrogen-ion concentration exceeding 1·0M, the second stage in such solutions is the displacement of cobaltous ion from its edta complex by hydrogen ions. Calculations based on established stability constants [6] and oxidation-reduction potentials [7] show that for solutions of low ionic strength a small positive change in free energy accompanies the first stage, $Co(Y)^- + Fe^{2+} \longrightarrow Co^{II}(hY)H_2O + Fe^{3+}$, and this also appears to be true under our experimental conditions. However, the free-energy change of the overall reaction, $Co(Y)^- + Fe^{2+} \longrightarrow Co^{2+} + Fe^{III}(hY)H_2O$, is sufficiently negative that $Co(Y)^-$ is quantitatively reduced by ferrous ion. Thus, the intermediates, $Co^{II}(hY)H_2O$ and ferric ion, can react in two ways by reactions which involve negative changes in free energy, giving either the products, cobaltous ion and $Fe^{III}(hY)H_2O$, or the reactants, $Co(Y)^-$ and ferrous ion. The extent of the competition between these two reactions will influence the rate of the overall reaction; only if the rate of formation of products greatly exceeds the rate of re-formation of reactants will the overall rate equal that of the first stage.

The importance of this competition was demonstrated by the following experiments. We mixed rapidly solutions of *ca.* 2 × 10^{-3}M-ferric perchlorate and *ca.* 2 × 10^{-3}M-$Co^{II}(hY)H_2O$ and investigated the products of the reaction. The ionic strength was 1·0M and the range of hydrogen-ion concentrations employed was 10^{-3} to 10^{-2}M. At higher

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[4] Dyke and Higginson, *J.*, 1960, 1998.

[5] Higginson, *J.*, 1962, 2761.

[6] "Stability Constants," *Chem. Soc. Special Publ.* No. 6, 1957, p. 76.

[7] Latimer, "Oxidation Potentials," 2nd edn., Prentice-Hall Inc., New York, 1952, pp. 213, 223.

hydrogen-ion concentrations than 10^{-2}M more than 5% of the total cobalt(II) is in the form of cobaltous ion, while below 10^{-3}M the proportion of dimeric iron(III) is appreciable and precipitation of iron(III) hydroxide tended to occur. The reaction was carried out at *ca.* 20° with solutions of the two reactants adjusted to the same pH before mixing. The optical density of the solution at several wavelengths was found after various intervals of time had elapsed from the time of mixing. These measurements showed that the main reaction was substantially complete within 2 min. after mixing, although small changes in optical density occurred for a few hours, indicating a slow subsidiary reaction. This was found to be the decomposition of $Co(hY)H_2O$, a minor product of the reaction, to $Co(Y)^-$. The main forms in which cobalt appeared were $Co(Y)^-$ and cobaltous ion. The proportion of cobalt(III) formed was increased with increase in pH; at pH 2·08 *ca.* 40% of the $Co^{II}(hY)H_2O$ was oxidised, at pH 2·66 *ca.* 75%. About 70% of this cobalt(III) appeared as $Co(Y)^-$, the rest being $Co(hY)H_2O$; the proportion of $Co(Y)^-$ increased slightly with increase in pH. Thus, these experiments showed that in solutions of pH exceeding 2 the reverse of the first stage of the reaction competes strongly with the second stage. Below pH 2 very little oxidation of $Co^{II}(hY)H_2O$ by ferric ion occurs; this is partly due to the instability of this complex in such solutions. When these experiments were repeated with *ca.* 2 × 10^{-3}M-ferrous ion present, *i.e.*, under conditions more similar to those of the kinetic experiments, the proportion of cobalt(III) appearing in the form of $Co(hY)H_2O$ was greatly reduced. Taking these observations into account, we can write the full kinetic scheme:

$$Co(Y)^- + Fe^{2+} \xrightleftharpoons[k_{-1}]{k_1} Co^{II}(hY)H_2O + Fe^{III} \qquad (1), (-1)$$

$$Co(Y)^- \xrightleftharpoons[k_b]{k_f} Co(hY)H_2O \qquad (f), (b)$$

$$Co(hY)H_2O + Fe^{2+} \xrightleftharpoons[k_{-2}]{k_2} Co^{II}(hY)H_2O + Fe^{III} \qquad (2), (-2)$$

$$Co^{II}(hY)H_2O + Fe^{III} \xrightarrow{k_3} Co^{2+} + Fe^{III}(hY)H_2O \qquad (3)$$

Here, Fe^{III} refers to Fe^{3+} and its partial hydrolysis products. From this scheme we have obtained the following kinetic equation:

$$\begin{aligned} k_{obs.} &= \{k_1[Fe^{2+}] + k_f k_2[Fe^{2+}]/(k_b + k_2[Fe^{2+}])\}k_3 \div (k_{-1} + k_3) \\ &= \{k_1[Fe^{2+}] + C\}k_3 \div (k_{-1} + k_3) \qquad (4) \end{aligned}$$

where $k_{obs.} = -d \ln [Co(Y)^-]/dt$, the other velocity constants refer to the correspondingly-numbered reactions in the scheme given above, and $C = k_f k_2[Fe^{2+}]/(k_b + k_2[Fe^{2+}])$.

Various assumptions have been made in deriving equation (4). By making the stationary-state assumptions $d[Co^{II}(hY)H_2O]/dt = 0$ and $d[Co(hY)H_2O]/dt = 0$, and taking into account all the reactions given in the kinetic scheme, we obtained equation (5); equation (4) is the special case of equation (5) with $k_{-2} = 0$.

$$k_{obs.} = \{k_1[Fe^{2+}] + D\}k_3 \div (k_{-1} + k_{-2} + k_3) \qquad (5)$$

where
$$D = \frac{k_2 k_f(k_{-1} + k_{-2} + k_3)[Fe^{2+}] + k_1 k_2 k_{-2}[Fe^{2+}]^2}{(k_b + k_2[Fe^{2+}])(k_{-1} + k_{-2} + k_3) - k_2 k_{-2}[Fe^{2+}]}$$

We used equation (4) to obtain k_1 and k_{-1}/k_3 from several experimental values of $k_{obs.}$; appropriate values of k_f and k_b were already known. Then, by means of equation (5), we calculated $k_{obs.}$ using these values of k_1 and k_{-1}/k_3, the corresponding values of k_f and k_b, and arbitrarily-chosen values of k_{-2}/k_3. We knew, from the experiments in which solutions of $Co^{II}(hY)H_2O$ and ferric ion were mixed, that k_{-1}/k_3 exceeds k_{-2}/k_3 since more $Co(Y)^-$ than $Co(hY)H_2O$ was formed, but in these calculations values of k_{-2}/k_3 up to twice that of k_{-1}/k_3 were chosen. In all cases we found that the value of $k_{obs.}$ calculated with a finite value of k_{-2}/k_3 did not differ significantly from that obtained by assuming that $k_{-2} = 0$. This justified our use of the simpler equation (4) rather than equation (5). Of the stationary-state assumptions, we can justify $d[Co^{II}(hY)H_2O]/dt = 0$ by comparing the rate of formation of $Co^{II}(hY)H_2O$ and ferric ion from the initial reactants with the relatively rapid rate of their disappearance; we calculate that the stationary concentration of $Co^{II}(hY)H_2O$ is less than 0·1% of the $Co(Y)^-$ concentration. The similar assumption $d[Co(hY)H_2O]/dt = 0$ can in principle be checked by the spectrophotometric determination of the concentration of $Co(hY)H_2O$ during kinetic experiments. We were unable to detect this complex, but we estimate that it must be present in at least 5% of the concentration of $Co(Y)^-$ before its presence can be established. Accordingly we compared the rate constants for the reactions leading to the formation of $Co(hY)H_2O$ with those leading to its disappearance and calculated that the ratio $[Co(hY)H_2O]/[Co(Y)^-]$ did not exceed *ca.* 0·01 in our experiments.

The various rate constants required for this comparison, and in using equations (4) and (5), were obtained in the following manner. Both k_f and k_b are composite constants; $k_f = k_f'[H^+] + k_f''$ where k_f' and k_f'' relate to the formation from $Co(Y)^-$ of $Co(HY)H_2O$ and $Co(Y)H_2O^-$, respectively, while $k_b = \{[H^+]/([H^+] + K_1)\}k_b' + \{K_1/([H^+] + K_1)\}k_b''$ where k_b' and k_b'' relate to the formation of $Co(Y)^-$ from $Co(HY)H_2O$ and $Co(Y)H_2O^-$, respectively. The terms in parentheses indicate the proportions of $Co(hY)H_2O$ in the acid and base forms, respectively, K_1 being the acid dissociation constant of $Co(HY)H_2O$. Values of k_f' and k_b' have been found previously,[4] and we have measured k_b'' under the conditions of temperature and ionic strength of our oxidation-reduction experiments by performing experiments similar to those described previously.[8] These experiments, conducted over the range pH 1—5, also enabled us to obtain K_1 from the dependence of k_b upon hydrogen-ion concentration. Values of k_f'' were calculated by using the relation $k_f'' = k_b''K_b = k_b''K_aK_1$, where $K_a = [Co(HY)H_2O]/[H^+][Co(Y)^-]$, and $K_b = [Co(Y)H_2O^-]/[Co(Y)^-]$; K_a is known under conditions similar to those of our experiments,[4] and k_b'' and K_1 were found as indicated above. The constant k_2 has been found in the manner described in the second part of this Paper, and a calculation based on the stability constants[6] for $Co(Y)^-$ and $Co^{II}(Y)H_2O^{2-}$, the oxidation-reduction potentials[7] for the couples $e^- + Co^{3+}/Co^{2+}$ and $e^- + Fe^{3+}/Fe^{2+}$, together with the value of K_b, has enabled us to show that k_{-2} is approximately one-third of k_2. The constant k_{-2} was not required accurately since it was used only in deciding whether the approximation $d[Co(hY)H_2O]/dt = 0$ is valid.

We used the following method in obtaining values of k_1 from our experimental results. First we calculated values of C [see equation (4)] appropriate to the particular hydrogen-ion concentration for a set of experiments at a given temperature. Since $k_2[Fe^{2+}]$ was found to be much larger than k_b, the values of C are similar to corresponding values of k_f, as reference to Table 1 shows. Although k_f and hence C varies with hydrogen-ion concentration, inspection showed that the changes in $k_{obs.}$ could not be ascribed to this variation alone, and hence that one or more of the constants k_1, k_{-1}, and k_3 must also vary with hydrogen-ion concentration. Several assumptions were made and the simplest which accords with our results is that k_1 is independent of the hydrogen-ion concentration while the ratio k_{-1}/k_3 varies inversely as the hydrogen-ion concentration. Equation (4) can therefore be written in the form

$$(k_{obs.} - C)/[Fe^{2+}] = k_1 - (k_{obs.}/[H^+][Fe^{2+}])E \qquad (6)$$

where $k_{-1}/k_3 = E/[H^+]$, E being a constant independent of the hydrogen-ion concentration. We obtained k_1 and E by plotting the left-hand side of equation (6) against $(k_{obs.}/[H^+][Fe^{2+}])$. From an Arrhenius plot we found $\log k_1 = (7{\cdot}21 \pm 1{\cdot}10) - (11{,}800 \pm 1500)/2{\cdot}303RT$, whence the activation entropy was found to be $\Delta S^‡_1 = -36 \pm 5$ cal. mole^{-1} deg.$^{-1}$. The values of k_1 quoted in Table 1 were obtained by using the mean values of these activation

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[8] Shimi and Higginson, *J.*, 1958, 260.

TABLE 1

$10^2[H^+]$ (M)	10^4k_f (min.$^{-1}$)	10^4C (min.$^{-1}$)	$10^3k_{calc.}$ (min.$^{-1}$)	$10^3k_{obs.}$ (min.$^{-1}$)
		At 20·0°		
4·60	5·4	4·7	1·81	1·83
3·60	4·5	3·8	1·70	1·72
2·60	3·6	3·1	1·59	1·61
1·60	2·9	2·5	1·46	1·47
0·80	1·9	1·8	1·22	1·25
0·40	1·6	1·5	0·97	0·98
k_1 = 0·0258 l. mole^{-1} min.$^{-1}$, E = 0·0026 mole l.$^{-1}$.				
		At 25·0°		
4·60	10·8	8·4	2·75	2·70
3·60	9·0	7·1	2·59	2·58
2·60	7·2	5·8	2·42	2·34
1·60	5·4	4·5	2·21	2·18
1·26	4·8	4·1	2·13	2·10 *
0·40	3·2	3·1	1·60	1·57 *
k_1 = 0·0362 l. mole^{-1} min.$^{-1}$, E = 0·0019 mole l.$^{-1}$.				
		At 30·0°		
4·60	20·2	15·8	4·27	4·29
3·60	17·0	13·6	4·02	4·06
2·60	13·4	10·7	3·68	3·77
1·80	10·7	9·8	3·52	3·54
0·80	7·3	6·8	3·00	3·04 *
k_1 = 0·0504 l. mole^{-1} min.$^{-1}$, E = 0·0014 mole l.$^{-1}$.				

* $[Fe^{2+}]$ = 0·0564M (0·0558M in all other experiments).

parameters. As well as the experimental values of $k_{obs.}$, Table 1 also contains values ($k_{calc.}$) of the same constant calculated by substituting the values of k_1, C, and E given in the Table into equation (7), which is equation (4) incorporating E instead of k_{-1} and k_3.

$$k_{calc.} = \{k_1[Fe^{2+}] + C\} \div (1 + E/[H^+]) \qquad (7)$$

Since k_1 is independent of hydrogen-ion concentration, then m, the velocity constant for the related reaction $Co^{II}(Y)H_2O^{2-} + Fe^{3+} \longrightarrow Co(Y)^- + Fe^{2+}$, must also be independent of hydrogen-ion concentration. By assuming that $Co^{II}(HY)H_2O^-$ is oxidised much more slowly than its conjugate base by ferric ion, we may deduce $k_{-1} = \{K_1/([H^+] + K_1)\}m$. It has been found [9] that $Co^{II}(HY)H_2O^-$ reacts very much faster than $Co^{II}(Y)H_2O^{2-}$ with Pb^{2+} to give $Pb(hY)H_2O$ and cobaltous ion. If we make a similar assumption about the reaction of these cobalt(II)–edta complexes with ferric ion to give $Fe^{III}(hY)H_2O$ and cobaltous ion, then $k_3 = \{[H^+]/([H^+] + K_1)\}n$ where n is the velocity constant for the reaction $Co^{II}(HY)H_2O^- + Fe^{3+} \longrightarrow Co^{2+} + Fe^{III}(hY)H_2O$. By combining these equations, which express k_{-1} and k_3 in terms of the hydrogen-ion concentration and constants which are independent of this concentration, we obtain equation (8)

$$k_{-1}/k_3 = (mK_1/n)/[H^+] = E/[H^+] \qquad (8)$$

which is in accordance with our experimental results. It seems probable that for both reactions (—1) and (3) the reactive form of iron(III) is the ferric ion, although for this interpretation to hold it is necessary only that the reactive form should be the same for both reactions. The presence of iron(III) in partly-hydrolysed, unreactive forms in addition to ferric ion does not affect the validity of equations (4)—(8).

The Reaction between $Co(hY)H_2O$ *and Ferrous Ion.*—In this system the same reactions must be taken into account as in the previous section. Owing to the formation of $Co(Y)^-$ by reaction (*b*) and the relatively slow rate of disappearance of this complex by reactions (1) and (*f*), it is formed as a by-product. Consequently we did not prepare solutions of $Co(hY)H_2O$ free from $Co(Y)^-$ by dissolving in dilute acid the solid $Na_2Co(Y)OH,3H_2O$ as

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[9] Tanaka, Osawa, and Kamada, *Bull. Chem. Soc. Japan*, 1963, **36**, 67.

in previous work,[8] since this material is difficult to prepare and is of low stability. Instead, a solution of the solid $NaCo(Y),4H_2O$ in 4M-perchloric acid was allowed to reach equilibrium through reactions (*f*) and (*b*) when the proportion of cobalt(III) in the form of $Co(HY)H_2O$ was found to be *ca.* 85%. Such a solution was used as the source of $Co(hY)H_2O$ in all experiments, the concentration of cobalt(III) being *ca.* 2×10^{-3}M in the reaction solutions. The range of hydrogen-ion concentrations was 0·03—0·20M; the reaction became inconveniently rapid at hydrogen-ion concentrations below this range, while above 0·20M considerable salt effects are likely, judging by the behaviour of the analogous system, Co(hY)Cl-ferrous ion.[2] In preliminary experiments, although the ionic strength was kept at 1·0M by the addition of sodium perchlorate, we observed a salt effect when the concentration of ferrous ion was changed. This effect was suppressed in all subsequent experiments by keeping the concentration of bivalent cations constant (0·084M) by the addition of zinc perchlorate when necessary; sodium perchlorate was used as before to maintain an ionic strength of 1·0M.

By taking spectrophotometric measurements at two wavelengths during a kinetic experiment we were able to find the concentrations of $Co(HY)H_2O$ and of $Co(Y)^-$ at any time during an experiment. The concentration of the latter rose with time from its initial value of *ca.* 15% of the initial cobalt(III) concentration to a flat maximum value of 25 to 40% and then fell off slowly. The concentration of $Co(hY)H_2O$ decreased approximately according to a first-order law and became equal to that of $Co(Y)^-$ after about half the time necessary for the latter to attain its maximum concentration. Now, we can write

$$-d[Co(hY)H_2O]/dt = k_2[Fe^{2+}][Co(hY)H_2O] + k_b[Co(hY)H_2O] - k_f[Co(Y)^-]$$

a term in k_{-2} being unnecessary since we have found that reaction (—2) is unimportant in solutions of hydrogen-ion concentration 0·03M or more. This equation can be rearranged to give

$$k'_{obs.} = -d \ln [Co(hY)H_2O]/dt = k_2[Fe^{2+}] + k_b - k_f[Co(Y)^-]/[Co(hY)H_2O] \qquad (9)$$

If the term in k_f is sufficiently small and ferrous ion is present in large excess over $Co(hY)H_2O$ then the disappearance of the latter should follow a first-order law. We obtained good first-order plots for the first half of the reaction; under these conditions the term in k_f did not exceed *ca.* 10% of $k_2[Fe^{2+}]$. In a set of experiments at the same hydrogen-ion concentration and temperature, but with three different concentrations of ferrous ion, the contribution of the term in k_f to $k'_{obs.}$ is approximately constant, provided the values of $k'_{obs.}$ are obtained from plots covering the same proportion of the reaction. Consequently a plot of $k'_{obs.}$ against ferrous concentration enables good values of k_2 to be obtained as the gradient, while the intercept differs from k_b by the mean contribution of the term in k_f to $k'_{obs.}$. We estimate that the errors in values of k_2 due to this approximate method of making allowance for the term in k_f do not exceed 2—3% of k_2.

At a given temperature the values of k_2 obtained in the above manner were found to increase with decrease in the hydrogen-ion concentration. We interpret this by suggesting that $Co(Y)H_2O^-$ reacts more rapidly than $Co(HY)H_2O$ with ferrous ion, in which case we can write

$$\begin{aligned} k_2 &= \{[H^+]/([H^+] + K_1)\}k_{2a} + \{K_1/([H^+] + K_1)\}k_{2b} \\ &= k_{2a} + \{K_1/([H^+] + K_1)\}(k_{2b} - k_{2a}) \qquad (10) \end{aligned}$$

where k_{2a} and k_{2b} are the velocity constants for the reduction by ferrous ion of $Co(HY)H_2O$ and $Co(Y)H_2O^-$, respectively. We had previously found values of K_1 at various temperatures (see p. 2119), $pK_1 = 3{\cdot}09 + (T - 25)0{\cdot}002 \pm 0{\cdot}05$, where T is the temperature from 5 to 30°, and so we were able to plot values of k_2 against the corresponding values of the term in parentheses in equation (10). At each temperature the plots were linear, confirming our interpretation and enabling us to find k_{2a} and k_{2b}. The values of these two constants are included in Table 2, together with the values of $k_{obs.}$ from which they are

TABLE 2

$[H^+]$(M)	$10^2k'_{obs.}$ (min.$^{-1}$)		
	At 5·6°		
0·030	0·89	1·73	2·64
0·050	0·77	1·43	1·90
0·075	0·68	1·21	1·76
0·115	0·57	1·08	1·59
0·180	0·56	1·02	1·49
($10^2[Fe^{2+}]$ =	2·83M	5·66M	8·49M)

k_{2a} = 0·138 l. mole^{-1} min.$^{-1}$;
k_{2b} = 4·43 l. mole^{-1} min.$^{-1}$

$[H^+]$(M)	$10^2k'_{obs.}$ (min.$^{-1}$)		
	At 10·0°		
0·032	1·46	2·50	4·00
0·052	1·10	2·05	3·09
0·077	1·00	1·87	2·98
0·117	0·93	1·55	2·39
0·182	0·78	1·52	2·28
($10^2[Fe^{2+}]$ =	2·79M	5·58M	8·37M)

k_{2a} = 0·217 l. mole^{-1} min.^{1};
k_{2b} = 7·9 l. mole^{-1} min.$^{-1}$

$[H^+]$(M)	$10^2k'_{obs.}$ (min.$^{-1}$)		
	At 20·0°		
0·032	4·23	7·0	11·0
0·052	3·15	6·1	8·2
0·077	3·25	5·2	7·4
0·117	2·47	4·4	6·4
0·182	2·36	3·9	5·3
($10^2[Fe^{2+}]$ =	2·80M	5·60M	8·40M)

k_{2a} = 0·390 l. mole^{-1} min.$^{-1}$;
k_{2b} = 34·3 l. mole^{-1} min.$^{-1}$

$[H^+]$(M)	$10^2k'_{obs.}$ (min.$^{-1}$)		
	At 25·0°		
0·042	6·8	10·7	15·0
0·072	5·0	8·6	10·2
0·115	4·3	6·7	8·8
0·197	3·8	5·9	7·9
($10^2[Fe^{2+}]$ =	2·87M	5·74M	8·61M)

k_{2a} = 0·510 l. mole^{-1} min.$^{-1}$;
k_{2b} = 54 l. mole^{-1} min.$^{-1}$

derived. From Arrhenius plots for k_{2a} and k_{2b} we obtained the following activation energies and entropies:

$$E^{\ddagger}_{2a} = 11{\cdot}1 \pm 0{\cdot}9,\ E^{\ddagger}_{2b} = 22{\cdot}1 \pm 1{\cdot}7 \text{ kcal. mole}^{-1};$$
$$\Delta S^{\ddagger}_{2a} = -33 \pm 3,\ \Delta S^{\ddagger}_{2b} = +27 \pm 6 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$$

The Reaction between Co(YOH)H_2O *and Ferrous Ion*.—The quinquedentate monoaquo-complex beteen heta and cobalt(III), Co(YOH)H_2O, showed relatively simple behaviour in its reaction with ferrous ion. As with the quinquedentate edta complexes, reaction must occur in two stages,

$$\text{Co(YOH)H}_2\text{O} + \text{Fe}^{2+} \longrightarrow \text{Co}^{\text{II}}\text{(YOH)H}_2\text{O} + \text{Fe}^{3+} \longrightarrow \text{Co}^{2+} + \text{Fe}^{\text{III}}\text{(YOH)H}_2\text{O}$$

but reversal of the initial stage and side-reactions leading to the formation of a sexidentate cobalt(III) complex are unimportant under our experimental conditions. Linear first-order plots for the disappearance of Co(YOH)H_2O were obtained in the presence of a sufficient excess of ferrous ion.

Values of $k_4 = -\{\text{d ln [Co(YOH)H}_2\text{O]}/\text{d}t\}/[\text{Fe}^{2+}]$ obtained under various conditions are

TABLE 3

$[H^+]$ (M)	k_4 †	$[H^+]$ (M)	k_4 †	$[H^+]$ (M)	k_4 †	$[H^+]$ (M)	k_4 †
At 20·0°		At 25·0°		At 30·0°		At 35·0°	
0·206	0·214	0·208	0·316	0·208	0·49	0·108	0·81
0·106	0·230	0·108	0·352	0·108	0·55	0·048	1·07
0·056	0·282	0·068	0·394	0·058	0·65	0·028	1·43
0·036	0·342	0·048	0·455	0·038	0·76		
0·026	0·412	0·038	0·50	0·028	0·94		
		0·028	0·57				

k_{4a} †	0·182	0·277	0·411	0·604
$10^3K_4k_{4b}$ *	5·5	9·0	14·3	22·6

$[Fe^{2+}]$ ~0·060M; [Co(YOH)H_2O] ~2·0 × 10^{-3}M.
* = min.$^{-1}$. † = l. mole^{-1} min.$^{-1}$.

shown in Table 3. The rate constant, k_4, shows a linear dependence upon the inverse of the hydrogen-ion concentration, which we interpret by assuming that Co(YOH)H_2O, the dominant form, is reduced much more slowly than its conjugate base, Co(YOH)OH^-. If

k_{4a} and k_{4b} are the second-order velocity constants for the reduction by ferrous ion of the acidic and basic forms, respectively, then by analogy with equation (10)

$$k_4 = k_{4a} + \{K_4/([H^+] + K_4)\}(k_{4b} - k_{4a}),$$

where K_4 is the acid dissociation constant of Co(YOH)H_2O. In this case, k_{4b} greatly exceeds k_{4a} and the lowest hydrogen-ion concentration employed greatly exceeds K_4. Consequently, the above equation becomes

$$k_4 = k_{4a} + K_4k_{4b}/[H^+] \qquad (11)$$

Our results fit this equation fairly well, and we include in Table 3 the values of k_{4a} and K_4k_{4b} which hold at the various temperatures employed. Values of K_4 needed to evaluate k_{4b} were obtained by measuring spectrophotometrically the ratio of the concentrations of Co(YOH)H_2O and its conjugate base at various pH values in buffered solutions of ionic strength 1·0M. We found $pK_4 = 8{\cdot}22 + (25 - T)0{\cdot}008 \pm 0{\cdot}03$ where T is the temperature from 20 to 35°. From Arrhenius plots for k_{4a} and k_{4b} we obtained $E^{\ddagger}_{4a} = 14{\cdot}2 \pm 0{\cdot}4$, $E^{\ddagger}_{4b} = 13{\cdot}7 \pm 1{\cdot}6$ kcal. mole^{-1}; $\Delta S^{\ddagger}_{4a} = -23{\cdot}5 \pm 1{\cdot}4$, $\Delta S^{\ddagger}_{4b} = +6 \pm 5$ cal. deg.$^{-1}$ mole^{-1}.

These kinetic experiments were conducted at hydrogen-ion concentrations from 0·03 to 0·2M, a similar range to that used in the experiments with Co(Y)H_2O^-. With the latter complex we did not take into account a route of reaction through the conjugate base Co(Y)OH^{2-}, although it must be present in the same proportion relative to Co(Y)H_2O^- as is Co(YOH)OH^- relative to Co(YOH)H_2O, since the acid dissociation constants of the two acid forms are very similar.[3] [The free carboxylate group in Co(Y)OH^{2-} is unlikely to lead to a reactivity very different from that of Co(YOH)OH^-; the situation is akin to that of Co(Y)Cl^{2-} and Co(HY)Cl^- which react with ferrous ion at very similar rates.[2]] The reason for neglecting Co(Y)OH^{2-} is that the rate constant for the reduction of Co(Y)H_2O^- is *ca.* 200 times greater than that for Co(YOH)H_2O and so at a given hydrogen-ion concentration the conjugate base will contribute proportionately less to the rate observed for the edta complex compared with that for the heta complex. Under our experimental conditions the contribution of Co(Y)OH^{2-} to the rate of reduction of Co(hY)H_2O by ferrous ion is negligible. These comparisons draw attention to the surprising difference between the rate constants for the reactions of Co(YOH)H_2O and Co(Y)H_2O^- with ferrous ion; we shall discuss this later.

Catalysis by hydrogen ion of the reduction of various polycarboxylatocobalt(III) complexes by chromous ion has been reported,[10] and it seemed possible that such catalysis might occur in the reduction by ferrous ion of edta and heta complexes of cobalt(III). An apparent catalysis by hydrogen ion of the reaction between Co(HY)Cl^- and ferrous ion was shown to be a salt effect,[2] but this system cannot be regarded as typical since it probably involves an inner-sphere transition complex with chlorine as the bridging atom. Owing to their complexity, a direct catalysis by hydrogen ion of the reductions of Co(Y)$^-$ and Co(hY)H_2O would be difficult to demonstrate, unless the effect were particularly marked, since these reactions show a pronounced dependence upon hydrogen-ion concentration for other reasons. On account of the simplicity of the reaction between Co(YOH)H_2O and ferrous ion we used it to find if this type of system is subject to catalysis by hydrogen ion. To make salt effects small, experiments were conducted with the sum of perchloric acid and lithium perchlorate concentrations equal to 1·0M, the ionic strength being made 3·0M by addition of sodium perchlorate. Concentrations of ferrous ion and Co(YOH)H_2O were similar to those in the main experiments with this system. Values of k_4 at 20·0° were 0·149, 0·151, 0·146 l. mole^{-1} min.$^{-1}$ at hydrogen-ion concentrations of 0·918, 0·736, 0·551M, respectively. After allowance had been made for the reaction path *via* Co(YOH)OH^- these velocity constants became 0·143, 0·143, 0·136 l. mole^{-1} min.$^{-1}$, respectively. These figures for k_{4a} suggest that there is a small catalysis by hydrogen ion, but it is only of the

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[10] Kopple and Miller, *Proc. Chem. Soc.*, 1962, 306; Fraser, *J. Amer. Chem. Soc.*, 1963, **85**, 1747.

magnitude of a salt effect and is much smaller than the effects observed in the reduction of other polycarboxylatocobalt(III) complexes by chromous ion. Consequently we have asumed that direct catalysis by hydrogen ion of the reduction by ferrous ion of the edta and heta complexes discussed in this Paper is negligible under the conditions adopted.

Although the reaction of the quinquedentate monoaquo-complex must occur in two stages,

$$\mathrm{Co(YOH)H_2O + Fe^{2+} \longrightarrow Co^{II}(YOH)H_2O^- + Fe^{3+} \longrightarrow Co^{2+} + Fe^{III}(YOH)H_2O},$$

the first stage is not reversible under our conditions. In the reaction of $\mathrm{Co(Y)^-}$ with ferrous ion, the reversibility of the corresponding first step, reaction (—1), is partly responsible for the decrease in the overall rate of reaction observed as the hydrogen-ion concentration is decreased. This reaction also accounts for the formation of $\mathrm{Co(Y)^-}$ as a by-product in the reaction between Co(hY)Cl and ferrous ions at pH ~3.[2] We believe that the reactive form of the cobalt(II)-edta complex for the reverse of the first step is $\mathrm{Co^{II}(Y)H_2O^{2-}}$, while that for the second step, reaction (2), is $\mathrm{Co^{II}(HY)H_2O^-}$. Since the behaviour of $\mathrm{Co^{II}(YOH)H_2O^-}$ is likely to resemble that of $\mathrm{Co^{II}(HY)H_2O^-}$ rather than $\mathrm{Co^{II}(Y)H_2O^{2-}}$, the reverse of the first stage is likely to be unimportant in the reduction of heta complexes, with consequent simplification of the kinetics compared with edta complexes.

DISCUSSION

The activation parameters for the reduction by ferrous ion of the edta and heta complexes we have studied are summarised in Table 4. The values quoted for $\mathrm{Co(HY)Cl^-}$ were obtained previously; values for $\mathrm{Co(Y)Cl^{2-}}$ are not included, but are believed to be very similar to those of its conjugate acid.[2] On the other hand, $\mathrm{Co(Y)H_2O^-}$ appears to be much more reactive than $\mathrm{Co(HY)H_2O}$. Among all the complexes, $\mathrm{Co(Y)H_2O^-}$ is unusual in its high activation energy. We suggest that the true activation parameters for the direct reduction of this complex are similar to those for $\mathrm{Co(HY)H_2O}$ and $\mathrm{Co(YOH)H_2O}$, and that the dominant route of reduction of $\mathrm{Co(Y)H_2O^-}$ is through its isomer, $\mathrm{Co(HY)OH^-}$, with which it is in labile equilibrium. The activation energy found for $\mathrm{Co(Y)H_2O^-}$ would therefore be high because it includes not only the activation energy for the reduction of $\mathrm{Co(HY)OH^-}$, which presumably would be *ca.* 13 kcal. mole^{-1}, but also a positive contribution from the heat of the isomerisation $\mathrm{Co(Y)H_2O^- \longrightarrow Co(HY)OH^-}$, the latter being present only in small proportion. Now, pK ~3 for the equilibrium $\mathrm{Co(HY)H_2O \rightleftharpoons H^+ + Co(Y)H_2O^-}$ and pK ~8 for $\mathrm{Co(Y)H_2O^- \rightleftharpoons H^+ + Co(Y)OH^{2-}}$.[8] Consequently we may assume pK ~8 as an upper limit for the equilibrium $\mathrm{Co(HY)H_2O \rightleftharpoons H^+ + Co(HY)OH^-}$, and p$K$ ~3 as a lower limit for $\mathrm{Co(HY)OH^- \rightleftharpoons H^+ + Co(Y)OH^{2-}}$. From these p$K$ values it is evident that at equilibrium the ratio $\mathrm{[Co(HY)OH^-]/[Co(Y)H_2O^-]}$ is not less than 10^{-5}. If $\mathrm{Co(HY)OH^-}$ has a reactivity similar to that of $\mathrm{Co(YOH)OH^-}$, then this ratio would have to be *ca.* 4×10^{-5} to account for the rate constant observed for $\mathrm{Co(Y)H_2O^-}$. Assuming that this ratio is 10^{-5} and that the entropy of isomerisation is small, the corresponding positive enthalpy change of *ca.* 7 kcal. mole^{-1} would lead to a value in the region of 20 kcal. mole^{-1} for the overall activation energy for $\mathrm{Co(Y)H_2O^-}$.

TABLE 4

Complex	$E^‡$ (kcal. mole^{-1})	$\Delta S^‡$ (cal. mole^{-1} deg.$^{-1}$)	k(25°) (l. mole^{-1} min.$^{-1}$)
$\mathrm{Co(Y)^-}$	11·8 ± 1·5	−36 ± 5	0·0362
$\mathrm{Co(HY)H_2O}$	11·1 ± 0·9	−33 ± 3	0·510
$\mathrm{Co(Y)H_2O^-}$	22·1 ± 1·7	+27 ± 6	53·9
$\mathrm{Co(YOH)H_2O}$	14·2 ± 0·4	−23·5 ± 1·4	0·277
$\mathrm{Co(YOH)OH^-}$	13·7 ± 1·6	+6 ± 5	$1{\cdot}45 \times 10^6$
$\mathrm{Co(HY)Cl^-}$	11·3 ± 0·4	−21·9 ± 1·5	81·7

It seems probable that hydrogen bonding will occur between the carboxylic acid group and the hydroxo-group in $Co(HY)OH^-$. On the other hand, hydrogen bonding between the free carboxylate group and the ligand water molecule in $Co(Y)H_2O^-$ seems to be small, since the pK of the acid $Co(HY)H_2O$ is similar to that of $Co(HY)L^-$, where L = Cl, Br, and NO_2; [11] such hydrogen bonding cannot occur in the conjugate bases of these complexes. In consequence, although the reactivity of $Co(HY)OH^-$ would be reduced, the proportion of this isomer in $Co(Y)H_2O^-$ is likely to be increased to well above 10^{-5} by such hydrogen bonding. We made a careful examination of the spectra of $Co(Y)^-$, $Co(HY)H_2O$, and $Co(Y)H_2O^-$ over a range of about 100 mμ on either side of the long-wavelength maximum occurring at *ca.* 550 mμ. [The main details of the spectra of $Co(Y)^-$, $Co(Y)H_2O^-$, and $Co(Y)OH^{2-}$ are given in ref. 8; the spectrum of $Co(HY)H_2O$ is similar to that of $Co(Y)H_2O^-$.] Compared with the spectra of the other two complexes, that of $Co(Y)H_2O^-$ showed a slight asymmetry which was consistent with the presence of a species having a spectrum similar to that of $Co(Y)OH^{2-}$, but present at a concentration of $\frac{1}{2}$—1% of that of $Co(Y)H_2O^-$. Unfortunately, the effects observed are too small to be acceptable as a satisfactory demonstration of the presence of $Co(HY)OH^-$ in these relatively high proportions. On the other hand, we have little doubt that the presence of this isomer in concentrations exceeding 10^{-5} times those of $Co(Y)H_2O^-$ is responsible for the latter's apparently anomalous activation parameters.

In the reduction of cobalt(III) complexes by chromous ion it is often possible to identify the bridging group for reactions involving an inner-sphere transition complex, owing to the substitution-inert character of chromium(III). For other cationic reducing agents this direct criterion is not available, but inferences have been drawn in various ways for reductions involving vanadium(II) and europium(II).[12] These usually involve a comparison between the kinetic or mechanistic behaviour of these reagents as reducing agents, and the corresponding behaviour, with the same cobalt(III) complexes, of chromous ion and trisbipyridylchromium(II); the last of these is presumed to react by an outer-sphere mechanism, while chromous ion can usually be shown to follow an inner-sphere mechanism except where the ligands of the cobalt(III) complex lack unshared electron pairs suitable for bridge formation. Our conclusions about the mechanisms of these reductions by ferrous ion are likewise somewhat speculative, but they do not depend entirely upon comparisons with the behaviour of chromous ion. First, we suggest that on account of its high reactivity, the species $Co(YOH)OH^-$ reacts with ferrous ion through an inner-sphere type of transition complex, with the hydroxo group acting as a bridge. This suggestion also applies to the reduction of $Co(HY)OH^-$. Here, we are proceeding by analogy with the observation that hydroxopenta-amminecobalt(III) is reduced very much more rapidly than aquopenta-amminecobalt(III) by chromous ion, the reactions being of the inner-sphere type, whereas these two complexes react at similar rates with trisbipyridylchromium(II) in a reaction believed to be of the outer-sphere type.[13]

Next, we consider the reduction of $Co(Y)^-$, $Co(HY)H_2O$, and $Co(YOH)H_2O$. In the case of $Co(Y)^-$, we suggest that the reaction is of the inner-sphere type in which the bridging carboxylato-group remains co-ordinated to the iron atom, but dissociates from the cobalt during electron transfer so that the formation of the cobalt(II)-edta complex in the unstable [14] sexidentate form is avoided. The two quinquedentate cobalt(III) complexes may react by an inner-sphere mechanism in which the aquo-group acts as the bridge, but we consider that a carboxylato bridge is likely to be more effective. The similarity of the activation parameters for these complexes is in accord with the view that all three proceed through inner-sphere transition complexes with carboxylato-groups acting as bridges.

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[11] Schwarzenbach, *Helv. Chim. Acta*, 1949, **32**, 839.

[12] Zwickel and Taube, *J. Amer. Chem. Soc.*, 1961, **83**, 793; Fraser and Taube, *ibid.*, p. 2242; Fraser, " Advances in the Chemistry of the Co-ordination Compounds," ed. Kirschner, Macmillan, New York, 1961, p. 287.

[13] Zwickel and Taube, *Discuss. Faraday Soc.*, 1960, **29**, 42.

[14] Hoard, Smith, and Lind, " Advances in the Chemistry of the Co-ordination Compounds," ed. Kirschner, Macmillan, New York, 1961, p. 296.

The comparative slowness of reaction of $Co(Y)^-$ is understandable since it is the most stable of the three complexes.

Supporting evidence that carboxylato-groups may act as bridges comes from the observation (p. 2118) that the major product of the oxidation of $Co^{II}(hY)H_2O$ by ferric ion is $Co(Y)^-$. It is difficult to imagine how an outer-sphere mechanism could lead to this product rather than $Co(hY)H_2O$. An inner-sphere mechanism in which the free carboxylate group of $Co^{II}(Y)H_2O^{2-}$ acts as the bridging entity, with displacement of the aquo-group, seems the most probable interpretation; this is the reverse of the inner-sphere mechanism we have postulated for the reduction of $Co(Y)^-$ by ferrous ion. The formation of $Co(hY)H_2O$ as a minor product of the reaction between $Co^{II}(hY)H_2O$ and ferric ion does not necessarily show that an outer-sphere type of reaction also occurs, with the corollary that outer-sphere reduction of $Co(hY)H_2O$ by ferrous ion is possible. Under the conditions of our experiments on the oxidation of $Co^{II}(hY)H_2O$, some $FeOH^{2+}$ is present and this could enable the kinetically favourable bridge through a hydroxyl group to be formed. The reaction $Co^{II}(HY)H_2O^- + FeOH^{2+} \longrightarrow [Co(HY)OHFe^+]^\ddagger \longrightarrow Co(HY)OH^- + Fe^{2+}$ is of course the reverse of the reaction thought to be responsible for the anomalous behaviour of $Co(Y)H_2O^-$. Finally, we have no conclusive evidence showing that the dominant path in the reduction of $Co(HY)Cl^-$ by ferrous is of the inner-sphere type with a chlorine-atom bridge. In view of the rapid rate of reaction of this complex compared with $Co(HY)H_2O$ we consider that a bridge through the chlorine atom is the most satisfactory interpretation.

These conclusions about bridging groups have led us to investigate the reduction of most of these complexes by chromous ion. A full comparison between the mechanisms followed by the two reducing agents is not yet possible, but it is pertinent to mention that several groups co-ordinated to a single cobalt(III) atom may be transferred to a single chromium atom in the oxidation-reduction. For example, under certain conditions three carboxylato-groups can be transferred from $Co(Y)^-$ to chromium.[15] Consequently, although we have tentatively identified one bridging group in each of several reductions by ferrous ion, we must accept that these reactions may involve doubly- or triply-bridged transition states. We are unable to reach any conclusions concerning the number of bridges in these reactions.

EXPERIMENTAL

Reagents were of AnalaR grade unless otherwise specified. Sodium perchlorate solutions were obtained either by neutralising cooled 60% perchloric acid with solid sodium carbonate, or by dissolving B.D.H. Ltd. solid sodium perchlorate, "low in chloride" grade, in water; the solutions were filtered before being used. Solutions of ferrous perchlorate were obtained by double decomposition between ferrous sulphate heptahydrate dissolved in dilute perchloric acid, and aqueous barium perchlorate solution. Ferric perchlorate solutions were obtained by oxidation of ferrous perchlorate solution with Laporte Ltd. stabiliser-free hydrogen peroxide; the solutions were heated on a water-bath to decompose excess of hydrogen peroxide. The various solutions were standardised by standard methods.

Sodium ethylenediaminetetra-acetatocobaltate(III) tetrahydrate, $NaCo(Y),4H_2O$, was prepared by Schwarzenbach's method.[11] Solutions of (ethylenediaminetriacetatoacetic acid)-aquocobalt(III), $Co(HY)H_2O$, were obtained by allowing $Co(Y)^-$ (0·2M), dissolved in 4·0M-perchloric acid, to stand overnight at 25°; such solutions contained *ca.* 15% of cobalt(III) in the form of $Co(Y)^-$. Solutions of (hydroxyethylethylenediaminetriacetato)aquocobalt(III), $Co(YOH)H_2O$, were prepared by heating aqueous solutions of $Co(YOH)Br^-$ to *ca.* 85° for several minutes.[3]

The kinetics of reduction of the various complexes by ferrous ion were followed spectrophotometrically; these and other optical density measurements were made by using Unicam S.P. 500 or S.P. 600 instruments equipped with temperature-controlled cell compartments. Wavelengths used in the oxidation-reduction experiments were, for $Co(Y)^-$, 535; for $Co(hY)H_2O$, 500 and 597; for $Co(YOH)H_2O$, 550 mμ. All these systems were studied under pseudo first-order conditions, ferrous ion being in considerable excess over the cobalt(III)

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[15] Wood and Higginson, *Proc. Chem. Soc.*, 1964, 109.

complex. Since the contributions to the optical density of ferrous ion, cobaltous ion, and $Fe^{III}(hY)H_2O$ were negligible at the wavelengths stated, the first-order velocity constants for these reactions were found from linear plots of the logarithm of the optical density against time. The decomposition of $Co(hY)H_2O$ to $Co(Y)^-$ at various pH values, used in obtaining values of K_1, was followed by the procedure previously described,[8] but experiments were conducted at ionic strength 1·0M; this reaction was followed at 500 mμ. In the evaluation of K_4 by the spectrophotometric determination of the ratio of acid to conjugate base for $Co(YOH)H_2O$, measurements were made at 420 and 620 mμ. The wavelengths used in investigating the products of reaction between ferric ion and $Co^{II}(hY)H_2O$ were 400, 500, and 597 mμ. These experiments were conducted in the absence of buffers, pH values being adjusted by the appropriate addition of perchloric acid or sodium hydroxide. In other experiments requiring values of pH exceeding 2·0, buffers were used, these being chloroacetate (2·0—3·5), acetate (4·0—5·5), phosphate (6·0—8·0), and borate (pH 8·5—10·0). The ionic strength due to the buffer constituents did not exceed 0·2M in solutions in which the total ionic strength was made 1·0M by the addition of sodium perchlorate. Values of pH were measured by meter, the reference solution being 0·0100N-perchloric acid, the ionic strength of which was made 1·00M by addition of sodium perchlorate. The pH of this solution was arbitrarily taken as 2·00, irrespective of the temperature.

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