MECHANISMS OF SOME OXIDATION-REDUCTION REACTIONS BETWEEN METAL CATIONS IN AQUEOUS SOLUTION

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Received 21*st January*, 1960

The main features of the kinetics of the following reactions in aqueous perchloric acid are briefly described: $Fe^{III}+V^{III}\rightarrow Fe^{II}+V^{IV}$; the preceding reaction, catalyzed by Cu^{II}; $Tl^{III}+2V^{IV}\rightarrow Tl^{I}+2V^{V}$; $Tl^{III}+2V^{III}\rightarrow Tl^{I}+2V^{IV}$; $2Ce^{IV}+(Hg^{I})_2\rightarrow 2Ce^{III}+2Hg^{II}$, catalyzed by Ag^{I}; $2Hg^{II}+2V^{III}\rightarrow (Hg^{I})_2+2V^{IV}$. The mechanisms of these and related reactions are discussed.

The significance of the positive entropies of activation found for some bimolecular oxidation-reduction processes occurring between metal cations is discussed.

Much of the interest in oxidation-reduction reactions between metal cations in solution relates to the nature of the electron-transfer process itself. Many of the reactions already studied, especially those of the isotopic-exchange type, involve only a single oxidation-reduction process. In this paper, however, we report our findings, in several cases of a preliminary nature only, concerning some reactions in which more than one oxidation-reduction step contributes to the total chemical change. Our emphasis is primarily upon the overall oxidation-reduction mechanism.

EXPERIMENTAL

Reactions were followed spectrophotometrically, as described previously,[1] except for the $Ce^{IV}+(Hg^{I})_2+Ag^{I}$ system in which Ce^{IV} was estimated by titrating samples of the reaction solution with Fe^{II}. All reactions were in dilute perchloric acid unless otherwise stated. Reaction solutions which included V^{III} were kept under nitrogen. The ionic strength I was made 3·0 M by the addition of $NaClO_4$, except in certain experiments with the $Ce^{IV}+(Hg^{I})_2+Ag^{I}$ system in which $I = 4·5$ M, and in mixing experiments with the $Tl^{III}+V^{III}$ system in which $I \simeq 6$ M.

The concentration equilibrium constant of the reaction

$$VO^{2+}+Fe^{3+}+H_2O \rightleftharpoons VO_2^{+}+Fe^{2+}+2H^{+}$$

was found by e.m.f. measurements using the cell

$$Pt\,|\,Fe^{3+}, Fe^{2+}, H^{+}\,\|\,VO_2^{+}, VO^{2+}, H^{+}\,|\,Pt,$$

the concentrations and ionic strength being similar to those in the related kinetic experiments.

RESULTS AND DISCUSSION

THE REACTION BETWEEN IRON(III) AND VANADIUM(III)

The reaction, $Fe^{III}+V^{III}\rightarrow Fe^{II}+V^{IV}$ at first appeared to involve a single-stage oxidation-reduction process, similarly to the reaction, $Co^{III}+Ce^{III}\rightarrow Co^{II}+Ce^{IV}$,[2]

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because preliminary experiments in the initial absence of the products showed the kinetic equation to be

$$-\mathrm{d}[\mathrm{Fe^{III}}]/\mathrm{d}t = -\mathrm{d}[\mathrm{V^{III}}]/\mathrm{d}t = k_0[\mathrm{Fe^{III}}][\mathrm{V^{III}}].$$

However, further work has shown [3] the full kinetic equation to be

$$-\mathrm{d}[\mathrm{Fe^{III}}]/\mathrm{d}t = -\mathrm{d}[\mathrm{V^{III}}]/\mathrm{d}t = k_1[\mathrm{Fe^{III}}][\mathrm{V^{III}}]+ k'[\mathrm{Fe^{III}}][\mathrm{V^{III}}][\mathrm{V^{IV}}]/[\mathrm{Fe^{II}}]. \quad (1)$$

If the products, $\mathrm{Fe^{II}}$ and $\mathrm{V^{IV}}$, are absent at the beginning of the reaction, then at any time during the reaction $[\mathrm{Fe^{II}}] = [\mathrm{V^{IV}}]$ and so $k_0 = k_1+k'$; hence the simple form of the kinetic equation under these conditions. In experiments at a high initial concentration of $\mathrm{Fe^{II}}$ the contribution of the term in k' (eqn. (1)) is negligible and k_1 can be found. We consider that this term relates to a single-stage process, analogous to that of the $\mathrm{Co^{III}}+\mathrm{Ce^{III}}$ reaction. The dependence of k_1 upon the hydrogen-ion concentration in the range 0·50-2·40 M is

$$k_1 = b+c/[\mathrm{H^+}]+d/[\mathrm{H^+}]^2,$$

but although individual values of k_1 are subject to relatively small errors, corresponding values of b, c and d are of low precision. From experiments at 15, 20, 25 and 30°C with $I = 3{\cdot}0$ we find that

$$b = \mathrm{antilog}_{10}\,(11{\cdot}8\pm2{\cdot}9)\times \exp -\{(17{\cdot}3\pm4{\cdot}1)10^3/RT\}\mathrm{M^{-1}\ min^{-1}},$$

$$c = \mathrm{antilog}_{10}\,(16{\cdot}4\pm3{\cdot}9)\times \exp -\{(23{\cdot}2\pm5{\cdot}4)10^3/RT\}\mathrm{min^{-1}},$$

$$d = \mathrm{antilog}_{10}\,(17{\cdot}1\pm2{\cdot}0)\times \exp -\{(24{\cdot}5\pm2{\cdot}8)10^3/RT\}\mathrm{M\ min^{-1}}.$$

The entropy of activation $\Delta S^\ddagger$ corresponding to the velocity constant b is -15 ± 13 cal mole^{-1} deg.$^{-1}$

It is not possible to obtain k' satisfactorily by finding k_0 from experiments in which neither $\mathrm{Fe^{II}}$ nor $\mathrm{V^{IV}}$ is present initially and then subtracting k_1, since this constant is several times larger than k'. We have found k' from experiments using a high initial concentration of $\mathrm{V^{IV}}$. The term involving this constant in eqn. (1) is interpreted as indicating a sequence of two reactions:

$$\mathrm{Fe^{III}}+\mathrm{V^{IV}} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{Fe^{II}}+\mathrm{V^{V}}$$

$$\mathrm{V^{V}}+\mathrm{V^{III}} \xrightarrow{k_3} 2\mathrm{V^{IV}}.$$

The stationary-state approximation, $\mathrm{d}[\mathrm{V^V}]/\mathrm{d}t = 0$, leads to

$$\frac{-\mathrm{d}[\mathrm{Fe^{III}}]}{\mathrm{d}t} = \frac{-\mathrm{d}[\mathrm{V^{III}}]}{\mathrm{d}t} = \frac{k_2k_3[\mathrm{Fe^{III}}][\mathrm{V^{III}}][\mathrm{V^{IV}}]}{k_{-2}[\mathrm{Fe^{II}}]+k_3[\mathrm{V^{III}}]},$$

and if $k_{-2}[\mathrm{Fe^{II}}]\gg k_3[\mathrm{V^{III}}]$ this corresponds to the second term in eqn. (1), with

$$k' = k_2k_3/k_{-2} = k_3K_2,$$

where K_2 is the concentration equilibrium constant for the reaction:

$$\mathrm{Fe^{3+}}+\mathrm{VO^{2+}}+\mathrm{H_2O} \rightleftharpoons \mathrm{Fe^{2+}}+\mathrm{VO_2^+}+2\mathrm{H^+}.$$

We have measured K_2 at temperatures corresponding to those of the kinetic experiments and so we obtain k_3. (The value, $K_2 = 8{\cdot}0\times10^{-6}\ \mathrm{M^2}$ at 25°C and $I = 3{\cdot}0$ M may be compared with the value, $1{\cdot}60\times10^{-5}\ \mathrm{M^2}$ recently obtained [4] at 25° and $I = 1{\cdot}0$ M. The thermodynamic constant is $9{\cdot}02\times10^{-5}\ \mathrm{M^2}$ at 25°C.) At 25°C in 1 M perchloric acid, $k_3 \simeq 1{\cdot}7 \times 10^4$ min^{-1}, thus it would be difficult to investigate the reaction between V^V and V^{III} directly by conventional methods. The dependence of k_3 upon the hydrogen-ion concentration in the range 0·60-2·40 M at 15-30°C is

$$k_3 = e + f/[H^+]$$

and

$$e = \text{antilog}_{10}\,(16{\cdot}2 \pm 1{\cdot}3) \times \exp -\{(16{\cdot}6 \pm 1{\cdot}8)10^3/RT\}\text{M}^{-1}\,\text{min}^{-1};$$

from the pre-exponential term, $\Delta S^{\ddagger} = 5 \pm 6$ cal mole^{-1} deg.$^{-1}$ Values of f are about two-thirds those of e at corresponding temperatures, but are subject to rather large errors.

CATALYSIS OF THE IRON(III)+VANADIUM(III) REACTION BY COPPER(II)

The oxidation-reduction reaction between Cu^{II} and V^{III} cannot be investigated directly, but can be studied by following the $Fe^{III}+V^{III}$ reaction in the presence of Cu^{II}.[3] At sufficiently high concentrations of Cu^{II}, the rate of reaction is independent of the concentrations of Fe^{III}, Fe^{II} and V^{IV}, the rate equation being

$$-d[Fe^{III}]/dt = -d[V^{III}]/dt = k_4'[V^{III}] = k_4[V^{III}][Cu^{II}]_{\text{initial}}.$$

This is consistent with a 2-stage mechanism:

$$Cu^{II} + V^{III} \xrightarrow{k_4} Cu^{I} + V^{IV},$$

$$Fe^{III} + Cu^{I} \xrightarrow{\text{rapid}} Fe^{II} + Cu^{II}.$$

The alternative possibility for the slow step, $Cu^{II}+V^{III} \rightarrow Cu^{\circ}_{\text{atom}} + V^V$, is regarded as improbable on energetic grounds. In most experiments it was convenient to use concentrations of Cu^{II} such that the rate of the uncatalyzed reaction, although small, was not negligible compared with the rate observed. However, knowing k_0, k_4 can be obtained from such experiments. At 10-25°C, 0·7-2·6 M hydrogen ion and $I = 3{\cdot}0$ we find that

$$k_4 = g + h/[H^+],$$

$$g = \text{antilog}_{10}\,(16{\cdot}1 \pm 1{\cdot}1) \times \exp -\{(21{\cdot}0 \pm 1{\cdot}5)10^3/RT\}\text{M}^{-1}\,\text{min}^{-1},$$

$$h = \text{antilog}_{10}\,(15{\cdot}1 \pm 0{\cdot}4) \times \exp -\{(19{\cdot}0 \pm 0{\cdot}6)10^3/RT\}\text{min}^{-1}.$$

The value of $\Delta S^{\ddagger}$ corresponding to the velocity constant g is 5 ± 5 cal mole^{-1} deg.$^{-1}$

SOME REACTIONS INVOLVING 2-EQUIVALENT CHANGES IN OXIDATION STATE IN A SINGLE PROCESS

The $Fe^{III}+V^{III}$ system is abnormal since reactions in which the change in oxidation number is unity for each reactant usually involve only one stage. However, in reactions in which at least one of the reactants changes its oxidation state by more than one unit, several steps are always to be expected. There is one major exception to this generalization, the system in which both reactants change their oxidation number by two units, since here a single-stage process may occur. Unfortunately, it is difficult to prove the occurrence of 2-equivalent (2-eq.) changes by straightforward kinetic methods. For example, the reaction $Tl^{III}+U^{IV} \rightarrow Tl^{I}+U^{VI}$ follows the rate law;[5]

$$-d[Tl^{III}]/dt = -d[U^{IV}]/dt = k[Tl^{III}][U^{IV}].$$

This equation is to be expected for a single-stage, 2-eq. process. However, it is possible that if initially the 1-eq. reaction $Tl^{III}+U^{IV} \rightarrow Tl^{II}+U^V$ were to occur, the subsequent reactions of the relatively reactive intermediates, Tl^{II} and U^V, so formed would be sufficiently rapid that the overall kinetics would follow the same simple law. In systems of this sort a possible approach would involve the prior demonstration of a reaction characteristic of an intermediate which would be formed if the initial reaction were of the 1-eq. type, e.g. the irreversible oxidation of a substrate, inert to reactants and products taken separately, in a system in which this intermediate is known to be produced. The presence or absence of this characteristic reaction on adding the substrate could then be sought in the system under investigation. Nevertheless, the indication of a 1-eq. reaction would be a more certain conclusion than that of a 2-eq. process based upon a negative result.

Occasionally a more positive indication of a 2-eq. change is possible, as in the reaction $\mathrm{Tl^{III}+2Cr^{II}\rightarrow Tl^{I}+(Cr^{III})_2}$, the mechanism being: [6]

$$\mathrm{Tl^{III}+Cr^{II}\rightarrow Tl^{I}+Cr^{IV}},$$

$$\mathrm{Cr^{IV}+Cr^{II}\rightarrow(Cr^{III})_2}.$$

The observation that almost all the $\mathrm{Cr^{III}}$ appears in a dimeric form provides the evidence for the intermediate formation of $\mathrm{Cr^{IV}}$ and hence makes the 2-eq. first stage probable. A review of the reactions of chromic acid [7] has shown that 2-eq. changes are common between oxidation states of chromium.

Another reaction believed to involve a 2-eq. change, $\mathrm{Tl^{III}+(Hg^{I})_2\rightarrow Tl^{I}+2Hg^{II}}$, does not proceed by a single step, but follows the mechanism: [8]

$$\mathrm{(Hg^{I})_2\rightleftharpoons Hg^{II}+Hg^{\circ}_{atom}},$$

$$\mathrm{Tl^{III}+Hg^{\circ}_{atom}\rightarrow Tl^{I}+Hg^{II}}.$$

Again, although the second reaction is probably a single-stage 2-eq. reaction, the evidence is not conclusive.

THE REACTION BETWEEN THALLIUM(III) AND VANADIUM(IV)

Although the examples quoted above suggest that $\mathrm{Tl^{III}}$ can act as a 2-eq. oxidant in its reactions with metal ions, the reactions, $\mathrm{Tl^{III}+2Fe^{II}\rightarrow Tl^{I}+2Fe^{III}}$ and $\mathrm{Tl^{III}+2V^{IV}\rightarrow Tl^{I}+2V^{V}}$, follow 1-eq. steps. The mechanism of the former reaction is [9]

$$\mathrm{Tl^{III}+Fe^{II}\rightleftharpoons Tl^{II}+Fe^{III}}$$

$$\mathrm{Tl^{II}+Fe^{II}\rightarrow Tl^{I}+Fe^{III}}.$$

The study of the $\mathrm{Tl^{III}+V^{IV}}$ reaction in dilute perchloric acid presents difficulties, since temperatures of 60-80°C are necessary to obtain a satisfactory rate of reaction and under these conditions $\mathrm{Tl^{III}}$ slowly decomposes to $\mathrm{Tl^{I}}$ and molecular oxygen. The rate equation is probably [3]

$$-\mathrm{d}[\mathrm{V^{IV}}]/\mathrm{d}t = k_5[\mathrm{Tl^{III}}][\mathrm{V^{IV}}]^2/\{k_6[\mathrm{V^{V}}]+[\mathrm{V^{IV}}]\},$$

where $k_5 \simeq 1{\cdot}34$ $\mathrm{M^{-1}}$ $\mathrm{min^{-1}}$ and $k_6 \simeq 42$ at 80°C, 1·8 M hydrogen ion and $I = 3{\cdot}0$. This is consistent with a mechanism similar to that of the $\mathrm{Tl^{III}+Fe^{II}}$ reaction:

$$\mathrm{Tl^{III}+V^{IV}\rightleftharpoons Tl^{II}+V^{V}},$$

$$\mathrm{Tl^{II}+V^{IV}\rightarrow Tl^{I}+V^{V}}.$$

The alternative reaction sequence,

$$\mathrm{2V^{IV}\rightleftharpoons V^{III}+V^{V}},$$

$$\mathrm{Tl^{III}+V^{III}\rightarrow Tl^{I}+V^{V}},$$

can only occur to a minor extent, if at all.

THE REACTION BETWEEN THALLIUM(III) AND VANADIUM(III)

The alternative mechanism mentioned above was considered owing to the rapidity of the second stage, the $\mathrm{Tl^{III}+V^{III}}$ reaction. When solutions 0·009 M in each of these species and 6 M in perchloric acid were mixed rapidly at *ca.* 5°C, reaction was complete [3] within the time of sampling, 45 sec. The products of this reaction were $\mathrm{Tl^{I}}$ and $\mathrm{V^{IV}}$; no $\mathrm{V^{V}}$ was detected. Plausible mechanisms are:

$$A{:}\quad \mathrm{Tl^{III}+V^{III}\rightarrow Tl^{II}+V^{IV}}, \quad \text{(1-eq. change)}$$

$$\mathrm{Tl^{II}+V^{III}\rightarrow Tl^{I}+V^{IV}}.$$

$$B{:}\quad \mathrm{Tl^{III}+V^{III}\xrightarrow{k_7}Tl^{I}+V^{V}}, \quad \text{(2-eq. change)}$$

$$\mathrm{V^{V}+V^{III}\xrightarrow{k_3}2V^{IV}}.$$

Under the conditions of the mixing experiment k_3, the velocity constant of the last-quoted reaction, cannot exceed 3×10^3 M^{-1} min^{-1}. (This value is obtained by extrapolation from the values of k_3 obtained as described earlier in this paper.) It can be shown that if the reaction follows mechanism *B*, k_7 must exceed 3×10^2 M^{-1} min^{-1} if 95 % of the initial concentration of $\mathrm{V^{III}}$ has been oxidized 45 sec after mixing. If $(k_3/k_7)<10$, it can also be shown that at least 5 % of $\mathrm{V^{III}}$ will have been oxidized to $\mathrm{V^{V}}$ when the reaction is complete. This is contrary to the experimental evidence and we conclude that mechanism *A* is dominant.

We have not observed the formation of $\mathrm{V^{V}}$ in dilute perchloric acid, but in similar experiments with dilute sulphuric acid as solvent and with excess of $\mathrm{Tl^{III}}$ present up to 3 % of $\mathrm{V^{III}}$ was converted to $\mathrm{V^{V}}$. This proportion could be increased to 10 % in experiments in which $\mathrm{V^{IV}}$ was present initially. We are unable to interpret this observation in terms of mechanism *B*, but it is consistent with mechanism *A* if the following steps are added:

$$\mathrm{Tl^{II}+V^{IV}\rightarrow Tl^{I}+V^{V}},$$

$$\mathrm{V^{V}+V^{III}\rightarrow 2V^{IV}}.$$

We originally expected the first stage of the $\mathrm{Tl^{III}+V^{III}}$ reaction to be of the 2-eq. type. However, if this were so, either extensive hydrolysis would occur owing to the formation of $\mathrm{VO_2^+}$, or a less hydrolyzed and hence less stable form of $\mathrm{V^{V}}$ would be produced. In either case, a relatively high activation energy is likely and so the occurrence of the alternative 1-eq. reaction seems less surprising. In the $\mathrm{Tl^{III}+U^{IV}}$ reaction, which is probably of the 2-eq. type,[5] the alternative 1-eq. initial step should not offer an easier route according to this interpretation, since $\mathrm{U^{V}}$ and $\mathrm{U^{VI}}$ are hydrolyzed to the same extent in their most stable forms ($\mathrm{UO_2^+}$ and $\mathrm{UO_2^{2+}}$), unlike $\mathrm{V^{IV}}$ and $\mathrm{V^{V}}$ ($\mathrm{VO^{2+}}$ and $\mathrm{VO_2^+}$).

CATALYSIS OF THE CERIUM(IV)+MERCURY(I) REACTION BY SILVER(I)

The $\mathrm{Ce^{IV}+Ag^{I}}$ system is similar to the $\mathrm{Cu^{II}+V^{III}}$ system in that no reaction is observed in the absence of a suitable substrate. In the presence of $\mathrm{(Hg^{I})_2}$ or $\mathrm{Tl^{I}}$ a reaction occurs and has been identified [10] as the oxidation of the one or the other of these species, catalyzed by $\mathrm{Ag^{I}}$:

$$\mathrm{2Ce^{IV}+(Hg^{I})_2\xrightarrow{(Ag^{I})}2Ce^{III}+2Hg^{II}},$$

$$\mathrm{2Ce^{IV}+Tl^{I}\xrightarrow{(Ag^{I})}2Ce^{III}+Tl^{III}}.$$

Under the conditions of our experiments, the direct reactions between $\mathrm{Ce^{IV}}$ and $\mathrm{(Hg^{I})_2}$ or $\mathrm{Tl^{I}}$ could be neglected. In the presence of a sufficiently large excess of $\mathrm{(Hg^{I})_2}$, the reaction followed the rate law:

$$-\mathrm{d[Ce^{IV}]}/\mathrm{d}t = -2\mathrm{d[(Hg^{I})_2]}/\mathrm{d}t = 2k_8'[\mathrm{Ce^{IV}}] = 2k_8[\mathrm{Ce^{IV}}][\mathrm{Ag^{I}}]_{\text{initial}}, \quad (2)$$

the rate of reaction being independent of the concentration of $(Hg^I)_2$. If Ce^{III} is present initially and $(Hg^I)_2$ is only in small excess, the plot of $\log_{10}[Ce^{IV}]$ against time is curved so that k'_8 decreases as the concentration of Ce^{III} increases. We conclude that the mechanism of the reaction is

$$Ce^{IV} + Ag^I \underset{k_{-8}}{\overset{k_8}{\rightleftharpoons}} Ce^{III} + Ag^{II},$$

$$Ag^{II} + (Hg^I)_2 \xrightarrow{k_9} Ag^I + Hg^I + Hg^{II},$$

$$Ce^{IV} + Hg^I \xrightarrow{\text{rapid}} Ce^{III} + Hg^{II},$$

and, by assuming $d[Ag^{II}]/dt = 0$, we can deduce that

$$\frac{-d[Ce^{IV}]}{dt} = \frac{-2d[(Hg^I)_2]}{dt} = \frac{2k_8[Ce^{IV}][Ag^I]_{\text{initial}}}{(k_{-8}/k_9)[Ce^{III}]/[(Hg^I)_2]+1}. \tag{3}$$

The integrated form of eqn. (3) is in good agreement with the results of a series of kinetic experiments in which different concentrations of Ce^{III} were present initially. The value of k_{-8}/k_9 (0·198 at 1·50 M hydrogen ion, $I = 3{\cdot}0$ M and 20°C) is such that the term in $[Ce^{III}]/[(Hg^I)_2]$ is negligible if $(Hg^I)_2$ is in large excess; eqn. (3) then reduces to eqn. (2).

If Tl^I is used as the substrate, the sequence of reactions is thought to be similar;

$$Ce^{IV} + Ag^I \underset{k_{-8}}{\overset{k_8}{\rightleftharpoons}} Ce^{III} + Ag^{II},$$

$$Ag^{II} + Tl^I \xrightarrow{k_{10}} Ag^I + Tl^{II},$$

$$Ce^{IV} + Tl^{II} \xrightarrow{\text{rapid}} Ce^{III} + Tl^{III}.$$

From this mechanism we similarly deduce that

$$\frac{-d[Ce^{IV}]}{dt} = \frac{-2d[Tl^I]}{dt} = \frac{2k_8[Ce^{IV}][Ag^I]_{\text{initial}}}{(k_{-8}/k_{10})[Ce^{III}]/[Tl^I]+1}. \tag{4}$$

The value of k_{-8}/k_{10}, 35·7, is very much larger than that of k_{-8}/k_9 under the same conditions and the term in $[Ce^{III}]/[Tl^I]$ cannot be neglected. Thus k_8 cannot be obtained from plots of $\log_{10}[Ce^{IV}]$ against time. By using the integrated form of eqn. (4) both k_{-8}/k_{10} and k_8 can be found and the latter is in good agreement with the corresponding value obtained when $(Hg^I)_2$ is the substrate. From k_{-8}/k_9 and k_{-8}/k_{10}, we find $k_9/k_{10} = 180$ at 1·50 M hydrogen ion and 20°C. This quantity is the ratio of the rate constants for oxidation of $(Hg^I)_2$ and of Tl^I by Ag^{II}. Under the same conditions, the ratio of the rate constants for oxidation of these two reductants by Co^{III} is 185.[11]

The dependence of k_8 upon the concentration of hydrogen ions has been investigated over the range 0·22-4·2 M with $I = 4{\cdot}5$ M at various temperatures from 9·8 to 30·0°C. The form of this dependence is complex and there is evidence for the presence of dimeric Ce^{IV} species in appreciable proportions in the less acid solutions. In the range 1·0-4·2 M hydrogen ion we find that

$$k_8 = j[H^+]^2/\{[H^+]^2 + K_3[H^+] + K_3K_4\}.$$

This result is most simply interpreted in terms of a bimolecular reaction between the least hydrolyzed monomeric Ce^{IV} species present and Ag^+. At 24·95°C, the rate constant for this reaction, j, is $6{\cdot}2 \pm 0{\cdot}7$ M^{-1} min^{-1} and the first hydrolysis constant of this Ce^{IV} species, K_3, is *ca.* 10·6 M. We find that

$$j = \text{antilog}_{10}\,(15{\cdot}4 \pm 0{\cdot}9) \times \exp - \{(20{\cdot}0 \pm 1{\cdot}2)10^3/RT\}$$

and $\Delta S^{\ddagger} = 1{\cdot}8 \pm 4$ cal mole^{-1} deg.$^{-1}$. Values of the first and second hydrolysis constants of Ce^{4+} have recently been obtained [11a] and by comparison we conclude that K_3 is the first hydrolysis constant of this ion. Hence j is the velocity constant for the bimolecular reaction between Ce^{4+} and Ag^{+}.

THE REACTION BETWEEN MERCURY(II) AND VANADIUM(III)

The reaction $2Hg^{II} + 2V^{III} \rightarrow (Hg^{I})_2 + 2V^{IV}$ follows a complex rate equation: [10]

$$\frac{-d[V^{III}]}{dt} = \frac{[Hg^{II}][V^{III}]^2}{p[V^{IV}] + q[V^{III}]} + \frac{[Hg^{II}][V^{III}]^2}{r[V^{IV}] + s[Hg^{II}]}, \qquad (5)$$

where $p = 2{\cdot}52 \pm 0{\cdot}15$, $q = 0{\cdot}20 \pm 0{\cdot}05$, $r = 3{\cdot}4 \pm 0{\cdot}6$ and $s = 6{\cdot}0 \pm 1{\cdot}5$ M min at 15°C, 0·20 M hydrogen ion and $I = 3{\cdot}0$ M. It was not possible to vary the concentrations of reactants and products as much as is desirable in a case where four constants are necessary to describe the rate of reaction. The form of the term in p and q in eqn. (5) seems certain, although the form of the second term, which contributes only 10-20 % of the total rate, may be erroneous. The first term is in accordance with the mechanism:

$$Hg^{II} + V^{III} \underset{k_{-11}}{\overset{k_{11}}{\rightleftharpoons}} Hg^{I} + V^{IV},$$

$$Hg^{I} + V^{III} \xrightarrow{k_{12}} Hg^{\circ}_{atom} + V^{IV},$$

$$Hg^{II} + Hg^{\circ}_{atom} \xrightarrow{rapid} (Hg^{I})_2.$$

The second term may indicate an alternative sequence of reactions:

$$2V^{III} \underset{k_{-13}}{\overset{k_{13}}{\rightleftharpoons}} V^{IV} + V^{II},$$

$$Hg^{II} + V^{II} \xrightarrow{k_{14}} Hg^{\circ}_{atom} + V^{IV},$$

$$Hg^{II} + Hg^{\circ}_{atom} \xrightarrow{rapid} (Hg^{I})_2.$$

The relations between the bimolecular velocity constants defined in these equations and the constants p, q, r and s are:

$$k_{11} = 1/2q; \; k_{-11}/k_{12} = p/q; \; k_{13} = 1/2s; \; k_{-13}/k_{14} = r/s.$$

COMMENTS ON THE FORMULATION OF REACTION MECHANISMS

As shown above, a complex form of the rate law may be sufficient to indicate the essentials of a reaction mechanism. Such complexity often occurs if the first stage in the sequence of reactions involves a positive change in free energy. A highly reactive species produced in this stage may either react further, ultimately yielding a final product, or may react in the reverse sense with the re-formation of the reactants. If the rates of these competing reactions are similar, kinetic complexity is observed and the overall mechanism of reaction is usually obvious. If, however, this reverse reaction is relatively slow and can be neglected, a simple form of kinetic equation is likely. Some reactions following a several-stage mechanism show simple kinetics which may be consistent in form with two or more reaction sequences. In certain cases of this type the probable mechanism can be inferred from the stability of the oxidation states adjacent to those of the reactants. For example, the reaction $2Fe^{III} + U^{IV} \rightarrow 2Fe^{II} + U^{VI}$ follows the rate law,[12]

$$-d[Fe^{III}]/dt = k[Fe^{III}][U^{IV}]$$

which is formally consistent with the rate-determining initial reactions,

$$\mathrm{Fe^{III}+U^{IV}\rightarrow Fe^{II}+U^{V}} \quad \text{and} \quad \mathrm{Fe^{III}+U^{IV}\rightarrow Fe^{I}+U^{VI}}.$$

The latter can be excluded owing to the lack of evidence for $\mathrm{Fe^{I}}$ in dilute acid solutions. Thus, in discussing mechanisms of oxidation-reduction reactions in solution it is helpful to consider the electronic structures of simple cations and other evidence about the stability of the parent elements in their various oxidation states. We may conclude that for homogeneous reactions in acid solutions monomeric forms of, e.g., $\mathrm{Ce^{III}}$, $\mathrm{Ce^{IV}}$, $\mathrm{Ti^{III}}$, $\mathrm{Fe^{III}}$, $\mathrm{Co^{II}}$, $\mathrm{Co^{III}}$ are very unlikely to undergo 2-eq. reactions as also are oxidizing agents including $\mathrm{V^{III}}$, $\mathrm{Cr^{III}}$, $\mathrm{Mn^{III}}$, $\mathrm{U^{IV}}$, $\mathrm{Np^{IV}}$, $\mathrm{Pu^{IV}}$ and reducing agents including $\mathrm{V^{IV}}$, $\mathrm{U^{V}}$, $\mathrm{Np^{V}}$, $\mathrm{Pu^{V}}$. On the other hand, the stable ionic oxidation states of non-transition metals usually differ by 2 units, so that 2-eq. changes are favoured.[13] Nevertheless, in reactions with reagents restricted to 1-eq. changes and in certain other cases, e.g., the $\mathrm{Tl^{III}+V^{III}}$ reaction, intermediate oxidation states, usually of low stability, can be produced with comparative ease from non-transition metals. Chromium, although a transition element, is also known to form unstable oxidation states.[6, 7] Such intermediate states, particularly those of non-transition metals, are analogous to the free radicals of the chemistry of non-metallic elements. In this connection, intermediate states produced in the reduction of $\mathrm{Cr^{VI}}$ have been shown to initiate vinyl polymerization.[14]

In the reactions mentioned in this paper, a series of bimolecular reactions seems adequate in formulating reaction mechanisms and the corresponding transition complexes contain only two metal ions. Examples are known in which three species undergo oxidation-reduction in a single transition complex,[15] but although two may be metal ions, the case in which all three species are metallic does not appear to have been observed. Such a three-fold transition complex may be possible if anions are also incorporated. Many partly-hydrolyzed metal ions form dimeric species [16] and it is conceivable that a dimeric ion, formed from a simple cation capable only of a 1-eq. change, may react in a single process with a cation favouring a 2-eq. change. For example, the reaction, $\mathrm{2Fe^{III}+Sn^{II}\rightarrow 2Fe^{II}+Sn^{IV}}$ has been studied [17] under conditions in which dimeric $\mathrm{Fe^{III}}$ [18] is almost certainly present. In any re-interpretation of the complicated behaviour observed in this system, the possibility should be considered of the reaction $\mathrm{(Fe^{III})_2+Sn^{II}\rightarrow 2Fe^{II}+Sn^{IV}}$, where $\mathrm{(Fe^{III})_2}$ represents $\mathrm{Fe_2(OH)_2^{4+}}$ or a related dimeric ion.

ENTROPIES OF ACTIVATION OF SOME BIMOLECULAR OXIDATION-REDUCTION REACTIONS

In table 1 we summarize entropies of activation $\Delta S^{\neq}$ for bimolecular reactions between metal cations in dilute perchloric acid solutions and for two reactions of anionic complexes. Since the reaction paths to which these entropies apply do not involve a dependence of rate upon hydrogen-ion concentration, the corresponding transition complexes can be regarded as composed of the two reactants and water molecules; in the cationic reactions, perchlorate ions may also be present. In group *A* the reactions are of the isotopic-exchange type and there is no net chemical change; the entropy of reaction ΔS can be taken as zero. In reactions in group *B*, chemical change occurs and ΔS is usually not zero. It can be seen that in group *B* there are several cases in which $\Delta S^{\neq}$ is positive. This seems surprising since there are experimental and theoretical reasons for expecting negative values of $\Delta S^{\neq}$ in bimolecular reactions between ions of like charge.[19, 20] A suggestion [21] that the positive value of $\Delta S^{\neq}$ observed in the $\mathrm{Co^{3+}+Tl^{+}}$ reaction is due to the incorporation of perchlorate ions in the transition complex has been shown to be incorrect and this interpretation is also unlikely for others of the reactions cited.[11]

A recent interpretation [22] of entropies of activation in the oxidation-reduction reactions of uranium, neptunium and plutonium has shown that the entropies of the transition complexes are related simply to their charge. The reactions in table 1B conform rather poorly with this type of relation, possibly because in many of them the transition complexes, lacking bridging groups between the metal atoms, are less compact. Following a similar approach to that of Halpern,[15] we suggest that in reactions of this type there may be a relation between $\Delta S^{\ddagger}$ and ΔS. Relationships between the free energy of activation and the free energy of reaction,

TABLE 1

reactants	I, mole/l.	$\Delta S^{\ddagger}$ cal mole^{-1} deg.$^{-1}$	charge on transition complex	ref.
A				
$NpO_2^{2+} + NpO_2^{+}$	3·0	−11·7	+3	22
$MnO_4^{-} + MnO_4^{2-}$	0·16	− 9	−3	30
$Tl^{3+} + Tl^{+}$	3·68	−20	+4	31
$Fe^{3+} + Fe^{2+}$	0·55	−25	+5	32
$V^{3+} + V^{2+}$	2·0	−25	+5	33
$Fe(CN)_6^{3-} + Fe(CN)_6^{4-}$	0·01	−41	−7	34
B				
$VO_2^{+} + V^{3+}$	3·0	+ 5±6	+4	3, 35
$Co^{3+} + Tl^{+}$	3·0	+13±6	+4	11
$Ce^{4+} + Ag^{+}$	4·5	+ 2±4	+5	10, 35
$Co^{3+} + Hg_2^{2+}$	3·0	+ 9±6	+5	1
$Co^{3+} + VO^{2+}$	3·0	+12±9	+5	1
$Cu^{2+} + V^{3+}$	3·0	+ 5±5	+5	3, 35
$PuO_2^{2+} + Pu^{3+}$	1·0	−40·4±0·6	+5	22
$Tl^{3+} + Fe^{2+}$	3·0	−5±6	+5	†
$Co^{3+} + V^{3+}$	3·0	>0	+6	11
$Fe^{3+} + V^{3+}$	3·0	−15±13	+6	3, 35

† calculated from Johnson's results [36] by using Biedermann's value [37] for the first hydrolysis constant of Tl^{3+}.

and between the activation energy and heat of reaction are well known.[23-25] Particularly for ionic reactions, in which entropies are largely determined by ionic charge, similar relationships may apply between the corresponding entropies. We therefore propose the relation,

$$\Delta S^{\ddagger} = \Delta S^{\ddagger}_{(0)} + \alpha \Delta S \qquad (6)$$

where $\Delta S^{\ddagger}$ and ΔS refer to the reaction under consideration, $\Delta S^{\ddagger}_{(0)}$ represents the entropy of activation of a reaction of similar nature and the same charge-type for which $\Delta S = 0$, and $0 < \alpha < 1$. From the values in table 1A, we assume $\Delta S^{\ddagger}_{(0)} = -19, -25, -32$ cal mole^{-1} deg.$^{-1}$ when the charge of the transition complex is 4, 5, 6, respectively. We cannot assign a value to α since, for a given reaction, this parameter presumably depends on the extent to which the distribution of charge in the transition complex resembles that of the reactants ($\alpha \rightarrow 0$) or the products ($\alpha \rightarrow 1$). Therefore, to test eqn. (6) we compare ($\Delta S^{\ddagger} - \Delta S^{\ddagger}_{(0)}$) with ΔS (table 2). Where possible, values of ΔS were calculated from accepted values of ionic entropies,[26] but for several reactants and products it has been necessary to estimate [11] ionic entropies, usually by following established procedures.[27] Many quoted values of ΔS are therefore imprecise and since most values of $\Delta S^{\ddagger}$ are also subject to large errors, we have rounded the values of ΔS and ($\Delta S^{\ddagger} - \Delta S_{(0)}$) to the nearest 10 units.

If eqn. (6) holds we should expect ΔS, whether of positive or negative sign, to be greater numerically than the corresponding value of $(\Delta S^{\ddagger} - \Delta S_{(0)})$ since α cannot exceed unity. Reference to reactions (1), (3), (4), (7), (8) (table 2) shows that corresponding values of these quantities are similar, suggesting that $\alpha \rightarrow 1$. However, in reactions (5*a*), (6*a*), (9*a*), (10*a*), in which ΔS is calculated by assuming the oxidation-reduction process is formally a simple electron-transfer, $(\Delta S^{\ddagger} - \Delta S^{\ddagger}_{(0)})$ is seen to be much greater than ΔS. In these reactions one of the products is taken to be a vanadium cation less hydrolyzed than the normal form and consequently in a less stable state. We therefore suggest that partial hydrolysis occurs within the corresponding transition complexes and in (5*b*), (6*b*), (9*b*), (10*b*) we record values of ΔS calculated on the assumption that sufficient hydrolysis to give stable vanadium oxy-cations occurs in the overall reactions. We now find ΔS exceeds $(\Delta S^{\ddagger} - \Delta S^{\ddagger}_{(0)})$. Possibly different values of ΔS should be used for reactions in which the number of solute species alters,[28] but neglect to do so will not affect the evident distinction between these reactions and the others. Reaction (2) is of a type different from the rest and we have assumed that the products are $2VO^{2+}$ rather than the other extreme, V^{4+} and VO_2; in the latter case ΔS would probably be negative.

TABLE 2

	reaction	ΔS cal mole^{-1}deg.$^{-1}$	$(\Delta S^{\ddagger} - \Delta S^{\ddagger}_{(0)})$ cal mole^{-1} deg.$^{-1}$
1	$Co^{3+} + Tl^{+} \rightarrow Co^{2+} + Tl^{2+}$	+30	+30
2	$VO_2^{+} + V^{3+} \rightarrow 2VO^{2+}$	+10	+20
3	$Ce^{4+} + Ag^{+} \rightarrow Ce^{3+} + Ag^{2+}$	+20	+30
4	$Co^{3+} + Hg_2^{2+} \rightarrow Co^{2+} + Hg^{+} + Hg^{2+}$	+40	+30
5*a*	$Co^{3+} + VO^{2+} \rightarrow Co^{2+} + VO^{3+}$	+10	+40
5*b*	$Co^{3+} + VO^{2+} + H_2O \rightarrow Co^{2+} + VO_2^{+} + 2H^{+}$	+60	+40
6*a*	$Cu^{2+} + V^{3+} \rightarrow Cu^{+} + V^{4+}$	−10	+30
6*b*	$Cu^{2+} + V^{3+} + H_2O \rightarrow Cu^{+} + VO^{2+} + 2H^{+}$	+50	+30
7	$PuO_2^{2+} + Pu^{3+} \rightarrow PuO_2^{+} + Pu^{4+}$	−40	−20
8	$Tl^{3+} + Fe^{2+} \rightarrow Tl^{2+} + Fe^{3+}$	+10	+20
9*a*	$Co^{3+} + V^{3+} \rightarrow Co^{2+} + V^{4+}$	+10	$\nless +30$
9*b*	$Co^{3+} + V^{3+} + H_2O \rightarrow Co^{2+} + VO^{2+} + 2H^{+}$	+70	$\nless +30$
10*a*	$Fe^{3+} + V^{3+} \rightarrow Fe^{2+} + V^{4+}$	0	+20
10*b*	$Fe^{3+} + V^{3+} + H_2O \rightarrow Fe^{2+} + VO^{2+} + 2H^{+}$	+60	+20

We do not consider that the data in table 2 provide a clear-cut demonstration of our hypothesis and we acknowledge that specific factors other than the entropy of reaction may contribute to the entropy of activation. However, this comparison does suggest that bond-breaking and making may occur together with electron transfer, even in cases where the formation of bridged transition complexes [29] seems improbable.

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