82. *Reducing Reactions of Tin(II) in Aqueous Solution. Part I. A Method for the Detection of Tin(III).*

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The consumption of trioxalatocobaltate(III), present in reaction systems in which tin(II) is oxidised to tin(IV), can be interpreted to show that tin(III) is formed as an intermediate. By this means it is shown that in dilute hydrochloric acid the dinuclear complex di-μ-hydroxobis{dioxalatocobaltate(III)} is split into mononuclear complex ions, tentatively identified as *cis*-dioxalatodiaquocobaltate(III). This conclusion is supported by measurements of the visible spectra of the di-μ-hydroxo-complex in neutral and acid solutions.

Recently it was suggested [1] that dinuclear products of the partial hydrolysis of transition-metal cations may react in a single-stage oxidation–reduction with metal ions for which a 2-equivalent change is possible; the example suggested was $Fe_2(OH)_2^{4+} + Sn^{II} \longrightarrow 2Fe^{II} + Sn^{IV}$. In the hope of providing evidence for this type of reaction we investigated that between di-μ-hydroxobis{dioxalatocobaltate(III)}, $\{(C_2O_4)_2Co^{III}(OH)_2Co^{III}(C_2O_4)_2\}^{4-}$, and tin(II). The bridged structure was originally assigned to this complex by Percival and Wardlaw.[2] Preliminary spectrophotometric experiments showed that in dilute solutions of hydrochloric acid, which were necessary to avoid precipitation of tin(IV), a slow oxidation–reduction leads to the simple cobalt(II) ion. Linear logarithmic plots of the concentration of the complex against time were obtained, tin(II) being in at least ten-fold excess. The gradients of these plots were proportional to the concentration of tin(II) after correction for the spontaneous first-order decomposition of the complex to cobalt(II) in acid solutions in the absence of tin(II). The second-order constant for the reaction of the complex with tin(II) was found to be 17 l. mole^{-1} min.$^{-1}$ in 0·25M-hydrochloric acid at 20°, and the decomposition constant was 0·02 min.$^{-1}$. For comparison, the rate of reduction of the mononuclear complex, trioxalatocobaltate(III), by tin(II) was found under similar conditions to be 0·13 l. mole^{-1} min.$^{-1}$. This large difference between the second-order constants seemed an indication that the di-μ-hydroxo-complex might be reacting by the single-stage mechanism, thereby avoiding the intermediate formation of tin(III). However, we performed several experiments in which excess of tin(II) was allowed to react with acid solutions of the di-μ-hydroxo-complex in the presence of similar concentrations of trioxalatocobaltate(III). In such experiments the consumption of the latter complex due to its direct reaction with tin(II) is almost negligible: nevertheless a considerable fraction was consumed. This implies that an active reducing intermediate, presumably tin(III), is produced in acid solutions of the di-μ-hydroxo-complex and tin(II), contrary to our original expectations. By analogy with the behaviour of di-μ-hydroxobis{tetra-amminecobalt(III)} ions,[3] we concluded that di-μ-hydroxobis{dioxalatocobaltate(III)} might similarly be split into two *cis*-dioxalatodiaquocobaltate(III) ions. This suggestion has also been made [4] to account for the form of pH-titration curves obtained with solutions of di-μ-hydroxobis{dioxalatocobaltate(III)}. On this basis we are able to interpret quantitatively the induced oxidation of trioxalatocobaltate(III) described above.

We assume that the reactions occurring are:

$$A + Sn^{II} \xrightarrow{k_1} Co^{II} + Sn^{III}$$

$$A + Sn^{III} \xrightarrow{k_2} Co^{II} + Sn^{IV}$$

$$B + Sn^{III} \xrightarrow{k'} Co^{II} + Sn^{IV}$$

[1] Higginson, Rosseinsky, Stead, and Sykes, *Discuss. Faraday Soc.*, 1960, **29**, 56.
[2] Percival and Wardlaw, *J.*, 1929, **132**, 2628.
[3] Werner, *Ber.*, 1907, **40**, 4434.
[4] Adamson, Ogata, Grossman, and Newbury, *J. Inorg. Nuclear Chem.*, 1958, **6**, 319.

where A represents dioxalatodiaquocobaltate(III) and B represents trioxalatocobaltate(III). By making the stationary-state approximation, $d[Sn^{III}]/dt = 0$, we obtain:

$$\frac{-d[A]}{dt} = \frac{k_1[A][Sn^{II}](2k_2[A] + k_3[B])}{k_2[A] + k_3[B]} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\frac{-d[B]}{dt} = \frac{k_1k_3[A][B][Sn^{II}]}{k_2[A] + k_3[B]} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

whence, by dividing (1) by (2),

$$d[A]/d[B] = 1 + 2k_2[A]/k_3[B] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Integration of eqn. (3) gives

$$P \log_{10} [B] = \log_{10} (1 + P[A]/[B]) + \text{Constant},$$

where $P = 2k_2/k_3 - 1$.

If Sn^{II} is in excess, $[A] = 0$, $[B] = [B]_\infty$ when the reaction is complete; initially, $[A] = [A]_0$, $[B] = [B]_0$, whence the integration constant can be eliminated, giving

$$P \log_{10} ([B]_0/[B]_\infty) = \log_{10} (1 + P[A]_0/[B]_0) \quad . \quad . \quad . \quad . \quad . \quad (4)$$

We have expressed our experimental results by plotting $\Delta[A]/\Delta[Sn^{II}]$ against $[B]_0/[A]_0$ (Fig. 1); $\Delta[Sn^{II}]$ is obtained from the relation $2\Delta[Sn^{II}] = \Delta[A] + \Delta[B]$, where $\Delta[B] = [B]_0 - [B]_\infty$, and, in a reaction proceeding to completion, $\Delta[A] = [A]_0$. The ratio $\Delta[A]/\Delta[Sn^{II}]$ is the number of gram-ions of the diaquo-complex consumed per gram-ion of Sn^{II} consumed; when $[B]_0 = 0$ this ratio is 2. By using eqn. (4) we have calculated $[B]_\infty$ and hence $\Delta[A]/\Delta[Sn^{II}]$ from $[A]_0$ and $[B]_0$ for various values of P. The solid curve in Fig. 1 was calculated by using $P = 3{\cdot}5$ ($k_2/k_3 = 2{\cdot}25$), and for comparison two other calculated curves are shown, corresponding to $k_2/k_3 = 3{\cdot}0$ and $1{\cdot}5$, respectively. It can be seen that the experimental points fit eqn. (4) well and we consider this a strong indication that the reaction scheme suggested is correct since this equation contains only one adjustable parameter. It is noteworthy, but not surprising, that although the diaquo-complex reacts with tin(II) over a hundred times faster than does trioxalatocobaltate(III) the rates of reaction of these complex ions with the active intermediate tin(III) do not differ greatly. This suggests that trioxalatocobaltate(III), on account of its very slow reaction with tin(II) and the ease with which its concentration can be measured spectrophotometrically, would be a suitable reagent for demonstrating the intermediate formation of tin(III) in other reducing reactions of tin(II), a kinetic treatment similar to that given here being used. Such use of a reagent which does not react with the reactants or products of a given reaction, but which reacts with an intermediate, follows similar methods used for example in the detection of chromium(IV) and chromium(V) in oxidising reactions of chromium(VI),[5] and of hydroxyl radicals in reactions of hydrogen peroxide.[6]

Spectra of Solutions of Oxalatocobaltate(III) *Complexes.*—Further evidence that di-μ-hydroxobis{dioxalatocobaltate(III)} is converted into dioxalatodiaquocobaltate(III) in acid solutions was obtained from the spectra of solutions of the former in various buffers and in dilute hydrochloric acid. The molecular extinction curves are shown in Fig. 2 for solutions of pH 7·0—7·6 (D), and 1·3—1·6 (A). For comparison we show a curve (B) for trioxalatocobaltate(III), this spectrum being almost invariant over a wide range of pH, and a curve (C) for the simple ion Co^{3+} in perchloric acid solutions of concentration greater than 1M. Curve C is due to Hargreaves and Sutcliffe.[7] It can be seen that in curve D

[5] Westheimer, *Chem. Rev.*, 1949, **45**, 419.
[6] Baxendale, Evans, and Park, *Trans. Faraday Soc.*, 1946, **42**, 155.
[7] Hargreaves and Sutcliffe, *Trans. Faraday Soc.*, 1955, **51**, 786.

an extra absorption band appears, centred at approx. 350 mμ. This may be ascribed to the presence of the OH groups in the di-μ-hydroxo-complex although we have not investigated whether this effect is given only by bridged OH groups. The curves A and B are very similar and we consider that this indicates similarity between trioxalatocobaltate(III) and the product formed from the di-μ-hydroxo-complex in dilute hydrochloric acid. Our provisional identification of this product as *cis*-dioxalatodiaquocobaltate(III) therefore seems justified, although the possibility that this complex isomerises rapidly to the *trans*-isomer is not excluded by our experiments.

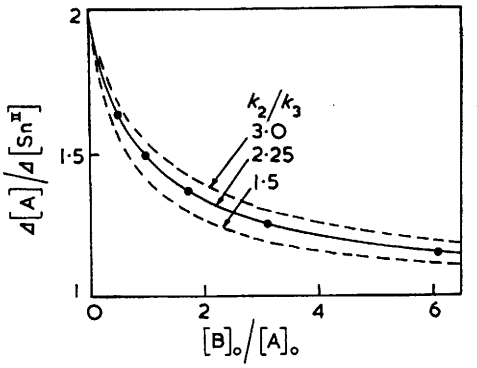

FIG. 1. Dependence of stoicheiometry of dioxalatodiaquocobaltate(III)–tin(II) reaction upon the ratio [trioxalatocobaltate(III)]$_0$/[dioxalatodiaquocobaltate(III)]$_0$.

[A] = [dioxalatodiaquocobaltate(III)], [B] = [trioxalatocobaltate(III)], $[Sn^{II}]_0$ = 11·1—25·8 × 10^{-3}M, $[A]_0$ = 0·60—3·83 × 10^{-3}M, $[B]_0$ = 1·39—4·44 × 10^{-3}M, $[H^+]$ = 0·25M; 20°.

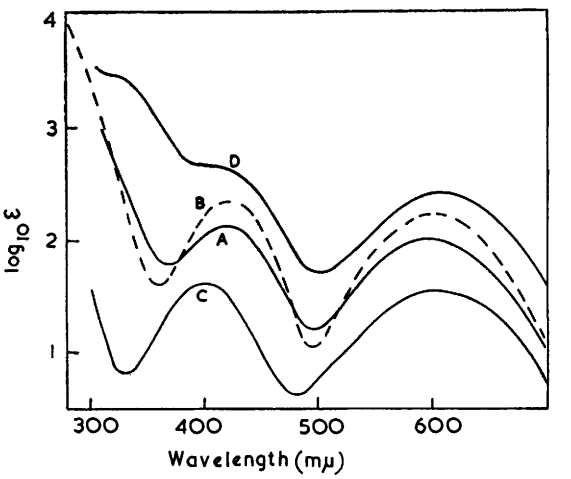

FIG. 2. Spectra of oxalatocobaltate(III) complexes.

A, Dioxalatodiaquocobaltate(III); B, trioxalatocobaltate(III); C, Co^{3+}; D, di-μ-hydroxobis{dioxalatocobaltate(III)}.

Interconversion of the Di-μ-hydroxo- and Diaquo-complexes.—The conversion of the di-μ-hydroxo-complex into the diaquo-complex is almost instantaneous at pH $\gtrsim$1·6. At higher pH values this reaction is slow and at pH 4·1 appears to follow first-order kinetics with a velocity constant of *ca.* 0·03 min.$^{-1}$ at 20°. The interpretation of the kinetics of this change is complicated by the slow decomposition of the diaquo-complex to cobalt(II), the velocity constant for this decomposition being 0·016 min.$^{-1}$ under these conditions. The chromium analogue of *cis*-dioxalatodiaquocobaltate(III) is easily converted into the conjugate base, *cis*-hydroxodioxalatoaquochromate(III), and this readily forms di-μ-hydroxobis{dioxalatochromate(III)}.[8] We attempted without success to accomplish the corresponding conversion of dioxalatodiaquocobaltate(III) into di-μ-hydroxobis{dioxalatocobaltate(III)} by increasing the pH of acid solutions of the former.

EXPERIMENTAL

Potassium trioxalatocobaltate(III) hydrate and potassium di-μ-hydroxobis{dioxalatocobaltate(III)} hydrate were prepared, purified, and analysed as described by Palmer.[9] Solutions of these complexes in water were freshly made up by weight for each experiment. Solutions of dioxalatodiaquocobaltate(III) were prepared by making an aqueous solution of the di-μ-hydroxo-complex at least 0·025M in hydrochloric acid; *ca.* 1 min. elapsed before any further reagents were added. Under these conditions the formation of the diaquo-complex is almost instantaneous. Other reagents were of "AnalaR" quality. Tin(II) chloride solutions in

[8] Werner, *Annalen*, 1914, **406**, 261.
[9] Palmer, "Experimental Inorganic Chemistry," Cambridge Univ. Press, 1954, pp. 550—554.

dilute hydrochloric acid were standardised by titration with potassium iodate in *ca.* 5M-hydrochloric acid (Andrews's procedure). A Unicam S.P. 500 spectrophotometer fitted with a thermostat-controlled cell-holder was used for the determination of spectra. Some decomposition of dioxalatodiaquocobaltate(III) occurred during determination of its spectrum. The time at which each reading of optical density was taken in scanning the spectrum was therefore noted, and every 5 min. the optical density was measured at 420 and 605 mμ, both of which wavelengths correspond to maxima. From the logarithmic plots of concentration against time, obtained from the measurements at these two wavelengths, the concentration of the complex remaining at any time was calculated, and hence the molecular extinction coefficients at other wavelengths were found. No correction was made for optical absorption due to Co^{2+}, the decomposition product of the complex, since its contribution to the optical densities did not exceed 5% and at most wavelengths was less than 2%. This procedure was unnecessary for di-μ-hydroxobis{dioxalatocobaltate(III)} in neutral solutions or for trioxalatocobaltate(III), both these complexes being relatively stable.

In preliminary kinetic experiments an " Eel " colorimeter was used at room temperature (*ca.* 20°), but most experiments were done by using thermostat-controlled optical cells in a Unicam S.P. 500 spectrophotometer. The rates of reaction of trioxalatocobaltate(III) and of dioxalatodiaquocobaltate(III) with tin(II) at 20·0°, and the rate of decomposition of the latter complex at various pH values were followed at one or other of the wavelengths 420 and 605 mμ which correspond to maxima in the spectra of both complexes. In the experiments with tin(II) initial concentrations were in the ranges 0·010—0·10M-tin(II), 1—5 × 10^{-3}M-complex, 0·10—0·50M-hydrochloric acid. The concentration of diaquo-complex was 2—5 × 10^{-3}M in the decomposition experiments, hydrochloric acid or acetate buffers being used to maintain a constant hydrogen ion concentration. A similar procedure was used for experiments in acetate buffers in which the rate of formation of the diaquo-complex from the di-μ-hydroxo-complex was measured.

The competition experiments in which trioxalatocobaltate(III), dioxalatodiaquocobaltate(III), and tin(II) were present together were performed by taking measurements of optical density at 605 mμ at various times after mixing. When the rate of change of optical density first assumed a steady low value, equal to the rate of the reaction between trioxalatocobaltate(III) and tin(II) under the experimental conditions, it was assumed that all the diaquo-complex had been consumed. The concentration of the trioxalatocobaltate(III) corresponding to complete consumption of the diaquo-complex was then calculated, a small correction (*ca.* 2% of its initial concentration) being applied for the loss of trioxalatocobaltate(III) due to its direct reaction with tin(II). Initial concentrations of trioxalatocobaltate(III), dioxalatodiaquocobaltate(III), and tin(II) were within the limits 1·39—4·44 × 10^{-3}M, 0·60—3·83 × 10^{-3}M, and 1·10—2·58 × 10^{-2}M, respectively. All these experiments were in 0·25M-hydrochloric acid at 20·0°. In connection with these experiments it was necessary to show that, in the absence of trioxalatocobaltate(III), two ions of dioxalatodiaquocobaltate(III) are equivalent to one ion of tin(II). This was difficult to establish directly on account of the instability of the diaquo-complex. However, several kinetic experiments were done under second-order conditions, initial concentrations being 2·50 × 10^{-3}M-tin(II) and *ca.* 4·4 × 10^{-3}M-dioxalatodiaquocobaltate(III). By assuming that one ion of tin(II) is equivalent to two of dioxalatodiaquocobaltate(III) ions we obtained kinetic plots from which we calculated rate constants for the second-order reaction between these two reagents within 5% of those found from experiments in which tin(II) was in large excess. The analysis of these second-order experiments also showed that the product of the first-order decomposition of the diaquo-complex, possibly oxalatotetraaquocobalt(III), is reduced rapidly by tin(II). This conclusion is important, for in certain of the competition experiments about 10% of the diaquo-complex must disappear by this first-order process. However, no modification of the kinetic scheme proposed appears necessary since tin(III) will be a product both of the first-order decomposition and of the direct reaction between the diaquo-complex and tin(II).

In an attempt to demonstrate the re-formation of di-μ-hydroxobis{dioxalatocobaltate(III)} from dioxalatodiaquocobaltate(III) we added buffer solutions to acid solutions of the latter and investigated the resulting mixtures spectrophotometrically. In solutions of pH 4·7 and less there was no evidence of substantial changes in the solution. At pH 7·1 ($H_2PO_4^-$–HPO_4^{2-} buffer) an immediate change of colour from the original green to yellow-green was observed on adding the buffer solution; a slow decomposition of the mixture took place, but there was no

evidence of the formation of the di-μ-hydroxo-complex. At pH 9·6 (HCO_3^-–CO_3^{2-} buffer) an instantaneous colour change to deep olive-green was observed. The mixture was unstable, ultimately depositing a dark precipitate, thought to be cobalt(III) hydroxide, and again there was no evidence of the formation of di-μ-hydroxobis{dioxalatocobaltate(III)}.

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