

**518. Kinetic Studies of Oxidation-Reduction of Cobalt-Ethylenediaminetetra-acetic Acid Complexes. Part I. The Reduction of Chloro(ethylenediaminetriacetatoacetic Acid)cobaltate(III) and its Conjugate Base by Ferrous Ion.**

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Chloro(ethylenediaminetriacetatoacetic acid)cobaltate(III) and its conjugate base are reduced to cobalt(II) at similar rates by ferrous ion in aqueous solution. These reactions are of the first order in both oxidant and reductant and the activation energy and entropy have been found. An increase in the rate of reaction with increase in hydrogen-ion concentration at constant ionic strength is interpreted as a salt effect.

RECENTLY the catalysis by various metal cations of the formation of ethylenediaminetetra-acetato-cobaltate(III)  $\text{Co(Y)}^-$  from chloro(ethylenediaminetriacetatoacetate)cobaltate(III)  $\text{Co(Y)Cl}^{2-}$  and its conjugate acid  $\text{Co(HY)Cl}^-$  was reported.<sup>1</sup> The behaviour of the ion  $\text{Fe}^{2+}$  as a potential catalyst was briefly investigated, but it was found that the dominant reaction occurring in the system  $\text{Fe}^{2+}$ - $\text{Co(HY)Cl}^-$  was the reduction of cobalt(III) to cobalt(II). Here we report a kinetic investigation by a conventional spectrophotometric method of this oxidation-reduction in dilute aqueous perchloric acid.

Most experiments were conducted in solutions of hydrogen-ion concentration exceeding 0.0050M in which the cobalt(III) is mainly in the form of the acid  $\text{Co(HY)Cl}^-$ . The principal reaction is  $\text{Co(HY)Cl}^- + \text{Fe}^{2+} \rightarrow \text{Co}^{2+} + \text{Fe}^{\text{III}}$ . Small amounts of  $\text{Co(Y)}^-$  which were found when the reaction was complete did not exceed 2% of the initial concentration of  $\text{Co(HY)Cl}^-$ . Although we might expect cobalt(II) to be formed initially as its complex with ethylenediaminetetra-acetic acid (EDTA), this complex is unstable under these conditions and rapidly forms  $\text{Co}^{2+}$ . The spectra of solutions of the products showed that at hydrogen-ion concentrations exceeding *ca.* 0.6M the larger part of the iron(III) appeared as  $\text{Fe}^{3+}$ , the remainder being a complex with the ligand EDTA. In product solutions of successively smaller hydrogen-ion concentration the proportion of uncomplexed iron(III) was also decreased, so that in solutions of less than 0.2M-hydrogen ion virtually all the iron(III) was in the form of its EDTA complex. We found that the oxidation-reduction followed the kinetic equation  $-\text{d}[\text{Co(HY)Cl}^-]/\text{d}t = k_h[\text{Co(HY)Cl}^-][\text{Fe}^{2+}]$ , good second-order plots being obtained up to 95% of reaction. The value of  $k_h$  was found to vary with hydrogen-ion concentration according to the relation  $\log k_h = \log k_0 + A[\text{H}^+]$ , where  $k_0$  and  $A$  are constant at a given ionic strength and temperature. We summarise the values obtained for  $k_h$  (l. mole<sup>-1</sup> min.<sup>-1</sup>) under various conditions by recording in the Table the values of  $\log k_0$  and  $A$  derived from groups of experiments, together with the highest and lowest hydrogen-ion concentration employed in each group. For experiments

|  |                     | At 15.1°          |                   |                   |                     | At 30.1°          |                   |                   |  |
|--|---------------------|-------------------|-------------------|-------------------|---------------------|-------------------|-------------------|-------------------|--|
| $\mu$ (M) .....                        | 0.20                | 1.00              | 2.00              | 3.00              | 0.20                | 1.00              | 2.00              | 3.00              |  |
| $\log k_0$ .....                       | 1.98 <sub>9</sub> * | 1.62 <sub>8</sub> | 1.45 <sub>9</sub> | 1.34 <sub>2</sub> | 2.35 <sub>8</sub> * | 2.05 <sub>4</sub> | 1.85 <sub>4</sub> | 1.78 <sub>2</sub> |  |
| $A$ .....                              | —                   | 0.14 <sub>4</sub> | 0.15 <sub>5</sub> | 0.16 <sub>5</sub> | —                   | 0.15 <sub>8</sub> | 0.17 <sub>0</sub> | 0.17 <sub>0</sub> |  |
| $[\text{H}^+]_{\text{max.}}$ (M) ..... | 0.185               | 0.98              | 1.98              | 2.98              | 0.140               | 0.98              | 1.98              | 2.98              |  |
| $[\text{H}^+]_{\text{min.}}$ (M) ..... | 0.0050              | 0.050             | 0.100             | 0.150             | 0.0050              | 0.050             | 0.100             | 0.300             |  |

\* Average values of  $\log k_h$  (see text).

in each group the ionic strength was made equal to the value ( $\mu$ ) quoted in the Table by addition of the appropriate amount of sodium perchlorate stock solution. In the experiments at ionic strength 0.20M the change in  $\log k_h$  over the range of hydrogen-ion concentration investigated was of the order of the experimental error, *ca.*  $\pm 0.013$  logarithmic unit, in individual values of  $\log k_h$ . Hence values of  $A$  could not be found and  $\log k_0$  is

<sup>1</sup> Dyke and Higginson, preceding paper.

taken as the mean of the values of  $k_h$  obtained over the range of hydrogen-ion concentrations studied at the specified temperature.

In an attempt to extend the kinetic measurements to solutions of considerably lower hydrogen-ion concentration than  $5.0 \times 10^{-3}M$  we found that the proportion of  $Co^{III}(Y)^-$  formed was greatly increased and the second-order rate plots were curved. The side-reactions responsible were partially suppressed by fluoride ions, employed in concentrations in the range 1.0— $10 \times 10^{-3}M$ . We did not continue with these experiments, but they showed that in solutions of  $pH \sim 4$ , in which the dominant form of the chloro-complex is  $Co(Y)Cl^{2-}$ , the value of the second-order velocity constant is similar to the corresponding value of  $k_0$ . An extensive series of experiments would be necessary to obtain a precise value of the velocity constant since this preliminary work led us to conclude that the fluoride ion is probably a weak catalyst of the oxidation-reduction. On the other hand, in solutions of hydrogen-ion concentration 0.10M and ionic strength 1.0M the rate of the reaction was unaffected by replacing part of the total perchlorate-ion concentration by an equal concentration (0.10M) of chloride ion.

*Discussion.*—Comparison of values of  $k_h$  obtained at a given hydrogen-ion concentration, but at different values of the ionic strength, shows that there is a marked negative salt effect. Bearing this in mind, we ascribe the relatively small increase in  $k_h$  with increase in hydrogen-ion concentration at constant ionic strength to a specific salt effect, rather than to catalysis involving a reaction path in which a proton enters into the transition complex. The empirical relations between  $\log k_h$  and  $[H^+]$  would arise if the logarithms of the activity coefficients of the reactant species and the transition complex show a linear dependence upon the hydrogen-ion concentration when sodium ions are replaced by hydrogen ions at constant ionic strength, *i.e.*, if  $\log f_h = \log f_0 + B[H^+]$ , where  $B$  is a constant characteristic of a particular ion and  $f_h$  and  $f_0$  are its activity coefficients at constant ionic strength in solutions of hydrogen-ion concentration  $h$  and zero, respectively. There is much experimental evidence for this type of relation;<sup>2</sup> in particular, an equation of this form has been postulated in the interpretation of e.m.f. cell measurements involving media similar to those of our experiments.<sup>3</sup> If we assume that specific salt effects are due principally to interactions between ions of opposite charge, then the increase in  $k_h$  on substitution of hydrogen ions for sodium ions is mainly due to a difference between their interactions with  $Co(HY)Cl^-$  since the other reactant,  $Fe^{2+}$ , and the transition complex are both positively charged. This increase can therefore be ascribed to a greater stabilisation of the species  $Co(HY)Cl^-$  by sodium ions than by hydrogen ions. This effect is in the sense to be expected from a comparison of the activity coefficients of acids which are strong electrolytes, such as hydrochloric, hydrobromic, hydriodic, and perchloric acid, and their sodium salts. For all these the mean ionic activity coefficients in moderately concentrated solutions of the acid exceed those in equimolar solutions of the corresponding salt, implying a stronger interaction of the anion with the sodium ion than with hydrogen ion.<sup>4</sup>

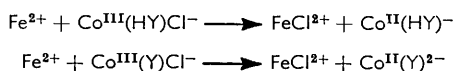
In solutions of hydrogen-ion concentration  $5.0 \times 10^{-3}M$  and 0.140M the proportions of the chloro-complex in the form of  $Co(Y)Cl^{2-}$  are 17% and 0.7%, respectively. Over this range  $k_h$  is almost constant, showing that  $Co(Y)Cl^{2-}$  and  $Co(HY)Cl^-$  react with  $Fe^{2+}$  at very similar rates and we calculate from our results that the value of  $k_0$  for  $Co(Y)Cl^{2-}$  lies between 0.75 and 1.33 of the corresponding value for  $Co(HY)Cl^-$ . This conclusion is in accord with the results of the exploratory experiments at  $pH \sim 4$  in the presence of fluoride ion. We infer that the free carboxylate group present in  $Co(Y)Cl^{2-}$  does not participate in the oxidation-reduction. Although we cannot offer direct experimental evidence, we consider

<sup>2</sup> Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ., Inc., New York, 3rd edn., 1958, pp. 595—602.

<sup>3</sup> Biedermann and Sillén, *Arkiv Kemi*, 1953, **5**, 425; McKay, Proc. Internat. Conf. Co-ordination Compounds, Amsterdam, 1955, p. 188.

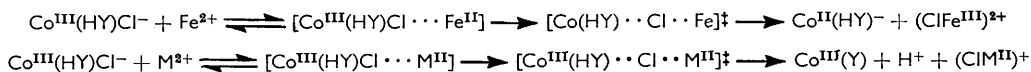
<sup>4</sup> Diamond, *J. Amer. Chem. Soc.*, 1958, **80**, 4808.

that the reaction proceeds through an inner-sphere transition complex, the chlorine atom acting as a bridge between the cobalt and the iron atom. In this connexion, it has been suggested that reactions involving such bridged transition complexes are unlikely to be susceptible to catalysis by chloride ion<sup>5</sup> and we note that the rate of reaction in the  $\text{Co}(\text{HY})\text{Cl}^- - \text{Fe}^{2+}$  system was not affected by the presence of this anion; however, this evidence in favour of a bridged transition complex is somewhat weakened by our observation of catalysis by fluoride ion. As the transition complex breaks up, the bridging chlorine atom is more likely to occur in association with iron(III) than with cobalt(II) and so we can represent the primary stages in the reaction as:



the chelation number<sup>6</sup> exhibited by EDTA in the cobalt(II) complexes produced being five. The aquocobalt(II) cation appears to be formed by subsequent rapid decomposition of these cobalt(II) complexes, and the rate of reaction is also unaffected by the final state in which iron(III) appears, *i.e.*, as the aquoiron(III) cation at the higher hydrogen-ion concentrations and as the iron(III)-EDTA complex at lower hydrogen-ion concentrations.

Several interesting features emerge on comparing the behaviour of this system with that of systems involving the cation-catalysed loss of chloride from these chlorocobalt(III) complexes without simultaneous oxidation-reduction:  $\text{M}^{2+} + \text{Co}^{\text{III}}(\text{Y})\text{Cl}^{2-} \longrightarrow \text{MCl}^+ + \text{Co}^{\text{III}}(\text{Y})^-$ . In the latter systems,  $\text{Co}(\text{Y})\text{Cl}^{2-}$  reacts much more rapidly than its conjugate acid with the cation, which suggests partial bond formation between the initially unbound carboxylate group and cobalt in the transition complex,<sup>1</sup> leading to formation of the sexidentate species  $\text{Co}(\text{Y})^-$  which is more stable than the quinqueidentate monoquo-complexes. However, it is probable that the stable form of the cobalt(II) complex with EDTA is the quinqueidentate monoquo-complex,<sup>6</sup> so that the lack of participation by the free carboxylate group of  $\text{Co}(\text{Y})\text{Cl}^{2-}$  in the reduction by iron(II) can be understood. By using values of  $k_0$  at  $15.1_5^\circ$  and  $30.1_7^\circ$  we calculate  $E^\ddagger = 11.3 \pm 0.4$  kcal. mole<sup>-1</sup> and  $\Delta S^\ddagger = -21.9 \pm 1.5$  cal. mole<sup>-1</sup> deg.<sup>-1</sup> for the oxidation-reduction at ionic strength 1.0M. Comparative figures for the abstraction of chloride from  $\text{Co}(\text{Y})\text{Cl}^{2-}$  by  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Ni}^{2+}$  are  $E^\ddagger \sim 26$  kcal. mole<sup>-1</sup>,  $\Delta S^\ddagger \sim +13$  cal. mole<sup>-1</sup> deg.<sup>-1</sup>; for these cations the rate of reaction with  $\text{Co}(\text{HY})\text{Cl}^-$  is too slow to permit evaluation of the activation parameters. For the more active catalysts  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$ ,  $E^\ddagger \approx 24$  kcal. mole<sup>-1</sup> and  $\Delta S^\ddagger \approx +14$  cal. mole<sup>-1</sup> deg. for the reaction of  $\text{Co}(\text{Y})\text{Cl}^{2-}$ , while slightly higher values of  $E^\ddagger$  and slightly lower values of  $\Delta S^\ddagger$  were obtained with  $\text{Co}(\text{HY})\text{Cl}^-$ . An oxidation-reduction involving a bridged transition complex may be regarded as proceeding through the intermediate formation of a bridged binuclear complex in equilibrium with the reactants, followed by the unimolecular electron-transfer stage.<sup>7</sup> This has been shown to occur in the azide-catalysed isotope exchange between iron(III) and iron(II).<sup>8</sup> It seems probable that a similar bridged intermediate will occur in the cation-catalysed chloride-abstraction reactions of  $\text{Co}(\text{HY})\text{Cl}^-$  and  $\text{Co}(\text{Y})\text{Cl}^{2-}$ ; evidence for such an intermediate was obtained in the catalysis by  $\text{Hg}^{2+}$ .<sup>1</sup> Thus we can represent the mechanisms of the systems now under discussion as:



Since the first stages are similar, the differences in overall activation parameters in the two cases reflect differences in the energetics of formation of the transition states from the corresponding binuclear intermediates. The much lower value of  $E^\ddagger$  obtained for the

<sup>5</sup> Zwickel and Taube, *J. Amer. Chem. Soc.*, 1961, **83**, 793.

<sup>6</sup> Higginson, *J.*, 1962, 2761.

<sup>7</sup> Taube, "Advances in Inorganic Chemistry and Radiochemistry," ed. Emeléus and Sharpe, Academic Press, New York, 1959, Vol. I, pp. 28-30.

<sup>8</sup> Bunn, Dainton, and Duckworth, *Trans. Faraday Soc.*, 1961, **57**, 1131.

reduction with  $\text{Fe}^{2+}$  is presumably a consequence of the extra weakening of the Co-Cl bond in the transition complex owing to the change in oxidation state of cobalt. On the other hand, the large difference in values of  $\Delta S^\ddagger$  implies much more stringent geometrical requirements, including the need for considerable re-orientation of solvent molecules, in the electron-transfer process than in the chloride-abstraction reaction.

At pH  $\sim 4$  in the absence of fluoride, *ca.* 20% of the chloro-complex was not converted into  $\text{Co}^{2+}$ , but appeared as  $\text{Co}^{\text{III}}(\text{Y})$ . We have not investigated the manner in which this by-product is formed. However, if the effect of  $\text{Fe}^{2+}$  as a catalyst of the reaction  $\text{Co}^{\text{III}}(\text{Y})\text{Cl}^{2-} \rightarrow \text{Co}^{\text{III}}(\text{Y})^-$  is similar to that of  $\text{Mn}^{2+}$  or  $\text{Co}^{2+}$ , then the extent of formation of  $\text{Co}^{\text{III}}(\text{Y})^-$  by this route would be negligible. Also, a calculation involving the known rate of catalysis of the reaction by  $\text{Fe}^{3+}$  produced in the oxidation-reduction would lead to conversion of only *ca.* 3% of the chloro-complex into  $\text{Co}^{\text{III}}(\text{Y})^-$ . We conclude tentatively that most of the  $\text{Co}^{\text{III}}(\text{Y})^-$  formed at pH  $\sim 4$  is produced by the reaction  $\text{Fe}^{\text{III}} + \text{Co}^{\text{II}}(\text{Y})\text{H}_2\text{O}^{2-} \rightarrow \text{Fe}^{2+} + \text{Co}^{\text{III}}(\text{Y})^-$ . The effect of fluoride in reducing the amount of  $\text{Co}^{\text{III}}(\text{Y})^-$  formed is presumably due to displacement of the equilibrium position in this reaction to the left-hand side owing to the formation of fluoride complexes of iron(III).

#### EXPERIMENTAL

Sodium chloro(ethylenediaminetriacetatoacetic acid)cobaltate(III) dihydrate was prepared and purified by Dwyer and Garvan's method.<sup>9</sup> The compound was shown to be pure by microanalysis for carbon, hydrogen, nitrogen, and chlorine and by pH titration. Iron(II) perchlorate solution was obtained by electrolytic reduction of 0.5M-iron(III) perchlorate (G. F. Smith's "Non-yellow" product) in 0.5M-perchloric acid by using a platinum cathode with a current density of *ca.* 0.06 amp. per sq. cm. The solution was filtered and diluted to *ca.* 0.05M-iron(II). This stock solution contained only traces of iron(III) and chloride and was standardised by titration against potassium permanganate. Other reagents used in kinetic experiments were of "AnalaR" quality or were prepared from "AnalaR" materials.

Sufficient solid chloro-complex was weighed for each kinetic experiment to give an initial concentration of *ca.*  $1.0 \times 10^{-3}\text{M}$ . For the experiments at 30.1°, in which the initial iron(II) concentration was also *ca.*  $1.0 \times 10^{-3}\text{M}$  the weight of complex was chosen so that its initial concentration was exactly equal to that of iron(II). The initial concentration of iron(II) was *ca.*  $2.0 \times 10^{-3}\text{M}$  in the experiments at 15.15° and also in the experiments at pH  $\sim 4$  which were conducted at 25.0° in pyridine buffers. Sodium perchlorate was used where necessary to bring the ionic strength to the required value. The reaction was followed spectrophotometrically at 584 m $\mu$  [ $\epsilon$  for  $\text{Co}(\text{HY})\text{Cl}^- = 230$ ] by using a Unicam S.P. 500 spectrophotometer equipped with a temperature-controlled cell compartment; 4 cm. optical cells were used. In experiments with equal initial concentrations of iron(II) and  $\text{Co}(\text{HY})\text{Cl}^-$  a 50% excess of iron(II) was added to the reaction mixture remaining after the sample for the optical cell had been removed. This mixture was kept at the same temperature as the optical cell and was used for finding the final value of the optical density; this procedure greatly reduced the time interval necessary between initial and final measurements. The final value of the optical density varied with hydrogen-ion concentration, but was not greater than 2% of the initial value except in solutions of pH  $\sim 4$ .

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<sup>9</sup> Dwyer and Garvan, *J. Amer. Chem. Soc.*, 1958, **80**, 4480.