1106. *Reducing Reactions of Tin*(II) *in Aqueous Solution. Part III.*[1] *The Reduction of Various Common Oxidising Agents*

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Evidence concerning the formation of tin(III) as an intermediate in the oxidation of tin(II) in aqueous solutions has been sought by observing whether induced reduction of cobalt(III) complexes occurs in various systems. Mainly by this means it is concluded that tin(III) or a related reducing intermediate is formed in the reactions of tin(II) with cerium(IV), iron(III), chromium(VI), and manganese(VII), but that tin(III) is absent in the reduction of hydrogen peroxide, iodine, bromine, thallium(III), and mercury(II). The latter reactions are thought to proceed through 2-equivalent changes in the oxidation states of the reactants.

The stable oxidation states of non-transition elements usually differ by two units in their mononuclear compounds,[2] and the mechanistic consequences in the oxidation or reduction of non-transition metal ions have already been discussed.[3,4] For our present purpose, the main feature is that most oxidation–reduction reactions of such elements involve either a 2-equivalent change with the direct formation of a stable oxidation state, or the reaction proceeds through successive 1-equivalent steps. In the latter case, an unstable intermediate oxidation state of the non-transition metal is produced and this may show some of the characteristics of a free radical, including the possibility of reaction with substrates which are inert to the reactants or the final products. It has been shown that in a system in which tin(II) is being oxidised, the transient existence of tin(III) may be demonstrated by its ability to reduce trioxalatocobaltate(III),[5] and we now describe further investigations of the oxidation of tin(II), mainly with the help of this method.

Although the method is appropriate to show the presence of a strongly reducing intermediate, it is not usually possible to identify this intermediate as tin(III) merely on the

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[1] Part II, D. J. Drye, W. C. E. Higginson, and P. Knowles, *J.*, 1962, 1137.

[2] W. C. E. Higginson and J. W. Marshall, *J.*, 1957, 454.

[3] W. C. E. Higginson, D. R. Rosseinsky, J. B. Stead, and A. G. Sykes, *Discuss. Faraday Soc.*, 1960, **29**, 49.

[4] J. Halpern, *Quart. Rev.*, 1961, **15**, 222.

[5] W. C. E. Higginson, R. T. Leigh, and R. Nightingale, *J.*, 1962, 435.

evidence of the consumption of a cobalt(III) complex. For example, the following three mechanisms for the oxidation of tin(II) by cerium(IV) involve different active intermediates, Sn^{III}, $(Ce\ Sn)^{VI}$, and Ce^{II}. If these intermediates are present

$$\text{(i)}\qquad Ce^{IV} + Sn^{II} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ce^{III} + Sn^{III}$$

$$Ce^{IV} + Sn^{III} \xrightarrow{k_2} Ce^{III} + Sn^{IV}$$

$$Co^{III} + Sn^{III} \xrightarrow{k_3} Co^{II} + Sn^{IV}$$

$$\text{(ii)}\qquad Ce^{IV} + Sn^{II} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (Ce\ Sn)^{VI}$$

$$Ce^{IV} + (Ce\ Sn)^{VI} \xrightarrow{k_2} 2Ce^{III} + Sn^{IV}$$

$$Co^{III} + (Ce\ Sn)^{VI} \xrightarrow{k_3} Co^{II} + Ce^{III} + Sn^{IV}$$

$$\text{(iii)}\qquad Ce^{IV} + Sn^{II} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ce^{II} + Sn^{IV}$$

$$Ce^{IV} + Ce^{II} \xrightarrow{k_2} 2Ce^{III}$$

$$Co^{III} + Ce^{II} \xrightarrow{k_3} Co^{II} + Ce^{III}$$

only in low concentrations, then for each mechanism the relationships between the consumptions of the reactants and of cobalt(III) can be deduced from the following equations (cf. ref. 5):

$$d[Ce^{IV}]/d[Co^{III}] = 1 + 2k_2[Ce^{IV}]/k_3[Co^{III}] \qquad (1)$$

$$2d[Sn^{II}] = d[Ce^{IV}] + d[Co^{III}] \qquad (2)$$

[It would be possible to distinguish between the three mechanisms by a kinetic investigation in the absence of cobalt(III), provided that the reverse of the first step is significant. Otherwise, the overall reaction would show simple kinetics, being of the first order in both cerium(IV) and tin(II), and no distinction could be made in this way.] However, the investigation of the induced oxidation of cobalt(III) complexes is useful as a simple means of deciding whether the oxidation of tin(II) involves 1- or 2-equivalent steps, a question of particular interest if the oxidant is not a transition element. In most cases studied, the conversion of the oxidising agent into a strongly reducing intermediate seems improbable, and, if an intermediate is found, it is likely to be either tin(III) or an association complex between tin(III) and the reduced form of the oxidising agent; we shall use the term tin(III) to represent either possibility.

The substrate used to demonstrate the presence of strongly reducing intermediates must not be a strong oxidising agent or it is likely to react fairly rapidly with tin(II) or the reduced form of the oxidising agent under investigation. Further, the reduced form of the substrate should be incapable of being oxidised back to its original form, or the sensitivity of the method will be impaired. The suitability of cobalt(III) complexes, most of which are weak oxidising agents, arises from the instability in acidic solutions of the substitution-labile cobalt(II) complexes to which they can be reduced. Some of the ligands will be weak bases and so their conjugate acids will be rapidly produced, together with cobaltous ion which is inert to oxidation or further reduction. The ease of estimation of low concentrations of cobalt(III) complexes by spectrophotometric methods is an added advantage. In previous work, only trioxalatocobaltate(III) was used as substrate, but we have briefly investigated the behaviour of a few other cobalt(III) complexes.

The integration of equation (1) gives

$$P \log [Co^{III}] = \log (1 + P[X]/[Co^{III}]) + \text{Constant},$$

where $P = 2k_2/k_3 - 1$; for generality we are using X in place of Ce^{IV}. We can eliminate the constant in this equation, and for the case in which tin(II) is present in excess, *i.e.*, in which the concentration of the oxidant X is zero when the reaction is completed, we obtain

$$P \log ([Co^{III}]_0/[Co^{III}]_\infty) = \log (1 + P[X]_0/[Co^{III}]_0), \qquad (3)$$

where subscripts zero and infinity refer, respectively, to initial and final concentrations. It is possible to compare the sensitivity of various substrates in detecting tin(III) by using equation (3) to obtain their values of P in the reduction of a given oxidant X by tin(II); the smaller its value of P, the more effectively does a substrate compete with X for tin(III). Experiments of this kind were conducted with dioxalatodiaquocobaltate(III) as X, following the procedure previously described,[5] and also with cerium(IV) as X. We found the following order of sensitivity: $Co(C_2O_4)_3^{3-} > Co(NH_3)_4(H_2O)Cl^{2+} > Co(YOH)H_2O > Co(Y)^- \gg Co(NH_3)_5H_2O^{3+}$, where $Co(YOH)H_2O$ represents (hydroxyethylethylenediaminetriacetato)-aquocobalt(III), and $Co(Y)^-$ represents ethylenediaminetetra-acetatocobaltate(III). Thus, trioxalatocobaltate is the most sensitive complex we have studied, and we think it unlikely that more sensitive cobalt(III) complexes can be found which are sufficiently inert to reduction by tin(II) and to decomposition in molar solutions of hydrogen ion. Trioxalatocobaltate(III) itself is sometimes unsuitable; we did not use it in studying the iron(III)–tin(II) system owing to the complication introduced by its reduction by the product, iron(II). Most of our experiments have been conducted in dilute solutions of hydrochloric acid, since this is the most common medium for using tin(II) as a reducing agent. Consequently we have restricted our study of cobalt(III) complexes to those which are sufficiently stable and soluble in this solvent. For example, we were unable to use chloropenta-amminecobalt(III) because it was insufficiently soluble in dilute hydrochloric acid for our purpose, although otherwise we should have expected it to prove a satisfactory substrate.

Reaction between Cerium(IV) *and Tin*(II).—This reaction has previously been studied,[6] but, although tin(III) is postulated as an intermediate, there is no experimental evidence for this. However, with mononuclear reactants, the formation of reducing intermediates through one of the mechanisms mentioned above seems probable, and this system was investigated primarily to test the value of the induced-reduction method for detecting these intermediates. Before it is concluded that such intermediates are not formed in a given system, it is necessary to be confident that lack of consumption of a cobalt(III) complex is not due to its inability to compete for them with a strong oxidising agent, and we chose cerium(IV) as a suitable example of the latter. The need for caution is illustrated by the observation that when solutions of *ca.* 10mM-tin(II) chloride in dilute hydrochloric acid and *ca.* 10mM-cerium(IV) sulphate in dilute sulphuric acid were rapidly mixed at 10° in the presence of *ca.* 3mM-aquopenta-amminecobalt(III) there was no consumption of the latter. Under similar conditions, with dioxalatodiaquocobaltate(III) as the oxidising agent, a small consumption of aquopenta-amminecobalt(III) was observed at *ca.* 18°, and by means of equation (3) a value of $P \sim 112$ was calculated. The conclusion that no reducing intermediates are present in the cerium(IV)–tin(II) system would be incorrect, for similar experiments with other substrates showed that induced reduction can occur in this system. With trioxalatocobaltate(III), P-values of *ca.* 127 were found at 10·0° for the cerium(IV)–tin(II) system, while, with the same substrate, $P \sim 2{\cdot}9$ at *ca.* 18° in the dioxalatodiaquocobaltate(III)–tin(II) system. Other substrates also gave much smaller values of P in the latter system compared with the cerium(IV)–tin(II) system. Consequently, the value of P for the competition for tin(III) between cerium(IV) and aquopenta-amminecobalt(III) is likely to be so large that consumption of the latter will be negligible, as observed. Hence this observation does not imply the absence of reducing intermediates in the system, whereas the consumption of trioxalatocobaltate(III) is evidence for such intermediates, probably in the form of tin(III).

[6] C. H. Brubaker and A. J. Court, *J. Amer. Chem. Soc.*, 1956, **78**, 5530.

Further experiments with the cerium(IV)–tin(II) system, using trioxalatocobaltate(III) as substrate, showed that the consumption of the latter was much reduced if cerium(IV) was present in excess. If some oxidant remains after reaction has ceased, the integrated equation corresponding to equation (3) is

$$P \log ([\mathrm{Co^{III}}]_0/[\mathrm{Co^{III}}]_\infty) = \log (1 + P[\mathrm{X}]_0/[\mathrm{Co^{III}}]_0) - \log (1 + P[\mathrm{X}]_\infty/[\mathrm{Co^{III}}]_\infty) \quad (4)$$

and calculations made by using this equation and

$$2[\mathrm{Sn^{II}}]_0 = [\mathrm{X}]_0 - [\mathrm{X}]_\infty + [\mathrm{Co^{III}}]_0 - [\mathrm{Co^{III}}]_\infty, \quad (5)$$

the integrated form of equation (2), confirmed that, if P is large, the use of oxidant in excess will cause a large decrease in the consumption of cobalt(III). With $P = 100$ and a 10% excess of oxidant, the theoretical consumption of substrate is approximately half that to be expected if tin(II) is present in excess and the initial concentrations of oxidant and cobalt(III) remain the same. Consequently, we restricted experiments with most other systems to conditions in which tin(II) was in excess of the oxidant. Under these conditions, both theory and experiment showed that the consumption of substrate depends only on the initial concentrations of oxidant and substrate, and the value of P, provided that mixing of the reactant solutions is efficient and the oxidising agent is of the 1-equivalent type.

As an alternative to mixing the reactants rapidly, it is possible to add the oxidant slowly to a well-stirred mixture of tin(II) and the cobalt(III) substrate. With a succession of infinitesimal additions of oxidant, the consumption of the substrate should equal that of the oxidant, because reaction of the latter with the reducing intermediate would be negligible. Although this limit cannot be closely approached, slow mixing does enable a much-increased consumption of substrate to be achieved. Thus, in experiments in which 10·0 ml. of 12·3mM-cerium(IV) were added smoothly during 40 min. to 20·0 ml. of a solution 9·0mM in tin(II) and 1·47mM in trioxalatocobaltate(III), the proportion of the latter consumed was 0·54. When similar solutions were mixed rapidly, the corresponding proportion consumed was 0·045. However, this method, which must be carried out in an atmosphere of nitrogen, does not in practice give the expected improvement in sensitivity of detection of tin(III), because with most substrates the corrections for reduction by tin(II) and for decomposition are much larger than in rapid-mixing experiments. In a control experiment in which the 10·0 ml. of cerium(IV) solution were replaced by the same volume of 0·545M-sulphuric acid [the same concentration as that present in the cerium(IV) solution], and with other concentrations and the time of addition the same as in the experiment quoted above, the proportion of trioxalatocobaltate(III) which had disappeared, mainly owing to the direct reaction with tin(II), was 0·13. Only in the case of the very stable and relatively insensitive substrate aquopenta-amminecobalt(III) was any improvement obtained by making use of the slow-mixing technique. By use of this technique at *ca.* 18° with cerium(IV) as oxidant, a small but significant consumption of 2 ± 1% of this complex was observed. There was no consumption in the control experiment, and it was also shown that this substrate was unaffected by cerium(IV). No consumption of this complex was observed in rapid-mixing experiments. However, the slow-mixing technique did not usually show any marked advantage over rapid-mixing, and so we did not normally use the slow-mixing technique in seeking evidence for tin(III). Our experiments with the cerium(IV)–tin(II) system showed that although the consumption of substrates such as trioxalatocobaltate(III) and $\mathrm{Co(Y)^-}$ was small when using the rapid-mixing method, it was more reliable than the alternative method, and it appeared adequate to detect tin(III) even in the presence of a strong oxidant. We have therefore assumed that in rapid-mixing experiments lack of consumption of trioxalatocobaltate(III), the most sensitive of the complexes employed, is evidence that tin(III) is not produced as an intermediate in a system in which tin(II) is being oxidised.

Reaction between Iron(III) *and Tin*(II).—Although earlier investigators [7–9] adopted the scheme

$$\mathrm{Fe^{III}} + \mathrm{Sn^{II}} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \mathrm{Fe^{II}} + \mathrm{Sn^{III}}$$

$$\mathrm{Fe^{III}} + \mathrm{Sn^{III}} \xrightarrow{k_5} \mathrm{Fe^{II}} + \mathrm{Sn^{IV}}$$

no decisive experimental evidence has hitherto been quoted in its favour. In perchlorate media, a marked decrease in the apparent second-order velocity constant was found as the reaction proceeded, if tin(II) was present in excess, whereas with iron(III) in excess there was relatively little change in this constant. Such behaviour is to be expected if a competition between iron(II) and iron(III) for tin(III) occurs in accordance with the above mechanism. However, these effects were interpreted [8] by assuming that ferric ion is hydrolysed slowly to give $\mathrm{Fe(OH)_2^+}$; at the relatively high temperatures used in these experiments, this conclusion is unacceptable.

In our experiments, trioxalatocobaltate(III) was not used for the detection of strongly reducing intermediates owing to its rapid reduction by ferrous ion.[10] We found $\mathrm{Co(YOH)H_2O}$ the most satisfactory complex; although it is reduced by ferrous ion and by tin(II), both these side-reactions are sufficiently slow to be disregarded. From six experiments at room temperature (*ca.* 18°) in 1·0M-hydrochloric acid with *ca.* 14mM-tin(II), 0·87—15·2mM-iron(III), and *ca.* 2·9mM-$\mathrm{Co(YOH)H_2O}$, a value of $P = 53 \pm 10$ was found.

As discussed above, the detection of reactive reducing intermediates may be insufficient evidence to determine a reaction mechanism, and so, on account of the importance of the iron(III)–tin(II) reaction, a brief kinetic study was undertaken. The reaction was followed spectrophotometrically at 335 mμ, absorption at this wavelength being due mainly to iron(III), with solutions containing 1·00M-hydrochloric acid. In a series of experiments, the initial concentrations were varied from 0·663 to 1·303mM-iron(III) and 0·293 to 1·22mM-tin(II); neither iron(II) nor tin(IV) was present initially in greater concentration than *ca.* 10% of the reactant concentrations. These experiments gave second-order plots of $\log\{[\mathrm{Fe^{III}}]/2[\mathrm{Sn^{II}}]\}_t$ against time t which were linear for at least 90% of reaction. We conclude that association between iron(III) and tin(II) must be small, and also that tin(II) is present mainly in a monomeric form. [In solutions of 3—6M-hydrochloric acid the behaviour of the reaction $2\mathrm{Re^{V}} + \mathrm{Sn^{II}} \longrightarrow 2\mathrm{Re^{IV}} + \mathrm{Sn^{IV}}$ has been interpreted on the assumption that tin(II) is largely dimeric.[11]] Similar experiments with *ca.* 10mM-iron(II) present initially again gave good second-order plots with values of the second-order constant closely similar to those obtained in the first series of experiments, *i.e.*, 169 l. mole^{-1} min.$^{-1}$ at 25·0°. Further experiments were conducted with *ca.* 100mM-iron(II) present initially. For comparison, experiments in which the iron(II) was replaced by the same concentration of calcium(II) were performed; calcium(II) was used because over a wide range of concentrations the mean ion activity coefficients of calcium(II) chloride solutions are very similar to those of iron(II) chloride at the same concentrations.[12] The average rate constant at 25·0° for the reference runs with 100mM-calcium(II) present was 260 l. mole^{-1} min.$^{-1}$, the initial concentrations of iron(III) and tin(II) both being *ca.* 0·9mM. With *ca.* 100mM-iron(II) present, a series of experiments was performed with initial iron(III) concentrations from 0·59 to 1·04mM, and initial tin(II) concentrations from 0·30 to 2·15mM. With tin(II) present in higher equivalent concentration than iron(III), plots of $\log\{[\mathrm{Fe^{III}}]/2[\mathrm{Sn^{II}}]\}_t$ against time showed curvature after *ca.* 75% of reaction, the apparent second-order constant

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[7] R. A. Robinson and N. H. Law, *Trans. Faraday Soc.*, 1935, **31**, 899.

[8] M. H. Gorin, *J. Amer. Chem. Soc.*, 1936, **58**, 1787.

[9] F. R. Duke and R. C. Pinkerton, *J. Amer. Chem. Soc.*, 1951, **73**, 3045.

[10] J. Barrett and J. H. Baxendale, *Trans. Faraday Soc.*, 1956, **52**, 210.

[11] D. Banerjea and M. S. Mohan, *J. Indian Chem. Soc.*, 1963, **40**, 188.

[12] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd edn., Butterworths, London, 1959, pp. 497, 499.

decreasing with time during the last 25% of reaction. With tin(II) present in lower equivalent concentration than iron(III), there was no departure from linearity. The average gradient of the linear portions was 233 l. mole^{-1} min.$^{-1}$, somewhat lower than the value obtained in the reference experiments with calcium(II) replacing iron(II). The situation is similar to that observed in the formally analogous reaction, $2Fe^{II} + Tl^{III} \longrightarrow 2Fe^{III} + Tl^{I}$,[13] although the departure from second-order kinetics (*i.e.*, curvature of the logarithmic plot) caused by a given concentration of the product iron(III) in the latter reaction is much greater than that caused by the corresponding product, iron(II), in the oxidation of tin(II) by iron(III).

The kinetic expression corresponding to the mechanism given at the beginning of this section is:

$$-d[Fe^{III}]/dt = -2d[Sn^{II}]/dt = 2k_4k_5[Sn^{II}][Fe^{III}]^2/\{k_{-4}[Fe^{II}] + k_5[Fe^{III}]\} \qquad (6)$$

and on integration we obtain

$$2{\cdot}303 \log \frac{[Fe^{III}]}{2[Sn^{II}]} - \frac{a+c}{k_5/k_{-4} - (b+c)/(b-a)} \times \frac{1}{[Fe^{III}]} = -\frac{(k_5/k_{-4})(b-a)}{k_5/k_{-4} - (b+c)/(b-a)} k_4t + \text{Constant} \qquad (7)$$

where a, b, and c represent the initial *equivalent* concentrations of iron(III), tin(II), and iron(II), respectively. If a suitable value of k_5/k_{-4} is chosen, a plot of the left-hand side of this equation against t will be a straight line and k_4 can be found from its gradient. By trial and error a value of $k_5/k_{-4} = 1280$ was obtained; this value was found to give plots linear for *ca.* 96% of reaction for all the experiments with 100mM-iron(II) present, and the average value of k_4 obtained was 266 l. mole^{-1} min.$^{-1}$, compared with 260 l. mole^{-1} min.$^{-1}$ for the reference experiments. The difference in extent of curvature between simple second-order plots with iron(III) present in excess and those with tin(II) in excess can be seen by referring to equation (8), which is equation (6) in a different form. In equation (8),

$$-d[Fe^{III}]/dt = 2k_4[Sn^{II}][Fe^{III}]/\{1 + ([Fe^{II}]/[Fe^{III}])/(k_5/k_{-4})\} \qquad (8)$$

if the term in braces is constant, the simple second-order plot of $\log\{[Fe^{III}]/2[Sn^{II}]\}_t$ against time will be linear. With $k_5/k_{-4} = 1280$ and $[Fe^{II}] \sim 100$mM it is evident that the term in braces will only show sufficient variation with $[Fe^{III}]$ for the second-order plot to exhibit curvature when the latter concentration becomes sufficiently small (less than *ca.* 0·3mM). This happened only in those reactions in which tin(II) was present in excess.

Thus, the use of cobalt(III) complexes has shown the presence of a strongly-reducing intermediate in the reduction of iron(III) by tin(II) in dilute hydrochloric acid, and the results of a brief kinetic study are in good agreement with the generally accepted mechanism involving tin(III) as an intermediate. Other mechanisms, involving the formation of $(Fe\ Sn)^V$ or Fe^I as intermediates [compare the various mechanisms discussed above for the cerium(IV)–tin(II) system], would show different kinetic behaviour and so can be eliminated. The greater tendency to curvature of the second-order logarithmic plots when tin(II) is present in excess is also evident in Gorin's experiments[8] in dilute perchloric acid. In his experiments it was not necessary to add iron(II) in high concentration; the iron(II) formed in the reaction was sufficient for curved plots to be obtained. Reference to equation (8) shows that the value of k_5/k_{-4} must be much smaller for experiments in perchlorate compared with those in chloride solutions, and we estimate that in Gorin's experiments k_5/k_{-4} is of the order of unity. We cannot give a complete explanation for the striking increase in this ratio on replacing perchlorate ion by chloride ion. However, some general observations concerning reactions of this type are relevant.

We consider the general case of an oxidation–reduction reaction between a 2-equivalent

[13] K. G. Ashurst and W. C. E. Higginson, *J.*, 1953, 3044.

and a 1-equivalent reagent which proceeds by a mechanism similar to that for the iron(III)–tin(II) reaction, *i.e.*, by two successive 1-equivalent steps of which the first is reversible. Deviations from simple second-order kinetics which appear as a retardation of the rate will be observed only if the velocity constant for the second stage does not exceed *ca.* 10^4 times that for the reverse of the first stage. In the case of the iron(III)–tin(II) system in dilute hydrochloric acid, $k_5/k_{-4} =$ *ca.* 10^3, and with a ratio as high as this it was necessary to use a very high concentration of iron(II), the product participating in the reverse of the first stage of the reaction, in order to detect the retardation of the overall reaction rate. If the kinetic behaviour of the system is consistent with the application of the stationary-state approximation to the concentration of the unstable intermediate state of the 2-equivalent reagent, then it should be possible to find a lower limit for the magnitude of the rate constant for the second stage of the reaction, relative to that for the forward first stage. However, calculations show that, for deviations from stationary-state kinetics to be detectable, this ratio, k_5/k_4 in the iron(III)–tin(II) system, could be as low as 10—10^2, corresponding to a maximum concentration of the unstable intermediate of 1—8% of the initial concentration of the 2-equivalent reagent. Such a high concentration of intermediate is improbable; it is evident that in these circumstances the mechanism we have assumed would not hold and the second stage would be disproportionation of the unstable intermediate. We know of no reaction between metal ions where this is the major route of disappearance of an unstable intermediate, and we conclude that the minimum value of the ratio of the rate constant of the second stage to that of the forward first stage is in general much larger than 10^2, without being able to suggest a definite value. Probably 10^4 is a conservative lower limit. We have thus placed limits on the rate constants of the forward and reverse first-stage reactions, relative to the second-stage rate constant, and so we conclude that the reverse first-stage rate constant must exceed that for the corresponding forward reaction, if deviations are observed from simple kinetics which can be ascribed to competition for an unstable intermediate. This condition can also be expressed by the statement that such deviations will be observed only if the first stage of the reaction involves a positive standard free-energy change in the forward direction. If this condition is met, then the thermodynamic instability (*i.e.*, the magnitude of the disproportionation constant) of the intermediate state of the 2-equivalent change reactant would not be expected to influence greatly the competition for this intermediate. An increase in its instability is likely to increase the rates of the competing reactions to a similar extent, and so their ratio, upon which the deviation from simple second-order kinetics depends, will be little changed. The reverse of the first stage of the reaction is likely to be more prominent in systems in which the negative standard free-energy change for the overall reaction is low. Thus, the possibility of demonstrating by kinetic experiments the presence of an unstable intermediate in systems of this type is more favourable for cases in which the (standard) oxidation–reduction potentials of the constituent couples are close together. In the iron(III)–tin(II) system, the decrease in importance of the reverse of the first stage in the more strongly-complexing chloride medium suggests that the iron and tin potentials have been moved further apart than they are in perchlorate solutions. This implies that complexing with chloride ions causes a bigger decrease in the tin(III)–tin(II) potential than in the iron(III)–iron(II) potential.

Reaction between Hydrogen Peroxide and Tin(II).—In this system, if tin(III) is formed as an intermediate, so also must the hydroxyl radical, and the reaction would probably be of the chain type, such as

$$\mathrm{Sn^{II}} + \mathrm{H_2O_2} \longrightarrow \mathrm{Sn^{III}} + \mathrm{OH}$$

$$\mathrm{Sn^{III}} + \mathrm{H_2O_2} \longrightarrow \mathrm{Sn^{IV}} + \mathrm{OH}$$

$$\mathrm{Sn^{II}} + \mathrm{OH} \longrightarrow \mathrm{Sn^{III}}$$

$$\mathrm{Sn^{III}} + \mathrm{OH} \longrightarrow \mathrm{Sn^{IV}}$$

The last step is one of several chain-terminating reactions which can be envisaged. Apart from a chain-breaking effect in removing tin(III), trioxalatocobaltate(III) might also remove OH radicals through a reaction such as

$$\mathrm{Co(C_2O_4)_3{}^{3-} + OH \longrightarrow Co^{2+} + 2C_2O_4{}^{2-} + 2CO_2 + OH^-}$$

This type of behaviour has been demonstrated with strong 1-equivalent oxidants and oxalatopenta-amminecobalt(III).[14]

The approximate rate of reaction between hydrogen peroxide and tin(II) was found by adding an excess of cerium(IV) to samples of the reaction mixture and titrating the remaining cerium(IV) with iron(II). This enabled the sum of the hydrogen peroxide and tin(II) concentrations to be determined. The stoicheiometry of the reaction between them was shown to be *ca.* 1·0 by colorimetric determination of hydrogen peroxide remaining after the termination of a reaction in which it was present in excess. Hence the separate concentrations of hydrogen peroxide and tin(II) could be found from the combined concentration. At 9·7° with *ca.* 6mM-hydrogen peroxide and *ca.* 2mM-tin(II) in 1·00M-hydrochloric acid solution, the second-order velocity constant is *ca.* 10^3 l. mole^{-1} min.$^{-1}$, on the assumption that the reaction is first-order in each of the reactants. With similar concentrations of the reactants and in the presence of *ca.* 1mM-trioxalatocobaltate(III) there was no consumption of the latter at room temperature. Also, the reaction was complete in 3 minutes whether the cobalt(III) complex was present or not. Other experiments were done in the presence of *ca.* 1mM-trioxalatocobaltate(III) or 3·5mM-aquopenta-amminecobalt(III), with higher concentrations of the reactants, *ca.* 10mM; again no consumption of cobalt(III) complex was observed. The procedure in these rapid-mixing experiments was similar to that used in the cerium(IV)–tin(II) system.

These observations do not appear consistent with the chain mechanism involving tin(III) suggested above. As a 1-equivalent oxidant, hydrogen peroxide is only of moderate strength and trioxalatocobaltate(III) should compete fairly readily with it for tin(III), even if aquopenta-amminecobalt(III) will not. Also, if the reaction involves chains, its rate would be slowed by the partial removal of carriers, but no change in rate was observed in the presence of the complexes. In previous investigations of this reaction, oxygen isotope fractionation is consistent with a 2-equivalent mechanism, in which the change $\mathrm{Sn^{II} + H_2O_2 \longrightarrow Sn^{IV}}$ involves only a single oxidation–reduction step.[15] However, the rates of reduction of hydrogen peroxide by various metal ions have been interpreted in terms of a 1-equivalent rate-determining step.[16] The latter conclusion seems inconsistent with the present results, but, although the rate of reaction may be related to the energetics of a 1-equivalent process, the resulting tin(III) and hydroxyl radical could undergo a further 1-equivalent change before they separate. Thus, as previously suggested,[1] it is possible that a 2-equivalent oxidation-state change can occur by successive 1-equivalent changes within the same collision complex. The methods described in the present Paper do not allow distinction to be made between a 2-equivalent change and a 1-equivalent change rapidly followed by a second such change before the intermediates separate. The formally analogous oxidation of uranium(IV) to uranium(VI) has been shown [17] to proceed by a chain reaction involving 1-equivalent changes in oxidation state. However, the stability of the intermediate state, uranium(V), is much greater than that of tin(III), so that the 1-equivalent change is more favourable in the uranium system.

Reactions of Bromine and of Iodine with Tin(II).—The solutions of the halogen and tin(II) were mixed rapidly at room temperature (*ca.* 18°); in all experiments observation of the colour change showed that reaction was complete within a few seconds. With bromine,

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[14] P. Saffir and H. Taube, *J. Amer. Chem. Soc.*, 1960, **82**, 13.
[15] A. E. Cahill and H. Taube, *J. Amer. Chem. Soc.*, 1952, **74**, 2312.
[16] W. C. E. Higginson, D. Sutton, and P. Wright, *J.*, 1953, 1380.
[17] F. B. Baker and T. W. Newton, *J. Phys. Chem.*, 1961, **65**, 1897.

the stock solution was 0·098M-bromine in 1·00M-hydrochloric acid, and after mixing with tin(II) solution concentrations were 2·46—6·15mM-bromine, 11mM-tin(II), and 1·00M-hydrochloric acid. In the presence of 1·00M-chloride, *ca.* 60% of the total bromine is in the form of Br_2Cl^- and the remainder is molecular bromine. With iodine, the concentration of hydrochloric acid after mixing was 1·00M in all experiments, but two stock solutions of iodine were used, one containing 1·43mM-iodine in 1·00M-hydrochloric acid and the other 30mM-iodine in 0·120M-potassium iodide. In the former stock solution about two-thirds of the iodine is in the form of I_2Cl^-, while in the stock solution in aqueous potassium iodide about 1·5% is in the form of molecular iodine, the remainder being tri-iodide. If, when the latter stock solution is mixed with the tin(II) solution in hydrochloric acid, equilibration between halogen species occurs before the oxidation–reduction, then *ca.* 85% of the iodine would occur as I_3^-, *ca.* 10% as I_2Cl^-, and *ca.* 5% as I_2. These proportions have been calculated from the values of the constants for the association of halide ions with molecular halogens in water given in Sidgwick's summary.[18] After mixing with tin(II), concentrations were 0·28—0·43mM-total iodine and 2·0—11·0mM-tin(II) for experiments with the iodine in hydrochloric acid stock solution, and 6·0mM-total iodine and 9·0mM-tin(II) for experiments with the tri-iodide stock solution.

Rapid-mixing experiments were also conducted in the presence of *ca.* 1mM-trioxalatocobaltate(III) and *ca.* 0·7mM-$Co(YOH)H_2O$; other concentrations were as given above. In no experiment was any consumption of cobalt(III) complex observed. Consequently, we conclude that the oxidations of tin(II) by bromine and iodine are of the 2-equivalent change type, similar to that by hydrogen peroxide. In the case of iodine this conclusion seems certain, as the following arguments show. From the bond-dissociation energy of molecular iodine,[19] and the oxidation–reduction potential for the iodine–iodide couple,[20] the potential of the couples $I_2 + e^- = I^- + I$, and $I + e^- = I^-$ are *ca.* −0·2 and +1·3 v, respectively. Even if the first couple is more correctly represented by $I_2 + e^- = I_2^-$, its potential is unlikely to exceed *ca.* +0·2 v. On the other hand, the behaviour of the iron(III)–tin(II) reaction in 1M-hydrochloric acid is consistent with a potential of not less than *ca.* +0·8 v for the tin(III)–tin(II) couple under these conditions. Thus, the standard free-energy change for a 1-equivalent first step in the oxidation of tin(II) by iodine is likely to be at least +14 kcal. mole^{-1}, and this step would be slow. With such a first step, the overall reaction would probably be of the chain type, analogous to that mentioned above as a possibility for the hydrogen peroxide–tin(II) system; only in this event could such a first step be consistent with the high overall rate of reaction observed. The chains would need to be long, and in the presence of potential chain-breakers such as cobalt(III) complexes the rate of reaction should be greatly reduced. However, reaction was complete within the time of mixing, a few seconds, even in the presence of these complexes. The chain-propagating step which the presence of cobalt(III) complexes would be expected to affect is $I_2(I_3^-) + Sn^{III} \longrightarrow I_2^- + Sn^{IV}\ (+I^-)$. Since molecular iodine, or tri-iodide ion, is a very weak 1-equivalent oxidant, there seems little doubt that the cobalt(III) complexes should be highly effective in the competition for tin(III).

Reaction between Thallium(III) *and Tin*(II).—This oxidation–reduction was found to be complete in less than 10 sec. at −6° in *ca.* 1·3M-hydrochloric acid with *ca.* 10mM-reactants. A small excess of tin(II) was used and rapid titration with cerium(IV) immediately after mixing gave titres consistent with completion of the reaction; cerium(IV) does not oxidise thallous ion or thallous chloride suspensions rapidly. The rapid-mixing technique was used for experiments with trioxalatocobaltate(III) or chloroaquotetra-amminecobalt(III) present and for the corresponding control experiments in the absence of a cobalt(III)

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[18] N. V. Sidgwick, "The Chemical Elements and Their Compounds," Oxford, 1950, vol. 2, p. 1193.

[19] T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd edn., Butterworths, London, 1958, p. 233.

[20] Standard oxidation–reduction potentials are taken from W. M. Latimer, "Oxidation Potentials," 2nd edn., Prentice-Hall, New York, 1952.

complex. The only modification of technique compared with that used with the cerium(IV)–tin(II) system was that *ca.* 2 min. after mixing the solution was rapidly filtered to remove solid thallous chloride before optical density measurements were made. These experiments were at room temperature, and concentrations of reagents immediately after mixing were 2·0—15mM-thallium(III), 2·0—15mM-tin(II), *ca.* 1mM-trioxalatocobaltate(III) or *ca.* 3mM-chloroaquotetra-amminecobalt(III), and 1·44M-hydrochloric acid. The concentrations of thallium(III) and tin(II) were not equal; in some experiments thallium(III) was present in excess, and tin(II) in others. After making allowance for the small changes in optical density obtained in control experiments in the absence of thallium(III), we found that there was no consumption of these complexes induced by the thallium(III)–tin(II) reaction. Finally, a few experiments were done at 9·7° using the slow-mixing technique, the time of addition of thallium(III) to a solution containing trioxalatocobaltate(III) and an excess of tin(II) being *ca.* 40 min. Concentrations were similar to those in the rapid-mixing experiments. Again no consumption of cobalt(III) complex was observed. Thus, the thallium(III)–tin(II) reaction appears to be of the single-stage 2-equivalent change type. Use was made of chloroaquotetra-amminecobalt(III) because in *ca.* 1M-hydrochloric acid thallium(III) is present in anionic forms [21] and tin(III) is likely to be similar in this respect. Consequently we thought that the competition between thallium(III) and a cobalt(III) complex for tin(III), if the latter were formed, might be improved in favour of the complex if it were positively charged.

Reaction between Mercury(II) *and Tin*(II).—When solutions of mercury(II) and tin(II) in dilute hydrochloric or perchloric acids are mixed, a fairly rapid oxidation–reduction occurs, as shown if tin(II) is present in excess by the formation of a grey precipitate of metallic mercury. If mercury(II) is present in excess in dilute hydrochloric acid, a white precipitate of mercurous chloride is obtained. No precipitate is observed if the reaction takes place in dilute perchloric acid, with mercury(II) in excess, but the formation of the ion Hg_2^{2+} was demonstrated spectrophotometrically. Such measurements showed that this reaction is virtually complete in 1 minute or less with reactant concentrations of the order of millimolar, and the rapid formation of precipitates in the other cases indicates that a similar conclusion applies to them also.

Rapid-mixing experiments were conducted with *ca.* 1mM-trioxalatocobaltate(III) present in 1·33M-perchloric acid with 0·61mM-mercury(II) and 0·30mM-tin(II), and in 1·00M-hydrochloric acid with 8·3mM-mercury(II) and 3·0mM-tin(II). No consumption of the complex was observed. Similar experiments showed that the reaction in perchloric acid was complete in *ca.* 1 minute in the presence of the cobalt(III) complex. However, in experiments with tin(II) present in excess a large consumption of cobalt(III) complex was found. Thus, in experiments using the rapid-mixing techniques in 1·00M-hydrochloric acid with initial concentrations of 1·67mM-mercury(II), *ca.* 16mM-tin(II), and *ca.* 4mM-trioxalatocobaltate(III) or 13·3mM-aquopenta-amminecobalt(III), *ca.* 90% of the former or *ca.* 10% of the latter complex was consumed at room temperature (*ca.* 18°). At 0° the proportions consumed were *ca.* 20% and less than 2%, respectively. Unusual features of these cobalt(III) consumptions are the marked dependence on temperature, which we have not observed in other systems, and the high consumption of trioxalatocobaltate(III) at room temperature. Even if two tin(III) species were produced for each mercury(II) reduced to mercury metal and these tin(III) species reacted solely with trioxalatocobaltate(III), the consumption of the latter would have been slightly lower than that observed. Experiments showed that, as reported previously,[22] cobalt(III) complexes may be reduced when shaken with metallic mercury. We found that the colour of a dilute aqueous solution of trioxalatocobaltate(III) was discharged in *ca.* 30 seconds on shaking with metallic mercury; the finely-divided metal formed in the reduction of mercury(II) is likely to be much more rapid in its reducing action. Because of this behaviour of mercury metal, we

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[21] "Stability Constants," *Chem. Soc. Special Publ.* No. 7, 1958, p. 107.

[22] J. Császár, L. Kiss, and J. Balog, *Acta Chim. Acad. Sci. Hung.*, 1962, **33**, 399.

cannot cite the consumption of cobalt(III) complexes as evidence of the formation of tin(III) in the mercury(II)–tin(II) system. With mercury(II) in excess, no cobalt(III) consumption was found, but our calculations and experiments with the cerium(IV)–tin(II) system have shown that the sensitivity of the method is decreased when the oxidising agent is present in excess of tin(II). Since mercury(II) is a much weaker oxidant than cerium(IV), the lack of consumption of cobalt(III) in the absence of a mercury metal precipitate points to the occurrence of a 2-equivalent reduction, but we did not regard this evidence as adequate. Accordingly we adopted another method for investigating the system.

If a dilute solution of mercuric perchlorate is rapidly mixed in a Y-shaped tube with an excess of dilute stannous perchlorate, the solution immediately becomes grey in colour, but remains transparent for a few seconds before becoming opaque and a darker grey as the droplets of mercury metal coalesce. In a similar experiment, mercurous perchlorate and tin(II) chloride were mixed; concentrations on mixing were 3·8mM-mercury(I), 17mM-tin(II), 1·0M-chloride, 1·0M-perchlorate, and 2·0M-hydrogen ion. A white precipitate formed instantaneously and immediately began to turn grey, the change in colour being complete after *ca.* 30 sec. This experiment shows that in such a system calomel is precipitated very rapidly from mercurous ion and is not immediately reduced by tin(II) to mercury metal. We then argued that if the mechanism of reduction of mercury(II) follows the scheme:

$$\mathrm{Hg^{II} + Sn^{II} \longrightarrow Hg^0{}_{(aq)} + Sn^{IV}}$$

$$\mathrm{Hg^{II} + Hg^0{}_{(aq)} \longrightarrow (Hg^I)_2 \xrightarrow{Cl^-} Hg_2Cl_2}$$

$$\mathrm{Hg^0{}_{(aq)} \longrightarrow Hg^0{}_{(liq)}}$$

where $\mathrm{Hg^0{}_{(aq)}}$ represents the mercury atom in aqueous solution, it might be possible to reduce mercury(II) by an excess of tin(II) in the presence of chloride ions without producing calomel. This would require careful mixing to avoid local excesses of mercury(II) which would permit the second reaction. Even with good mixing and a large excess of tin(II), the avoidance of calomel formation would only be possible if the values of the rate constants for the various stages were appropriately related to one another. When solutions of mercuric perchlorate and tin(II) chloride were rapidly mixed in the Y-shaped tube, a white precipitate was formed even with the highest ratio of tin(II) to mercuric ion concentrations which was used, the concentrations immediately after mixing being 94mM-tin(II), 0·42mM-mercury(II), and 1·90M-hydrochloric acid. With these concentrations, the white precipitate became grey in *ca.* 10 sec. To improve the mixing the mercury(II) solution was added rapidly by means of a small syringe to a well-stirred solution of tin(II). Concentrations after mixing were as given above for the highest-ratio experiment conducted in the Y-shaped tube. Under these conditions no transient formation of a white colour was observed; the system showed the same deepening grey colour change due to precipitation of metallic mercury as was observed on mixing an excess of stannous perchlorate with mercurous perchlorate. For comparison, a similar experiment was done by using the syringe-mixing technique with mercurous perchlorate in place of mercuric perchlorate. Concentrations immediately after mixing were 94mM-tin(II), 0·35mM-mercury(I), and 1·90M-hydrochloric acid. Here an immediate white precipitate was observed. The change in colour of this precipitate to grey, complete in *ca.* 15 sec., was more rapid than that observed when mixing was done in the Y-shaped tube, but this is probably due to the better mixing giving a smaller particle size of the calomel, with a consequently more rapid reduction by tin(II).

The observation that the formation of calomel can be avoided in the reduction of mercury(II) by tin(II) in the presence of chloride is consistent with the occurrence of a 2-equivalent change in the initial stage. It is necessary to show that the formation of calomel would be improbable if the first stage is of the 1-equivalent type. In this case the mechanism is likely to be of the chain type:

$$\begin{aligned}
\mathrm{Hg^{II}} + \mathrm{Sn^{II}} &\rightleftharpoons \mathrm{Hg^{I}} + \mathrm{Sn^{III}} \\
\mathrm{Hg^{I}} + \mathrm{Sn^{II}} &\longrightarrow \mathrm{Hg^{0}{}_{(aq)}} + \mathrm{Sn^{III}} \\
\mathrm{Hg^{II}} + \mathrm{Sn^{III}} &\longrightarrow \mathrm{Hg^{I}} + \mathrm{Sn^{IV}} \\
\mathrm{Hg^{I}} + \mathrm{Sn^{III}} &\longrightarrow \mathrm{Hg^{0}{}_{(aq)}} + \mathrm{Sn^{IV}} \\
2\mathrm{Sn^{III}} &\longrightarrow \mathrm{Sn^{II}} + \mathrm{Sn^{IV}} \\
2\mathrm{Hg^{I}} &\longrightarrow (\mathrm{Hg^{I}})_2 \\
\mathrm{Hg^{II}} + \mathrm{Hg^{0}{}_{(aq)}} &\longrightarrow (\mathrm{Hg^{I}})_2 \\
\mathrm{Hg^{0}{}_{(aq)}} &\longrightarrow \mathrm{Hg^{0}{}_{(liq)}}
\end{aligned}$$

in which the second and third reactions are chain carriers, and the fourth, fifth, and sixth are chain-terminating reactions. As discussed for the alternative scheme involving a 2-equivalent change in the first step, the formation of dimeric mercury(I) through the penultimate reaction in the above mechanism is likely to be avoided under the conditions of mixing employed. However, the rate constants of oxidation–reduction reactions, apart from those involving low-spin transition-metal complexes, are in general of such a magnitude that it would be surprising if the disappearance of monomeric mercury(I) through the second reaction in the series could occur so rapidly as to exclude the competing dimerisation reaction. Thus, some dimeric mercury(I) and hence some calomel formation are to be expected if the reaction scheme involves a 1-equivalent reaction as the first stage, even though tin(II) is present in considerably higher initial concentration than mercury(II).

Finally, some evidence can be gained by comparing oxidation–reduction potentials in the mercury and tin systems. Those potentials of interest have not been measured, but can be estimated in various ways with sufficient accuracy for our purpose. From the solubility of mercury metal in water [23] and the standard oxidation–reduction potential for the couple $\mathrm{Hg^{2+}} + 2e^- = \mathrm{Hg^0{}_{(liq)}}$,[20] we can calculate a value of +0·66 v for the couple $\mathrm{Hg^{2+}} + 2e^- = \mathrm{Hg^0{}_{(aq)}}$. Now, the dimeric ion $\mathrm{Hg_2{}^{2+}}$ dissociates heterolytically in solution, rather than homolytically to give monomeric $\mathrm{Hg^+}$.[23] Consequently, monomeric $\mathrm{Hg^+}$ will be less stable than the products of its disproportionation, $\mathrm{Hg^{2+}}$ and $\mathrm{Hg^0{}_{(aq)}}$, so that we can deduce that the potentials of the couples $\mathrm{Hg^{2+}} + e^- = \mathrm{Hg^+}$, and $\mathrm{Hg^+} + e^- = \mathrm{Hg^0{}_{(aq)}}$ are less than +0·66 and exceed +0·66 v, respectively. The oxidation of ferrous ion by mercuric ion involves the primary step $\mathrm{Fe^{2+}} + \mathrm{Hg^{2+}} \longrightarrow \mathrm{Fe^{3+}} + \mathrm{Hg^+}$ and is slow at 80°.[24] This is in accord with a considerably lower potential for the couple $\mathrm{Hg^{2+}} + e^- = \mathrm{Hg^+}$ than that, +0·77 v,[20] for the couple $\mathrm{Fe^{3+}} + e^- = \mathrm{Fe^{2+}}$. On the other hand, the dominant primary step in the oxidation of aquovanadium(III) ion by mercuric ion is thought to be $\mathrm{V^{3+}} + \mathrm{Hg^{2+}} \longrightarrow \mathrm{VO^{2+}} + \mathrm{Hg^+} + 2\mathrm{H^+}$, and there is evidence of retardation by $\mathrm{VO^{2+}}$.[25] Since the reverse of this primary step is important, the standard free-energy change in the forward direction must be positive, but it can only be small because the overall reaction occurs fairly readily at 15°. Accordingly, we suggest a value of *ca.* +0·2 v for the couple $\mathrm{Hg^{2+}} + e^- = \mathrm{Hg^+}$, slightly lower than the value of +0·36 v for the couple $\mathrm{VO^{2+}} + 2\mathrm{H^+} + e^- = \mathrm{V^{3+}}$.[20] In this case, the potential of the couple $\mathrm{Hg^+} + e^- = \mathrm{Hg^0{}_{(aq.)}}$ will be *ca.* +1·1 v. These figures correspond to a positive standard free-energy change of *ca.* 33 kcal. mole⁻¹ for the dissociation $\mathrm{Hg_2{}^{2+}} \longrightarrow 2\mathrm{Hg^+}$ in aqueous solution; this value may be compared with the previously suggested [26] value of 42 kcal. mole⁻¹. It should be noted that we are using indiscriminately both standard potentials and potentials estimated from the behaviour of reactions carried out in solutions of high ionic strength. However, errors due to differences in medium are likely to be of small importance compared with the errors inherent in estimates based on kinetic evidence.

[23] H. C. Moser and A. F. Voigt, *J. Amer. Chem. Soc.*, 1957, **79**, 1837.
[24] A. W. Adamson, *Discuss. Faraday Soc.*, 1960, **29**, 125.
[25] W. C. E. Higginson, D. R. Rosseinsky, J. B. Stead, and A. G. Sykes, *Discuss. Faraday Soc.*, 1960, **29**, 55.
[26] G. H. Cartledge, *J. Amer. Chem. Soc.*, 1941, **63**, 906.

In estimating the potentials of couples involving tin(III) in perchlorate solutions we can make use of observations [8] on the oxidation of stannous ion by ferric ion in this medium. The reaction is slow at 55° and we have concluded earlier in this Paper that accumulation of the product ferrous ion causes a marked reversal of the first stage of the reaction, $Fe^{3+} + Sn^{2+} \longrightarrow Fe^{2+} + Sn^{3+}$. This reaction evidently involves a positive standard free-energy change in the forward direction, and by comparison with the potential of +0·77 v for the couple $Fe^{3+} + e^- = Fe^{2+}$, we estimate a value of *ca.* +1·2 v for the couple $Sn^{3+} + e^- = Sn^{2+}$. We then obtain a value of *ca.* −0·4 v for the couple $Sn^{4+} + e^- = Sn^{3+}$ by assuming a value of *ca.* +0·4 v for the couple $Sn^{4+} + 2e^- = Sn^{2+}$ in perchloric acid. The value of +0·15 v quoted [20] for the tin(IV)–tin(II) couple refers to solutions in aqueous hydrochloric acid.

Our estimated values for the potentials of the couples $Hg^{2+} + e^- = Hg^+$ and $Sn^{3+} + e^- = Sn^{2+}$ suggest that a 1-equivalent first step in the oxidation–reduction between mercuric and stannous ions would be accompanied by a positive standard free-energy change of *ca.* 23 kcal. mole^{-1}. The overall reaction is therefore unlikely to be as rapid as that observed unless the mechanism involves long chains. However, we should expect dimerisation of Hg^+ to restrict the chain length; moreover, the reaction was still rapid in the presence of trioxalatocobaltate(III) which should be an effective chain terminator by removing tin(III). To summarise, although none of our evidence leads to a clear-cut conclusion on its own, on balance we consider that a 2-equivalent primary reaction is highly probable in the mercury(II)–tin(II) system.

Reaction between Chromium(VI) *and Tin*(II).—The reaction is $2Cr^{VI} + 3Sn^{II} \longrightarrow 2Cr^{III} + 3Sn^{IV}$, and it has been suggested [27] that the formally analogous reaction between chromium(VI) and arsenic(III) involves only 2-equivalent oxidation of the arsenic:

$$Cr^{VI} + As^{III} \longrightarrow Cr^{IV} + As^{V}$$
$$Cr^{VI} + Cr^{IV} \longrightarrow 2Cr^{V}$$
$$Cr^{V} + As^{III} \longrightarrow Cr^{III} + As^{V}$$

If the reaction with tin(II) involves a similar mechanism, then neither of the intermediates formed would be sufficiently reactive to reduce trioxalatocobaltate(III) during the short time, less than *ca.* 1 sec., necessary for completion of the reaction. A few experiments were done in the presence of trioxalatocobaltate(III), in all cases by using the rapid-mixing technique. Similar control experiments were performed in the absence of the complex because the chromium(III) product absorbed light at 605 mμ, the wavelength used for determining the concentration of the complex. The final concentration of complex was found by subtracting from the optical density observed at this wavelength the optical density found in the corresponding control experiment. In a series of experiments at 20° in 1M-hydrochloric acid with 1·25—6·25mM-chromium(VI), 3·0—12·5mM-tin(II), and *ca.* 1·0mM-trioxalatocobaltate(III), relatively large consumptions of the complex were observed, showing that it was competing fairly strongly with other oxidising species for a reducing intermediate. In a second series of experiments with 1·25mM-chromium(VI) and 12·5mM-tin(II), the trioxalatocobaltate(III) concentration was varied from 0·96mM to 19·2mM. The ratio of cobalt(III) consumed to chromium(VI) consumed rose rapidly to the region of 0·5 cobalt(III) per chromium(VI) with increase in the total trioxalatocobaltate(III) concentration up to *ca.* 5mM, but a further increase in the trioxalatocobaltate(III) concentration to 19·2mM caused little further increase in this ratio.

These results show that the chromium(VI)–tin(II) system does not follow the same type of mechanism as that postulated with arsenic(III) as the reducing agent. However, values of P obtained by using equation (3) varied for experiments in the first series from 4·6 with 6·25mM-chromium(VI) to 10·8 with 1·25mM-chromium(VI). This shows that the stoicheiometry of the reaction in the presence of cobalt(III) is not satisfactorily described

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[27] F. H. Westheimer, *Chem. Rev.*, 1949, **45**, 419.

by equation (3) although several mechanisms can be suggested which would lead to an equation of this form. Owing to the many competing reactions which are possible in a system in which tin(III), chromium(V), chromium(IV), and even chromium(II) may be intermediates, it seems unlikely that such stoicheiometry measurements can give positive evidence about the reaction mechanism. A further difficulty is the presence of part of the chromium(VI) in the dimeric form which may be kinetically significant and could lead to a complicated dependence of stoicheiometry upon total chromium(VI) concentration. Also, the assumption that the light absorption of the chromium(III) product is unaffected by participation of cobalt(III) in the reaction may be false, for it has been shown that the spectrum of chromium(III) produced by the reduction of chromium(VI) by tin(II) is abnormal and is sensitive to the conditions under which the reaction takes place.[28]

Apart from this experimental demonstration that a mechanism similar to that suggested for the chromium(VI)–arsenic(III) system does not hold with tin(II) as the reductant, there is a general objection to this mechanism. The second stage, $Cr^{VI} + Cr^{IV} \longrightarrow 2Cr^{V}$, although it is frequently postulated,[27,29] seems most unlikely. The reduction of chromium(VI) by ferrous ion in acid solution shows a strong retardation by ferric ion,[30] implying that the first stage, $Fe^{2+} + Cr^{VI} \longrightarrow Fe^{3+} + Cr^{V}$, involves a positive standard free-energy change. The oxidation–reduction potential for the couple $Cr^{VI} + e^- = Cr^{V}$ is in consequence less than that of the couple $Fe^{3+} + e^- = Fe^{2+}$ and is probably *ca.* +0·5 v. Similarly, the oxidation of chromic ion by cerium(IV) in dilute sulphuric acid is subject to retardation by cerous ion.[31] Consequently the potential of the couple $Cr^{IV} + e^- = Cr^{3+}$ must exceed that of $Ce^{IV} + e^- = Ce^{3+}$ in sulphuric acid, +1·44 v,[20] and is likely to be in the region of +1·8 v. By using these two estimated potentials, and the potential of +1·33 v [20] for the couple $Cr^{VI} + 3e^- = Cr^{3+}$, we obtain *ca.* +1·7 v for the couple $Cr^{V} + e^- = Cr^{IV}$. It seems difficult to produce any reasonable estimate of these potentials which would make the couple $Cr^{V} + e^- = Cr^{IV}$ substantially less than 1·0 v more positive than the couple $Cr^{VI} + e^- = Cr^{V}$. Hence the reaction $Cr^{VI} + Ce^{IV} \longrightarrow 2Cr^{V}$ will involve a positive standard free-energy change of not less than 20 kcal. mole^{-1} and will in consequence be too slow to be significant. Chromium(IV) as a powerful oxidant seems most likely to disappear through reduction by the reducing agent; there is also the possibility of disproportionation to chromium(V) and chromium(III). Finally, by combining our estimated $Cr^{IV} + e^- = Cr^{3+}$ potential with that of the couple $Cr^{3+} + e^- = Cr^{2+}$, —0·41 v,[20] we obtain the value of *ca.* +0·7 v for the couple $Cr^{IV} + 2e^- = Cr^{2+}$. This is sufficiently more positive than the potential of the couple $Sn^{IV} + 2e^- = Sn^{II}$ in chloride solutions, 0·15 v,[20] to make the formation of chromium(II) a possibility in this system.

Reaction between Permanganate and Tin(II).—The reaction was carried out by the usual rapid-mixing technique in the presence of $Co(YOH)H_2O$ in 1·00M-hydrochloric acid at 20°, and consumption of the complex was observed. Aqueous permanganate was used in one limb of the mixing tube, and tin(II) chloride and the cobalt(III) complex dissolved in dilute hydrochloric acid in the other. Experiments in the absence of complex showed that the reaction was complete within the time of mixing and that absorption of light by the products was negligible at the wavelength, 550 mμ, used to determine the concentration of complex. Owing to the stability of the complex in the presence of tin(II), no extrapolation procedure was necessary. Initial concentrations were in the ranges 0·43—2·15mM-permanganate, 3·6—9·0mM-tin(II), and 0·34—2·48mM-$Co(YOH)H_2O$. If the mechanism of the reaction involves the formation of tin(III) and its subsequent reaction with permanganate, then it can be shown that in the presence of a cobalt(III) complex the consumption of the latter is described by equation (3), if tin(II) is present in excess. By using this equation, values of P were obtained varying from 38 to 73. Although the value of

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[28] M. T. Beck and I. Bárdi, *Acta Phys. et Chem. Szeged.*, 1958, **4**, 54.
[29] R. Stewart, "Oxidation Mechanisms," Benjamin, New York, 1964, ch. 4.
[30] J. Y. Tong and E. L. King, *J. Amer. Chem. Soc.*, 1960, **82**, 3805.
[31] J. H. Espenson and E. L. King, *J. Amer. Chem. Soc.*, 1963, **85**, 3328.

P was constant, within the expected error of ±20%, for changes in the permanganate or cobalt(III) concentrations, there was a trend of P to higher values as the initial concentration of tin(II) was decreased. For most systems P is independent of changes in tin(II) concentration. We have not investigated whether this effect is a genuine feature of the permanganate–tin(II) system, or whether it is a consequence of the particular experimental conditions, *e.g.*, inefficient mixing or the presence of air. Owing to the many possible mechanisms which can be suggested for the system, we can conclude from our experiments only that tin(III) is produced as an intermediate. Known oxidation–reduction potentials [20,32] show that none of the intermediate states of manganese is likely to be sufficiently active to account for the reduction of $Co(YOH)H_2O$ in this system. The potentials also show that the standard free-energy change for the reaction $Mn^{VII} + Sn^{II} \longrightarrow Mn^{V} + Sn^{IV}$ is negative, whereas, accepting our estimate of *ca.* +0·8 v for the potential of the couple $Sn^{III} + e^- = Sn^{II}$ in hydrochloric acid, the standard free-energy change of the reaction $Mn^{VII} + Sn^{II} \longrightarrow Mn^{VI} + Sn^{III}$ is positive. Consequently, we think that the first stage in the reaction mechanism is possibly the formation of Mn^{V} by a 2-equivalent change. The step $Mn^{V} + Sn^{II} \longrightarrow Mn^{IV} + Sn^{III}$ then seems likely as the source of Sn^{III}.

EXPERIMENTAL

All chemicals were of AnalaR or other pure grade, or were prepared from such materials unless otherwise stated. *cis*-Chloroaquotetra-amminecobalt(III) sulphate, potassium trioxalatocobaltate(III) hydrate, and potassium di-μ-hydroxobis[dioxalatocobaltate(III)] hydrate were prepared and purified as described by Palmer.[33] Aquopenta-amminecobalt(III) perchlorate was prepared by hydrolysis of carbonatopenta-amminecobalt(III) nitrate in dilute perchloric acid; [34] the carbonato-complex was prepared by a standard method.[35] Sodium ethylenediaminetetra-acetatocobaltate(III) hydrate was prepared by Schwarzenbach's method.[36] Solutions of (*N*-hydroxyethylethylenediamine-*NN'N'*-triacetato)aquocobalt(III) were prepared by heating with charcoal aqueous solutions of sodium bromo-(*N*-hydroxyethylethylenediamine-*NN'N'*-triacetato)cobaltate(III) monohydrate to *ca.* 60° for *ca.* 10 min.; the solutions were then filtered. The solid bromo-complex was prepared and purified as previously described.[37] The trisodium *N*-hydroxyethylethylenediamine-*NN'N'*-triacetate used in the preparation was obtained from L. Light and Co.

Stock solutions of tin(II) chloride in dilute hydrochloric acid were prepared by dissolving AnalaR stannous chloride dihydrate in concentrated hydrochloric acid and diluting with boiled-out water; these solutions were kept under nitrogen and were fairly stable. Stannous perchlorate stock solutions were prepared by the reaction between an excess of pure granulated tin metal and a solution of cupric perchlorate in dilute perchloric acid.[38] These solutions were used on the day of their preparation since over longer periods a precipitate was slowly formed. The cupric perchlorate solution was obtained by dissolving pure cupric oxide in an excess of dilute perchloric acid. Cerium(IV) stock solutions were prepared by dissolving B.D.H. ammonium cerium(IV) sulphate (" low in other rare earths " grade) in dilute sulphuric acid and filtering after allowing to stand for several days. Thallium(III) chloride stock solution was obtained by dissolving freshly-precipitated thallic oxide in an excess of dilute hydrochloric acid and filtering; the oxide was obtained by oxidation of thallous chloride by potassium bromate in hydrochloric acid solution, followed by precipitation with aqueous ammonia.[39] Mercuric perchlorate stock solution was prepared by dissolving pure mercuric oxide in an excess of dilute perchloric acid. Mercurous perchlorate stock solution was obtained by shaking such a mercuric perchlorate solution with an excess of mercury metal for several hours. Iron(II) chloride stock solution was made by dissolving Hilger high purity iron powder in dilute hydrochloric acid. The solution was kept under nitrogen at *ca.* 0° in absence of light. Stock solutions of other oxidising agents

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[32] A. Carrington and M. C. R. Symons, *J.*, 1956, 3373.
[33] W. G. Palmer, " Experimental Inorganic Chemistry," Cambridge Univ. Press, 1954, pp. 545, 550, 551.
[34] A. C. Rutenberg and H. Taube, *J. Chem. Phys.*, 1952, **20**, 825.
[35] *Inorg. Synth.*, 1953, **4**, 171.
[36] G. Schwarzenbach, *Helv. Chim. Acta*, 1949, **32**, 839.
[37] M. L. Morris and D. H. Busch, *J. Amer. Chem. Soc.*, 1956, **78**, 5178.
[38] R. S. Tobias, *Acta Chem. Scand.*, 1958, **12**, 198.
[39] M. S. Sherrill and A. J. Haas, *J. Amer. Chem. Soc.*, 1936, **58**, 952.

were obtained by dissolving the appropriate pure reagent in water or dilute hydrochloric acid as required. A solution of titanium(IV) in sulphuric acid, for use in the spectrophotometric determination of hydrogen peroxide, was made as described by Belcher and Nutten.[40] The concentrations of reagents in stock solutions were determined by standard volumetric procedures. Solutions of the cobalt(III) complexes were made up by weight, and the concentrations were checked spectrophotometrically by making use of the extinction coefficients determined by previous workers. The spectrophotometer used for this and other purposes was a Unicam S.P. 500 fitted with a temperature-controlled cell holder.

The experiments with dioxalatodiaquocobaltate(III), produced by acidifying solutions of di-μ-hydroxobis[dioxalatocobaltate(III)], were conducted as described earlier.[5] This method was not suitable for most of the oxidants used in the present work, owing to their rapid reduction by tin(II), and we employed the " rapid-mixing " method, similar to that described for the tin(II)–vanadium(V) system.[1] Essentially the same technique was used for all except the iron(III)–tin(II) system. Into one limb of an inverted Y-shaped vessel, with lower limbs *ca.* 3 cm. in diameter and *ca.* 6 cm. long, a solution of tin(II) chloride was placed, and in the other the oxidising agent solution. The cobalt(III) complex was present in the tin(II) solution in some experiments and in the oxidising agent solution in others. The concentrations of hydrochloric acid in the solutions in the two limbs were each *ca.* 1M, except for experiments with cerium(IV) or permanganate as oxidant. Cerium(IV) stock solutions were in sulphuric acid, and the final concentration of this acid after mixing was 0·182M, that of hydrochloric acid, which was initially present with the tin(II) solution, being 1·30M. The solution of permanganate was made up in water and was not brought into contact with hydrochloric acid until the final mixing with tin(II); the final concentration of hydrochloric acid was 1·00M. Mixing was effected by rapid agitation of the vessel after the contents had come to temperature equilibrium in thermostats at 0 or 10°, or had attained room temperature (*ca.* 18°). Since the reactions are rapid, they were substantially complete shortly after mixing, and part of the solution was transferred to an optical cell maintained at a constant temperature, for the spectrophotometric determination of the concentration of cobalt(III) complex. Wavelengths used for this purpose were 605 for $Co(C_2O_4)_3^{3-}$, 550 for $Co(YOH)H_2O$, 536 for $Co(Y)^-$, 510 for $Co(NH_3)_4(H_2O)Cl^{2+}$, and 492 mμ for $Co(NH_3)_5H_2O^{3+}$. In experiments with the oxidants mercury(II) and thallium(III), filtration was necessary before the optical cell was filled. Owing to the slow reduction of $Co(C_2O_4)_3^{3-}$ and $Co(NH_3)_4(H_2O)Cl^{2+}$ by tin(II), readings were taken over a period of time, and the optical density immediately after reaction had occurred was found by extrapolation to the time of mixing. For each experiment a control was done with the same volumes of the same tin(II) and cobalt(III) solutions, but with the oxidant absent, in order to find the initial concentration of cobalt(III) after mixing, but before its induced reduction.

With cerium(IV) and with thallium(III) as oxidants, " slow-mixing " experiments were conducted in the following manner. The elongated tip of a 10-ml. burette was passed through a rubber bung in the neck of a small cylindrical vessel and was terminated in a fine jet just below the level which would be reached by 20 ml. of liquid in the vessel. An efficient screw-type glass stirrer was fitted to the vessel and pure nitrogen gas could be passed continuously into the vessel, escaping through the collar holding the stirrer rod. The vessel, containing 10·0 ml. of tin(II) solution and 10·0 ml. of a solution of cobalt(III) complex in boiled-out water was immersed in a thermostat; the burette was not thermostatted. During 5 min., allowed for the mixture to attain a steady temperature, nitrogen gas was passed into the vessel and the stirrer was operated slowly. Then, with good stirring, 10 ml. of oxidising agent solution was run in from the burette. With the tap fully open, the time of addition was 39 ± 1 min. When the addition was complete, the solution was filtered and the concentration of cobalt(III) was determined spectrophotometrically in the usual way. For each experiment a corresponding control was performed with the same concentration of reactants, but with the oxidising agent solution replaced by a dilute acid solution of the same concentration as the acid present in the oxidising agent solution.

With concentrations of iron(III) and tin(II) chlorides of *ca.* 10mM, the reaction between them takes several minutes for completion at 25° in 1M-hydrochloric acid. Rapid-mixing experiments, conducted in the absence of cobalt(III) complex, in which the total concentration of reducing species was found after the reaction was complete, showed that oxidation by molecular

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[40] R. Belcher and A. J. Nutten, " Qualitative Inorganic Analysis," Butterworths, London, 1955, p. 289.

oxygen must occur. This change in the total reducing strength of the mixture of iron(III) and tin(II) was not observed if the reaction took place in the absence of air. Consequently, mixing was done in the optical cell itself. The cell was fitted with a serum cap and one-way exit for gas, and could be flushed with nitrogen gas. Addition of solutions was made by hypodermic syringe through the serum cap, and stirring was effected by passing nitrogen gas through the solution by means of a hollow needle inserted through the cap. The cobalt(III) complex was $Co(YOH)H_2O$ which is quite stable to tin(II) solutions, but is slowly reduced by the iron(II) formed in the reaction. After mixing, readings of optical density at 550 mμ were taken over a period of time so that by extrapolation allowance could be made for the loss of cobalt(III) through reaction with iron(II). The same technique was used for mixing iron(III) and tin(II) solutions in the absence of cobalt(III) for measurements of the rate of the reaction. In the latter experiments the reactant concentrations were *ca.* 1mM, and the extent of reaction was found by spectrophotometric measurement at 335 mμ of the iron(III) concentration.

In the mercury(II)–tin(II) system, the completion of the reaction when excess of mercury(II) was present was established by spectrophotometric measurement at 236·5 mμ; at this wavelength the mercurous ion has a much greater extinction coefficient than any of the other species present except trioxalatocobaltate(III). For experiments in the presence of this complex additional measurements were made at 605 mμ, enabling the concentration of complex to be found. Knowing its extinction coefficient at 236·5 mμ, the appropriate correction could be made to obtain the contribution of mercurous ion to the optical density at this wavelength, and hence the mercurous concentration. More effective mixing of mercury(II) and tin(II) solutions than was found with the normal rapid-mixing technique was obtained by using a vessel equipped with a screw-type stirrer similar to that employed in the slow-mixing method. Mercury(II) perchlorate solution was added through a syringe fitted with a fine stainless steel needle, the tip of which was held below the surface of the tin(II) chloride solution during the addition.

The rate of the reaction between hydrogen peroxide and tin(II) was found by quenching the reaction mixture in an excess of cerium(IV) sulphate solution and titrating the remaining cerium(IV) with a standard ferrous ammonium sulphate solution, using ferroin as indicator. For experiments in the presence of trioxalatocobaltate(III) the completion of the reaction within 3 min. of mixing the tin(II) and hydrogen peroxide solutions was shown by adding a portion of the reaction mixture to a titanium(IV) solution and determining the optical density at 415 mμ. The titanium(IV)–hydrogen peroxide complex scarcely absorbs at 605 mμ, so that the trioxalatocobaltate(III) concentration could be found from a measurement at this wavelength and hence a correction made for the absorption due to this complex at 415 mμ. The method was calibrated by the use of solutions of known strength.

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