218. *Reducing Reactions of Tin*(II) *in Aqueous Solution. Part II.*[1] *The Reaction between Tin*(II) *and Vanadium*(V) *in Dilute Hydrochloric Acid.*

By D. J. Drye, W. C. E. Higginson, and P. Knowles.

Reduction of vanadium(V) by an excess of tin(II) in dilute hydrochloric acid yields a mixture of vanadium(III) and vanadium(IV). The dependence of the concentrations of these products upon reactant concentrations shows that the dominant initial step involves a 2-equivalent change in oxidation states, giving vanadium(III). Three distinct routes leading to the formation of vanadium(IV) are postulated.

When solutions of tin(II) and vanadium(V) in dilute hydrochloric acid are mixed, rapid oxidation–reduction occurs. If the initial concentration of vanadium(V) exceeds twice that of tin(II), vanadium(IV) is formed in concentration equal to twice the initial concentration of tin(II) and the excess of vanadium(V) remains unchanged. If the initial concentration of tin(II) exceeds that of vanadium(V), none of the latter remains and both vanadium(IV) and vanadium(III) appear as products. We summarise in Fig. 1 the results of several experiments in which an excess of a solution of tin(II) was mixed rapidly with a solution of vanadium(V); here, and subsequently, subscripts zero and infinity denote respectively initial and final concentrations. In all these experiments the solutions were mixed at −10° to avoid a slight irreproducibility found at 20°; otherwise the results obtained at these two temperatures were very similar. Changes in hydrochloric acid concentration from 0·50 to 0·95M caused only small changes in the proportions of products and we have included results obtained at both concentrations in Fig. 1. It can be seen that the proportion of vanadium(V) reduced to vanadium(III) is almost constant except for values of the ratio $[\mathrm{V^{V}}]_0/[\mathrm{Sn^{II}}]_0$ approaching unity. We attempted to interpret these observations in terms of the mechanism given in eqns. (1)—(4)

$$\mathrm{V^{V}} + \mathrm{Sn^{II}} \xrightarrow{k_1} \mathrm{V^{IV}} + \mathrm{Sn^{III}} \tag{1}$$

$$\mathrm{V^{V}} + \mathrm{Sn^{III}} \xrightarrow{k_2} \mathrm{V^{IV}} + \mathrm{Sn^{IV}} \tag{2}$$

$$\mathrm{V^{IV}} + \mathrm{Sn^{III}} \xrightarrow{k_3} \mathrm{V^{III}} + \mathrm{Sn^{IV}} \tag{3}$$

$$\mathrm{V^{V}} + \mathrm{V^{III}} \xrightarrow{k_4} 2\mathrm{V^{IV}} \tag{4}$$

Although we have rejected this mechanism, we include a simple kinetic analysis based on it since the reasons which led to its rejection are part of the evidence for the mechanism ultimately adopted. Reaction (4) must be included in considering experiments in which initially vanadium(V) is present in at least twice the concentration of tin(II) to account for the absence of vanadium(III) as a product. However, to simplify the analysis of systems in which tin(II) is in excess, we have omitted this reaction in the following treatment.

Considering reactions (1)—(3), we obtain

$$-\mathrm{d}[\mathrm{V^{V}}]/\mathrm{d}t = \{2k_1k_2[\mathrm{V^{V}}]^2[\mathrm{Sn^{II}}] + k_1k_3[\mathrm{V^{IV}}][\mathrm{V^{V}}][\mathrm{Sn^{II}}]\} \div \{k_2[\mathrm{V^{V}}] + k_3[\mathrm{V^{IV}}]\} \tag{5}$$

and

$$\mathrm{d}[\mathrm{V^{IV}}]/\mathrm{d}t = 2k_1k_2[\mathrm{V^{V}}]^2[\mathrm{Sn^{II}}] \div \{k_2[\mathrm{V^{V}}] + k_3[\mathrm{V^{IV}}]\} \tag{6}$$

by making the stationary-state approximation, $\mathrm{d}[\mathrm{Sn^{III}}]/\mathrm{d}t = 0$. By dividing eqn. (5) by eqn. (6) we then obtain

$$-\mathrm{d}[\mathrm{V^{V}}]/\mathrm{d}[\mathrm{V^{IV}}] = 1 + Q[\mathrm{V^{IV}}]/[\mathrm{V^{V}}], \tag{7}$$

where $Q = k_3/2k_2$.

---

[1] Part I, Higginson, Leigh, and Nightingale, *J.*, 1962, 435.

Integration of eqn. (7) gives

$$\frac{1}{\sqrt{Q-\frac{1}{4}}}\tan^{-1}\left\{\frac{[\mathrm{V^V}]/[\mathrm{V^{IV}}]+\frac{1}{2}}{\sqrt{Q-\frac{1}{4}}}\right\}$$
$$=\log_e\{[\mathrm{V^V}]^2+[\mathrm{V^V}][\mathrm{V^{IV}}]+Q[\mathrm{V^{IV}}]^2\}+\text{Constant.}$$

Initially, $[\mathrm{V^V}]=[\mathrm{V^V}]_0,[\mathrm{V^{IV}}]=[\mathrm{V^{IV}}]_0$, and at the end of the reaction, if tin is in excess, $[\mathrm{V^V}]=0$, $[\mathrm{V^{IV}}]=[\mathrm{V^{IV}}]_\infty$. We can therefore eliminate the constant of integration and so we obtain

$$\frac{1}{\sqrt{Q-\frac{1}{4}}}\left(\tan^{-1}\left\{\frac{[\mathrm{V^V}]_0/[\mathrm{V^{IV}}]_0+\frac{1}{2}}{\sqrt{Q-\frac{1}{4}}}\right\}-\tan^{-1}\left\{\frac{\frac{1}{2}}{\sqrt{Q-\frac{1}{4}}}\right\}\right)$$
$$=\log_e\left\{\frac{[\mathrm{V^V}]_0^2+[\mathrm{V^V}]_0[\mathrm{V^{IV}}]_0+Q[\mathrm{V^{IV}}]_0^2}{Q[\mathrm{V^{IV}}]_\infty^2}\right\}.$$

This equation can be written in the form

$$\frac{1}{2\sqrt{Q-\frac{1}{4}}}\left(\tan^{-1}\left\{\frac{R_0^{-1}+\frac{1}{2}}{\sqrt{Q-\frac{1}{4}}}\right\}-\tan^{-1}\left\{\frac{\frac{1}{2}}{\sqrt{Q-\frac{1}{4}}}\right\}\right)$$
$$=\log_e\frac{[\mathrm{V^V}]_0}{[\mathrm{V^{IV}}]_\infty}+\frac{1}{2}\log_e\left\{\frac{1}{Q}+\frac{R_0}{Q}+R_0^{\,2}\right\},\quad(8)$$

where $R_0=[\mathrm{V^{IV}}]_0/[\mathrm{V^V}]_0$.

It is evident from eqn. (8) that the proportion of vanadium(v) reduced to vanadium(IV) should be independent of the initial concentrations of tin(II) and vanadium(v), and should depend only on Q and R_0. The position of the broken line in Fig. 1 was calculated by using $R_0=0{\cdot}013$, the value in our experiments, and $Q=21$. Except at the higher values of $[\mathrm{V^V}]_0/[\mathrm{Sn^{II}}]_0$ the calculated line is in good accord with the experimental points. However, we have rejected this mechanism for several reasons. First, the value of Q necessary to fit our results corresponds to $k_3/k_2=42$, *i.e.*, tin(III) must react very much faster with vanadium(IV) than with vanadium(v). Our omission of reaction (4) does not alter this qualitative conclusion, for if this reaction is important the ratio k_3/k_2 must exceed 42. Now, vanadium(IV) reacts extremely slowly with tin(II), whereas the reaction between vanadium(v) and tin(II) is too fast for measurement by conventional methods. Although we should expect a smaller reactivity ratio between vanadium(v) and vanadium(IV) in their reduction by an active intermediate such as tin(III), it would be surprising if the order of reactivity were reversed to such an extent. Secondly, eqn. (8) predicts an increase in $[\mathrm{V^{III}}]_\infty/[\mathrm{V^V}]_0$ if R_0 is increased; a value of $R_0=0{\cdot}30$ with $Q=21$ corresponds to $[\mathrm{V^{III}}]_\infty/[\mathrm{V^V}]_0=0{\cdot}935$. The average value $[\mathrm{V^{III}}]_\infty/[\mathrm{V^V}]_0=0{\cdot}848$ was obtained from three experiments with $R_0=0{\cdot}30$ under otherwise similar conditions to those summarised in Fig. 1, the corresponding value with $R_0=0{\cdot}013$ being 0·825. This shows that eqn. (8) does not satisfactorily describe all our experimental results.

The strongest evidence against the mechanism given above was obtained by using trioxalatocobaltate(III) as a reagent for tin(III), as suggested previously.[1] Solutions of vanadium(v) containing trioxalatocobaltate(III) were mixed rapidly at 20° with solutions of tin(II). In each experiment the concentration of vanadium(IV) produced and the change in the concentration of the complex were measured spectrophotometrically. The initial concentrations of reagents were $4{\cdot}58\times10^{-3}$M-tin(II), $9{\cdot}96\times10^{-3}$M-vanadium(v), $0{\cdot}35$—$1{\cdot}09\times10^{-3}$M-trioxalatocobaltate(III), and 0·25M-hydrochloric acid. Similar experiments were also done with tin(II) present in slightly higher concentrations than vanadium(v). In all these experiments the concentration of vanadium(IV) produced was the same as in parallel experiments in the absence of trioxalatocobaltate(III) and the consumption of the latter did not exceed 2% of its initial concentration. Before concluding that these experiments indicate the absence of tin(III) as a major intermediate it was necessary to show that trioxalatocobaltate(III) can compete effectively with vanadium(V) and vanadium(IV) for tin(III). We already knew that if the vanadium(V)–tin(II) reaction follows reactions (1)—(4), then reaction (3) must be dominant compared with reaction (2), since $k_3/k_2 = 42$, and so we wished to find whether reaction (9)

$$\mathrm{Co(C_2O_4)_3}^{3-} + \mathrm{Sn^{III}} \xrightarrow{k_9} \mathrm{Co^{II}} + \mathrm{Sn^{IV}} \tag{9}$$

proceeds at a rate comparable with reaction (3). The value of k_3/k_9 could not be obtained by a direct experiment, but was found in the following way. We allowed dioxalatodiaquocobaltate(III) to react at 20° with tin(II) in the presence of vanadium(IV). In these experiments all the diaquo-complex was reduced to cobalt(II), tin(II) being in large excess, and a part of the vanadium(IV) was reduced to vanadium(III). Independent experiments showed that under similar conditions the extent of reduction of vanadium(IV) by tin(II) was negligible and that only a small correction was necessary to allow for the reduction of dioxalatodiaquocobaltate(III) by vanadium(III). The only major reactions which need to be considered are therefore

$$\mathrm{Co(C_2O_4)_2(H_2O)_2}^- + \mathrm{Sn^{II}} \xrightarrow{k_{10}} \mathrm{Co^{II}} + \mathrm{Sn^{III}} \tag{10}$$

$$\mathrm{Co(C_2O_4)_2(H_2O)_2}^- + \mathrm{Sn^{III}} \xrightarrow{k_{11}} \mathrm{Co^{II}} + \mathrm{Sn^{IV}} \tag{11}$$

$$\mathrm{V^{IV}} + \mathrm{Sn^{III}} \xrightarrow{k_3} \mathrm{V^{III}} + \mathrm{Sn^{IV}} \tag{3}$$

The induced reduction of vanadium(IV) in this system is exactly analogous to the induced reduction of trioxalatocobaltate(III) in tin(II)–dioxalatodiaquocobaltate(III) mixtures and is therefore described by an equation of the same form as eqn. (4) of Part I.[1] In the present case the equation is

$$P \log_{10}\{[\mathrm{V^{IV}}]_0/[\mathrm{V^{IV}}]_\infty\} = \log_{10}\{1 + P[\mathrm{Co(C_2O_4)_2(H_2O)_2}^-]_0/[\mathrm{V^{IV}}]_0\}, \tag{12}$$

where $P = 2k_{11}/k_3 - 1$. In a typical experiment, $[\mathrm{Sn^{II}}]_0 = 0{\cdot}055$M, $[\mathrm{Co(C_2O_4)_2(H_2O)_2}^-]_0 = 2{\cdot}26 \times 10^{-3}$M, $[\mathrm{V^{IV}}]_0 = 3{\cdot}82 \times 10^{-3}$M, and $[\mathrm{V^{IV}}]_\infty = 2{\cdot}56 \times 10^{-3}$M. By substitution in eqn. (12) we found $P = 1{\cdot}84$. The mean value of P obtained from this and four similar experiments, all in 0·25M-hydrochloric acid, was 1·90, hence $k_{11}/k_3 = 1{\cdot}45$ at 20°. We previously[1] found $k_{11}/k_9 = 2{\cdot}25$ at 20°, whence $k_3/k_9 = 1{\cdot}55$ under conditions identical with those in the competition experiments with the tin(II)–vanadium(V)–trioxalatocobaltate(III) system. This low value of k_3/k_9 indicates that a considerable proportion of trioxalatocobaltate(III) should be consumed in these competition experiments if the scheme given by reactions (1)—(4) and (9) is valid. An estimate of the expected consumption was made by a kinetic analysis similar to that described in Part I. For simplicity we omitted reaction (2) which plays a minor part in this scheme and, with $k_3/k_9 = 1{\cdot}55$, found that *ca.* 65% of the trioxalatocobaltate(III) should be consumed in the competition experiments in which vanadium(V) was present in excess. Since less than 2% was consumed, this provided the third indication that the mechanism summarised in reactions (1)—(4) is incorrect.

The most obvious alternative mechanism which avoids postulating the intermediate formation of tin(III) as a free entity involves a 2-equivalent change in the oxidation states of the reactants, eqn. (13):

$$\mathrm{V^{V}} + \mathrm{Sn^{II}} \xrightarrow{k_{13}} \mathrm{V^{III}} + \mathrm{Sn^{IV}}. \tag{13}$$

The formation of vanadium(IV) can then be attributed to reaction (4). A kinetic analysis based on this scheme leads to eqn. (14) for cases in which the initial concentration of tin(II) exceeds that of vanadium(V):

$$\frac{k_{13}}{k_4}\log_{10}\left\{1 - \frac{[\mathrm{V^V}]_0}{2[\mathrm{Sn^{II}}]_0} - \left(\frac{2k_4}{k_{13}} - 1\right)\frac{[\mathrm{V^{III}}]_\infty}{2[\mathrm{Sn^{II}}]_0}\right\} = \log_{10}\left\{1 - \frac{[\mathrm{V^V}]_0}{2[\mathrm{Sn^{II}}]_0} - \frac{[\mathrm{V^{III}}]_\infty}{2[\mathrm{Sn^{II}}]_0}\right\}. \tag{14}$$

We omit the derivation of this equation since it is a particular case, with $k_1 = 0$, of eqn. (20) which is derived later. In Fig. 2 we show as curves corresponding values of $[V^{III}]_\infty/[Sn^{II}]_0$ and $[V^V]_0/[Sn^{II}]_0$ which were calculated by substituting in eqn. (14) the values of k_{13}/k_4 indicated. The experimental points are those shown in Fig. 1. It can be seen that the predictions of the simple 2-equivalent mechanism are not in accord with our results. However, we have found that the following combination of reaction (13) and certain of the reactions originally suggested leads to an equation in reasonable agreement with experiment.

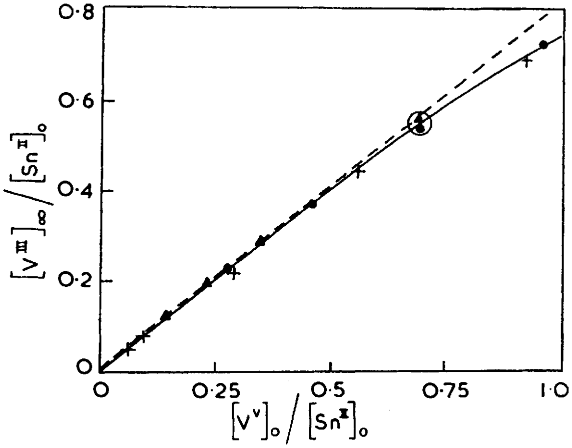

Fig. 1.
– – –, calc. from eqn. (8)
——, calc. from eqn. (20)

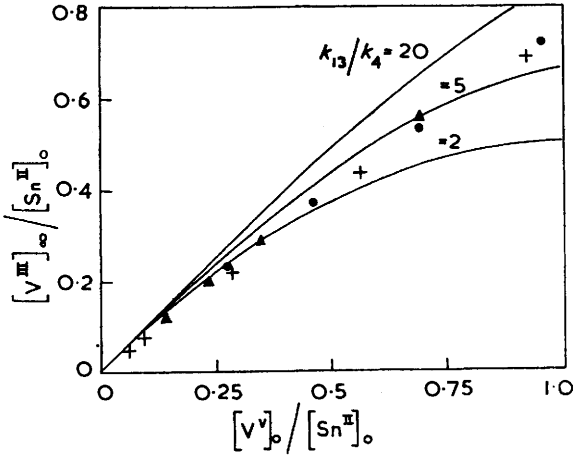

Fig. 2.
Curves calculated from eqn. (14).

FIGS. 1 and 2. Dependence of $[V^{III}]_\infty/[Sn^{II}]_0$ upon $[V^V]_0/[Sn^{II}]_0$.

Both Figs. ●, $[V^V]_0 = 19{\cdot}9 \times 10^{-3}$M, $[H^+] = 0{\cdot}50$M; ▲, $[V^V]_0 = 9{\cdot}96 \times 10^{-3}$M, $[H^+] = 0{\cdot}50$M; +, $[V^V]_0 = 3{\cdot}99 \times 10^{-3}$M, $[H^+] = 0{\cdot}95$M.

$$V^V + Sn^{II} \xrightarrow{k_{13}} V^{III} + Sn^{IV} \qquad (13)$$

$$V^V + Sn^{II} \xrightarrow{k_1} V^{IV} + Sn^{III} \qquad (1)$$

$$V^V + Sn^{III} \xrightarrow{k_3} V^{IV} + Sn^{IV} \qquad (2)$$

$$V^V + V^{III} \xrightarrow{k_4} 2V^{IV} \qquad (4)$$

For simplicity, we have omitted reaction (3) from the proposed scheme. Our justification is that we have already shown that if this reaction is important a considerable consumption of trioxalatocobaltate(III) should be observed in the competition experiments. Since the consumption of trioxalatocobaltate(III) was very small it follows that the contribution of reaction (3) must likewise be small. We have previously referred to the small increase in the yield of vanadium(III) obtained by greatly increasing the initial concentration of vanadium(IV); this effect also shows that reaction (3) occurs only to a minor extent. The conclusion that reaction (2) is the dominant route for the disappearance of tin(III) accords with the greater reactivity as an oxidising agent to be expected of vanadium(V) when compared with vanadium(IV).

From the above scheme we can write

$$\mathrm{d}[\mathrm{V^{III}}]/\mathrm{d}t = k_{13}[\mathrm{V^V}][\mathrm{Sn^{II}}] - k_4[\mathrm{V^V}][\mathrm{V^{III}}] \tag{15}$$

and, by using the stationary-state approximation, $\mathrm{d}[\mathrm{Sn^{III}}]/\mathrm{d}t = 0$, we obtain

$$-\mathrm{d}[\mathrm{V^V}]/\mathrm{d}t = (k_{13} + 2k_1)[\mathrm{V^V}][\mathrm{Sn^{II}}] + k_4[\mathrm{V^V}][\mathrm{V^{III}}]. \tag{16}$$

By dividing eqn. (16) by eqn. (15) we obtain

$$-\mathrm{d}[\mathrm{V^V}]/\mathrm{d}[\mathrm{V^{III}}] = \{(k_{13} + 2k_1)[\mathrm{Sn^{II}}] + k_4[\mathrm{V^{III}}]\} \div \{k_{13}[\mathrm{Sn^{II}}] - k_4[\mathrm{V^{III}}]\}\ . \tag{17}$$

If vanadium(III) is absent initially, we obtain from the stoicheiometry of the reaction the relation

$$[\mathrm{Sn^{II}}] = [\mathrm{Sn^{II}}]_0 + \tfrac{1}{2}[\mathrm{V^V}] - \tfrac{1}{2}[\mathrm{V^V}]_0 - \tfrac{1}{2}[\mathrm{V^{III}}]. \tag{18}$$

By using eqn. (18) to eliminate $[\mathrm{Sn^{II}}]$ from eqn. (17) we then obtain

$$-\frac{\mathrm{d}[\mathrm{V^V}]}{\mathrm{d}[\mathrm{V^{III}}]} = \frac{(k_{13} + 2k_1)([\mathrm{V^V}] + 2[\mathrm{Sn^{II}}]_0 - [\mathrm{V^V}]_0) + (2k_4 - k_{13} - 2k_1)[\mathrm{V^{III}}]}{k_{13}([\mathrm{V^V}] + 2[\mathrm{Sn^{II}}]_0 - [\mathrm{V^V}]_0) - (k_{13} + 2k_4)[\mathrm{V^{III}}]}\ . \tag{19}$$

On integration, eqn. (19) gives

$$\left(\frac{k_{13}}{k_4} + \frac{k_1}{k_4}\right)\log_{10}\left\{[\mathrm{V^V}] - [\mathrm{V^V}]_0 + 2[\mathrm{Sn^{II}}]_0 - \left(\frac{2k_4}{k_{13}} - 1 - \frac{2k_1}{k_{13}}\right)[\mathrm{V^{III}}]\right\}$$
$$= \log_{10}\{[\mathrm{V^V}] - [\mathrm{V^V}]_0 + 2[\mathrm{Sn^{II}}]_0 - [\mathrm{V^{III}}]\} + \text{Constant}.$$

Initially, $[\mathrm{V^V}] = [\mathrm{V^V}]_0$, $[\mathrm{V^{III}}] = 0$, and, if $[\mathrm{V^V}]_0 < [\mathrm{Sn^{II}}]_0$, when the reaction is complete $[\mathrm{V^V}] = 0$, $[\mathrm{V^{III}}] = [\mathrm{V^{III}}]_\infty$. The integration constant can therefore be eliminated, giving:

$$\left(\frac{k_{13}}{k_4} + \frac{k_1}{k_4}\right)\log_{10}\left\{1 - \frac{[\mathrm{V^V}]_0}{2[\mathrm{Sn^{II}}]_0} - \left(\frac{2k_4}{k_{13}} - 1 - \frac{2k_1}{k_{13}}\right)\frac{[\mathrm{V^{III}}]_\infty}{2[\mathrm{Sn^{II}}]_0}\right\}$$
$$= \log_{10}\left\{1 - \frac{[\mathrm{V^V}]_0}{2[\mathrm{Sn^{II}}]_0} - \frac{[\mathrm{V^{III}}]_\infty}{2[\mathrm{Sn^{II}}]_0}\right\}. \tag{20}$$

If we assume values of k_{13}/k_4 and k_1/k_{13} we can use eqn. (20) to calculate corresponding values of $[\mathrm{V^{III}}]_\infty/[\mathrm{Sn^{II}}]_0$ and $[\mathrm{V^V}]_0/[\mathrm{Sn^{II}}]_0$. The full line in Fig. 1 was obtained in this way, by assuming $k_{13}/k_4 = 20$ and $k_1/k_{13} = 0{\cdot}10$. Curves calculated by using values of k_1/k_{13} in the range 0·08—0·12 also fitted the experimental points reasonably well, the values of k_{13}/k_4 corresponding to these extremes being 14 and 30, respectively. On this basis we can conclude that about 90% of effective encounters between tin(II) and vanadium(V) lead directly to the formation of tin(IV) and vanadium(III) and that the remaining 10% give tin(III) and vanadium(IV) as primary products. Although the dominant reaction, (13), can be regarded kinetically as involving a 2-equivalent change in oxidation states, it is possible that the primary process is the formation of tin(III) and vanadium(IV), but that these remain adjacent long enough for a second 1-equivalent change giving tin(IV) and vanadium(III) to occur in the majority of encounters. A "sticky" collision between tin(II) and vanadium(V) seems possible in solutions containing 0·5M-free chloride ions, for about two-thirds of the total tin(II) is in anionic or uncharged forms.[2] Also, spectrophotometric evidence has been adduced[3] for the presence in low concentrations of a 1 : 1 association complex between tin(II) and uranium(VI) in solutions of these species in hydrochloric acid. We therefore suggest that the initial product of an encounter between tin(II) and vanadium(V) may be a similar association complex which we denote $(\mathrm{Sn + V})^{\mathrm{VII}}$. In this connection, eqn. (20) shows that for a given value of $[\mathrm{V^{V}}]_0/[\mathrm{Sn^{II}}]_0$ the corresponding value of $[\mathrm{V^{III}}]_\infty/[\mathrm{Sn^{II}}]_0$ should be independent of the absolute concentrations of the reactants. However, we found that the latter ratio decreases slightly with increase in the concentrations of reactants at constant $[\mathrm{V^{V}}]_0/[\mathrm{Sn^{II}}]_0$. This effect can be seen in the two ringed experimental points in Fig. 1. We suggest that apart from its decomposition to tin(IV) and vanadium(III) or to tin(III) and vanadium(IV), the association complex $(\mathrm{V + Sn})^{\mathrm{VII}}$ may persist sufficiently long for reaction (21) to occur to a limited extent.

$$(\mathrm{V + Sn})^{\mathrm{VII}} + \mathrm{V^{V}} \longrightarrow 2\mathrm{V^{IV}} + \mathrm{Sn^{IV}} \qquad (21)$$

About 20% of the vanadium(IV) formed in the reaction can be accounted for in this way and the probable value of k_1/k_{13} will in consequence be reduced to *ca.* 0·08. A kinetic analysis of the type given above showed that reactions (13) and (21) alone cannot account for our experimental results since much bigger changes than those observed in $[\mathrm{V^{III}}]_\infty/[\mathrm{Sn^{II}}]_0$ are predicted if $[\mathrm{V^{V}}]_0$ is altered at constant $[\mathrm{V^{V}}]_0/[\mathrm{Sn^{II}}]_0$. This analysis shows that reaction (4) may be less important in mixtures with tin(II) in excess than the ratio $k_{13}/k_4 = 20$ indicates, *i.e.* k_{13}/k_4 may exceed 20.

Summarising, we suggest that the primary processes in the reaction between tin(II) and vanadium(V) in dilute hydrochloric acid can be represented by

$$\begin{tikzcd}
 & & \mathrm{V^{III} + Sn^{IV}} & A \\
\mathrm{V^{V} + Sn^{II}} \arrow[r] & (\mathrm{V + Sn})^{\mathrm{VII}} \arrow[ur] \arrow[r] \arrow[dr, "+\mathrm{V^{V}}"'] & \mathrm{V^{IV} + Sn^{III}} & B \\
 & & 2\mathrm{V^{IV} + Sn^{IV}} & C
\end{tikzcd}$$

where $A > B > C$ indicates the relative extent of the three modes of decomposition of $(\mathrm{V + Sn})^{\mathrm{VII}}$. Although we have suggested that the dominant reaction A may involve the transitory intermediate formation of tin(III) and vanadium(IV) before their ultimate separation as tin(IV) and vanadium(III), we believe that this type of problem cannot be solved by kinetic studies. According to our reaction mechanism, vanadium(IV) is formed by three distinct routes, of which B followed by reaction (2) is the most important. The second route involves the oxidation by vanadium(V) in reaction (4) of part of the vanadium(III) produced in reaction A. The proportion of vanadium(IV) formed by this route increases with increase in the ratio $[\mathrm{V^{V}}]_0/[\mathrm{Sn^{II}}]_0$ and this is the main route for the formation of vanadium(IV) in mixtures in which the initial concentration of vanadium(V) considerably exceeds that of tin(II). The proportion of vanadium(IV) formed via the third route, C, is small under our experimental conditions, but should be substantial at high initial concentrations of vanadium(V).

EXPERIMENTAL

With the exception of vanadium stock solutions, reagents were prepared and standardised as described in Part I.[1] Vanadium(V) stock solutions in hydrochloric acid were prepared by dissolving a weighed quantity of " AnalaR " ammonium metavanadate in a small amount of M-sodium hydroxide and then adding sufficient dilute hydrochloric acid to give a final concentration of 0·5M-hydrochloric acid. These solutions were kept in the dark at 0° to minimise the formation of vanadium(IV). The concentration of vanadium(V) was determined by

---

[2] Vanderzee and Rhodes, *J. Amer. Chem. Soc.*, 1952, **74**, 3552.

[3] Moore, *J. Amer. Chem. Soc.*, 1955, **77**, 1504.

reduction with sulphur dioxide followed by spectrophotometric determination at 755 mμ of the vanadium(IV) produced. A Unicam S.P. 500 spectrophotometer, fitted with a thermostat-controlled cell-holder, was used for this and all other spectrophotometric determinations. A correction was applied for small concentrations of vanadium(IV), *ca.* 1% of the concentration of vanadium(V), present in the solutions of the latter. Stock solutions of vanadium(IV) in dilute hydrochloric acid were prepared and standardised by the same methods. Vanadium(III) solutions were obtained by shaking solutions of vanadium(V) in hydrochloric acid with zinc amalgam until vanadium(II) was present. After removal of the amalgam, a current of filtered air was passed through the solution for *ca.* 5 min. The presence of low concentrations of vanadium(IV), estimated spectrophotometrically, then showed that all the vanadium(II) had been removed. The concentration of vanadium(III) was found by mixing a sample with an excess of a vanadium(V) solution and determining the concentration of vanadium(IV) formed in the mixture spectrophotometrically. These vanadium(III) solutions were used immediately after standardisation, either to determine the molecular extinction coefficient of vanadium(III) in hydrochloric acid solutions at 400 mμ, or for kinetic experiments.

An inverted Y-shaped vessel with lower limbs *ca.* 3 cm. in diameter and 6 cm. long was used when mixing solutions of reactants in all experiments involving tin(II) and vanadium(V). Up to 20 ml. of a tin(II) solution was introduced into one limb, a similar volume of a vanadium(V) solution into the other, and the solutions were mixed by rapid agitation of the vessel. In certain experiments a vanadium(IV) solution was added either to the tin(II) solution, with which it does not react, or to the vanadium(V) solution before the contents of the two limbs were mixed. To avoid a slight irreproducibility obtained on mixing at 20°, the solutions in most experiments with an excess of tin(II) present were cooled to −10° in the vessel immediately before mixing. These mixtures were warmed to 20° before spectrophotometric determination of the products, vanadium(III) and vanadium(IV), at 400 mμ and 755 mμ, respectively. With this procedure, the variation in product concentrations found in duplicate experiments did not exceed the error of an individual determination, *ca.* ±1%. Similar experiments at 20° with an excess of vanadium(V) present showed that the initial concentration of tin(II) was equivalent to the concentration of vanadium(IV) produced; no vanadium(III) was obtained under these conditions. A similar procedure was also used in the experiments at 20° in the presence of trioxalatocobaltate(III) and in corresponding control experiments in the absence of this complex. In these experiments, measurements were made at 605 and 755 mμ which correspond respectively to maxima in the spectra of trioxalatocobaltate(III) and vanadium(IV); corrections were made for the absorption of light by trioxalatocobaltate(III) at 755 mμ and by vanadium(IV) at 605 mμ.

Competition experiments from which we obtained the relative rate of reduction of vanadium(IV) and dioxalatodiaquocobaltate(III) by tin(III) at 20° were performed by mixing solutions of this complex and vanadium(IV) with a large excess of tin(II). Special methods of mixing were unnecessary. The progress of the reaction was followed spectrophotometrically at 605 mμ and 755 mμ. After 20—30 min. the optical densities became constant and we assumed that all the diaquo-complex had been consumed. We then obtained the final concentrations of vanadium(III) and vanadium(IV) from measurements at 400 and 755 mμ. We also found the rate of reduction of dioxalatodiaquocobaltate(III) by vanadium(III) under similar conditions. This enabled us to calculate approximately the proportion of vanadium(III) lost in the competition experiments owing to its reaction with dioxalatodiaquocobaltate(III). The value of the final concentration of vanadium(III) was accordingly increased by an amount found to be *ca.* 5% and the value of the initial concentration of dioxalatodiaquocobaltate(III) was reduced by *ca.* 2% before using these concentrations to calculate *P*.

Robert Robinson Laboratory,
The University, Manchester, 13.

[*Received, July* 18*th*, 1961.]