519. *Kinetic Studies of Oxidation–Reduction of Cobalt–Ethylenediaminetetra-acetic Acid Complexes. Part II.* The Oxidation of the Cobalt*(II)*–Ethylenediaminetetra-acetic Acid Complex by Hexachloroiridate*(IV).

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The oxidation of the aquoquinquedentate complex between cobalt(II) and ethylenediaminetetra-acetic acid by hexachloroiridate(IV) in aqueous solution yields a mixture of the corresponding sexidentate and the aquoquinquedentate cobalt(III) complex. It is suggested that reaction proceeds through an inner-sphere type of transition complex with a chlorine atom bridge between the cobalt and the iridium atom.

Oxidation of the cobalt(II)–ethylenediaminetetra-acetic acid complex in aqueous solution by reagents such as hydrogen peroxide or molecular bromine yields the quinquedentate complexes $Co(Y)OH^{2-}$ and $Co(Y)Br^{2-}$ in which a part of the oxidant is incorporated in the substitution-inert complex produced.[1,2] It is of interest to investigate the nature of the cobalt(III) complex produced when the oxidant, either in part or whole, is unlikely to be so incorporated. We report here some observations on the oxidation of the cobalt(II)–ethylenediaminetetra-acetic acid complex by hexachloroiridate(IV), $IrCl_6^{2-}$, which, together with its reduced form $IrCl_6^{3-}$, is a substitution-inert complex.

Approximate measurements of the rate of reaction were made by using a " stopped-flow " apparatus. The reaction was found to be of the first order in both reactants, and in solutions of pH 3·9 and ionic strength 1·0M the second-order velocity constant was $(2{\cdot}4 \pm 0{\cdot}2) \times 10^5$ l. mole^{-1} min.$^{-1}$ at 22°. Thus the oxidation–reduction was very rapid compared with the rate of conversion[3] of quinquedentate cobalt(III) complexes into sexidentate $Co(Y)^-$ which was the most stable form under our conditions. Hence it was possible to determine the nature and proportions of the cobalt(III) species formed as immediate products of the oxidation–reduction by taking measurements of optical density at various times after mixing $IrCl_6^{2-}$ and the cobalt(II) complex and making a suitable extrapolation to zero time. We found from such experiments at 25·0° and ionic strength 1·0M that the products were 11 ± 4% of $Co(Y)H_2O^-$ and 89 ∓ 4% of $Co(Y)^-$, these proportions being independent of pH over the range pH 3·9—5·4. In these experiments the cobalt(II)–EDTA complex (EDTA = ethylenediaminetetra-acetic acid) was initially present in slightly higher concentration than $IrCl_6^{2-}$ (*ca.* 6×10^{-4}M). In a further series of experiments at pH 4·9, the ratio of initial concentrations $[Co^{II}]/[IrCl_6^{2-}]$ was varied between 1·2 and 5·0 and the proportions of products were found to remain constant within the limits quoted above. As the pH was reduced below 3·9, the proportion of $Co(Y)^-$ obtained was found to decrease; typical values of this proportion were 75% (pH 3·2), 65% (pH 3·0), and 34% (pH 2·7). Measurements were not made below pH 2·7 since an appreciable fraction of cobalt(II) would be in the form of the simple cation.

The cobalt(II)–EDTA complex is believed[4] to occur in the aquoquinquedentate form, $Co(Y)H_2O^{2-}$ and its conjugate acid $Co(HY)H_2O^-$, the p*K* of the latter being[5] *ca.* 3·0. In view of the unfavourable radius of Co^{2+} for six-fold co-ordination with EDTA[6] we consider it unlikely that the high proportional yield of $Co^{III}Y^-$ obtained at pH 3·9—5·4 is due to the presence, in rapid equilibrium with $Co^{II}(Y)H_2O^{2-}$, of a small amount of

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* Part I, preceding paper.

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

[2] Yalman, *J. Phys. Chem.*, 1961, **65**, 556.

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

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

[5] Schwarzenbach, Gut, and Anderegg, *Helv. Chim. Acta*, 1954, **37**, 937.

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

sexidentate $Co^{II}(Y)^{2-}$ which is oxidised more rapidly to $Co^{III}(Y)^-$ than is $Co^{II}(Y)H_2O^{2-}$ to $Co^{III}(Y)H_2O^-$. On the other hand, if only quinquedentate cobalt(II) species are present, then electron transfer *via* an outer-sphere-type of transition complex would be expected to lead to $Co^{III}(Y)H_2O^-$ as the dominant product since less re-organisation would be necessary for the formation of this quinquedentate complex than for formation of $Co^{III}(Y)^-$. Hence we conclude that the reaction proceeds through a bridged transition complex $[Cl_5IrCl \cdots Co(Y)]^{4-}$ in which the labile ligand water present in $Co^{II}(Y)H_2O^{2-}$ is displaced by $IrCl_6^{2-}$. As this transition complex breaks up we expect the bridging chlorine atom to remain attached to the iridium atom, as observed[7] in the oxidation of chromium(II) by $IrCl_6^{2-}$. At the same time the unbound carboxylate group of EDTA can move into the cobalt co-ordination site vacated by the bridging chlorine atom thus giving $Co^{III}(Y)^-$. This process is similar to that observed in the catalysis of the ligand-replacement reaction $Co^{III}(Y)Cl^{2-} \longrightarrow Co^{III}(Y)^-$ by metal cations, M, in which a chlorine atom-bridged transition complex $[M \cdots Cl \cdots Co^{III}(Y)]$ has been postulated.[8] In the latter reaction 100% conversion into $Co^{III}(Y)^-$ was obtained in catalysis by Hg^{2+} and Pb^{2+} and this is probably true of other cations. Although the product $Co^{III}(Y)^-$ dominates in the oxidation-reduction at high pH, a small proportion of $Co^{III}(Y)H_2O^+$ is produced. We ascribe this to a more negative polarity of the leaving chlorine atom in the oxidation–reduction compared with the ligand-replacement reaction (in the former reaction the chlorine atom forms part of $IrCl_6^{3-}$, in the latter the chlorine atom is thought to leave the transition complex in the form of a zero- or positively-charged complex with the catalyst cation). Thus, we conclude that charge repulsion between the unbound carboxylate group and the leaving chlorine atom does not prevent partial bond formation between the free carboxylate group and cobalt in the transition complex, but is sufficient to enable a solvent water molecule to compete with this carboxylate group as an entering ligand. It is possible that rupture of the cobalt–chlorine bond is complete, with the formation of an intermediate in which the co-ordination number of cobalt is five, before the commencement of bond formation with the entering carboxylate or water ligand. In view of the high proportion of $Co^{III}(Y)^-$ produced we prefer the former interpretation. The correct alternative might be established by investigating product proportions in systems involving suitable oxidants other than hexachloroiridate(IV). If the second alternative is correct the proportions of products should be unaffected by changes in the oxidant, otherwise we should expect these proportions to vary with the oxidant.

If the complex $Co^{II}(HY)H_2O^-$ is oxidised through a bridged intermediate little or no $Co^{III}(Y)^-$ is likely to be formed since the carboxylic acid group cannot interact strongly with the cobalt atom and in consequence $Co^{III}(HY)H_2O$ should be the major product. The pK of the carboxylic acid group in $Co^{II}(HY)H_2O^-$ is 3·0, so that as the pH of reaction mixtures is reduced below *ca.* 4 the proportion of this reactant becomes appreciable. Thus the observation that the proportion of aquoquinquedentate cobalt(III) species increases as the pH is reduced below 4 can be understood.

Experimental.—Reagents were of " AnalaR " quality with the exception of disodium hexachloroiridate(IV) hexahydrate which was obtained from Johnson Matthey and Co. Sodium perchlorate solution was prepared by neutralising perchloric acid with sodium carbonate, then boiling and filtering the solution. The cobalt(II)–EDTA complex was prepared in solution by mixing equivalent amounts of solutions of cobalt(II) sulphate and the disodium salt of EDTA.

All experiments were conducted in acetate buffers and the ionic strength was made 1·0M with sodium perchlorate. Measurements of the rate of reaction between $IrCl_6^{2-}$ and $Co(Y)H_2O^{2-}$ were made in collaboration with Dr. R. Westbury with the " stopped-flow " apparatus designed and constructed by him and Dr. J. H. Baxendale; concentrations of the reactants were *ca.* 10^{-2}M. The products of the reaction were determined by mixing an aqueous solution of hexachloroiridate(IV) with a buffered solution of the cobalt(II) complex at 25° and then

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[7] Taube and Myers, *J. Amer. Chem. Soc.*, 1954, **76**, 2103.

[8] Dyke and Higginson, *J.*, 1963, 2788.

transferring the mixture to a 1 cm. optical cell in the temperature-controlled cell-compartment of a Unicam S.P. 600 spectrophotometer. Successive measurements of optical density at each of several wavelengths in the range 500—600 mμ were made at various times after mixing until constant values were attained at each wavelength. The initial concentration of the cobalt(II) complex was greater than that of the hexachloroiridate, so that all of the latter was converted into its reduced form, $IrCl_6^{3-}$. By subtracting the contribution of $IrCl_6^{3-}$ from the observed optical densities we obtained the optical densities due to the absorption by the remaining cobalt(II) complex and the cobalt(III) products. When the system had reached equilibrium the only cobalt(III) species present was $Co(Y)^-$ and we found the total cobalt(III) concentration from the final optical-density measurements. This concentration was invariably a few percent lower than the apparent initial iridium(IV) concentration, but we did not investigate whether the $IrCl_6^{2-}$ stock solution contained a small proportion of $IrCl_6^{3-}$ or whether a side-reaction was responsible for this discrepancy. The corrected optical densities, *i.e.*, those due to cobalt species only, found before equilibrium was reached were consistent with the presence of only two types of cobalt(III) complex, $Co(Y)^-$ and $Co(Y)H_2O^-$ (with the conjugate acid of the latter in solutions of pH <4). The slow change in these optical densities with time was due to the slow formation of $Co(Y)^-$ from aquoquinquedentate cobalt(III) species produced in the rapid oxidation of the cobalt(II) complex. This was demonstrated by plotting log $(D_e - D_t)$ against time t, where D_e and D_t represent the optical density at a given wavelength at equilibrium and at time t, respectively; from the gradients of these linear plots we obtained first-order velocity constants which, after allowance for the difference in ionic strength, were in agreement with those previously established [9] at ionic strength 0·10M for the conversion of aquoquinquedentate cobalt(III) species into $Co(Y)^-$ in solutions of corresponding pH. These plots were used to obtain values of optical density at zero time by linear extrapolation; the proportions of the immediate products of the oxidation were then calculated by using the appropriate molecular extinction coefficients for $Co(Y)^-$, $Co(Y)H_2O^-$, and $Co(HY)H_2O$.

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