Evidence for One- and Two-electron Paths in the Reaction of Vanadium(II) with Mercury(II)

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Summary One- and two-electron transfer steps have been shown to occur concurrently in the reaction of vanadium(II) with mercury(II), and kinetic parameters have been obtained for both paths.

THERE has been much discussion as to whether simultaneous or near simultaneous transfer of two electrons is possible for reactions between metal ions in aqueous solutions.[1,2] In this context the redox reactions of sub-group B metal ions, in particular those of tin(II)[3] and thallium(III),[4] have proved most relevant, and much interest has centred around the exchange between thallium(I) and thallium(III).[5] The theoretical approach of Hush[6] has enabled the activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the disproportionation mechanism, $\mathrm{Tl^{I}} + \mathrm{Tl^{III}} \rightleftharpoons 2\mathrm{Tl^{II}}$, (involving one-electron transfers and intermediate formation of $\mathrm{Tl^{II}}$), to be calculated. These were found to be in good agreement with the experimental values. The value of $\Delta H^{\ddagger}$ which is obtained for the two-electron step by considering energy requirements for the re-organization of co-ordinated solvent molecules is 4—5 kcal mole^{-1} higher.[1] The above considerations support the view that the thallium(I)–thallium(III) exchange is a two-step process involving thallium(II) as an intermediate. Experimental evidence which has been interpreted in terms of a two-electron step,[7] may not be valid if newly formed thallium(II) ions are unable to diffuse apart.[2,8] Thus it is possible that the transfer of a second electron may occur before the ions are able to escape from their solvent cage and react with a substrate ion.[9] The absence of experimental $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values for one- and two-electron paths in the same (or similar) systems has not helped to clarify some of the arguments involved.

Kinetic data for the reaction of vanadium(II) *with mercury*(II) *in perchlorate media*, $\mu = 2{\cdot}0\mathrm{M}$ ($\mathrm{LiClO_4}$)

Reactants	k(l mole^{-1}sec^{-1})[a]	$\Delta H^{\ddagger}$(kcal mole^{-1})	$\Delta S^{\ddagger}$(e.u.)
$\mathrm{V^{2+} + Hg^{2+} \xrightarrow{k_1}}$ (1 electron)	1·32 ± 0·08	15·2 ± 0·8	−7·2 ± 2·9
$\mathrm{V^{2+} + Hg^{2+} \xrightarrow{k_2}}$ (2 electrons)	1·85 ± 0·05	10·9 ± 0·7	−20·6 ± 2·3
$\mathrm{V^{2+} + HgOH^{+} \xrightarrow{k_3}}$ (2 electrons)	3·2 (±0·6) × 10^4 [b]	7·9 ± 0·4[b]	−11·5 ± 1·4[b]

[a] 25°.

[b] Using $K_a = 2{\cdot}75 \times 10^{-4}$ mole^{-1} l^{-1} (at 25°) $\Delta H_a = 7{\cdot}23$ (±0·18) kcal mole^{-1} and $\Delta S_a = 7{\cdot}9 \pm 0{\cdot}7$ e.u. $\mu = 3\mathrm{M}$ ($\mathrm{NaClO_4}$), from R. Arnek and W. Kakolowicz, *Acta Chem. Scand.*, 1967, **21**, 1449.

We report the identification of one- and two-equivalent paths in the reaction of vanadium(II) with mercury(II). The reaction has been studied under pseudo first-order conditions [large excess of mercury(II)] at 10—25°, $\mu = 2{\cdot}0\mathrm{M}$ ($\mathrm{LiClO_4}$), using the stopped-flow technique. The one-electron path proceeds with the formation of $\mathrm{Hg^{I}}$ as an intermediate

$$\mathrm{V^{II} + Hg^{II} \xrightarrow{k_1} V^{III} + Hg^{I}} \qquad (1)$$

Subsequent reactions as in (2) and (3) are rapid

$$\mathrm{V^{II} + Hg^{I} \xrightarrow{\text{fast}} V^{III} + Hg^{0}} \qquad (2)$$

$$\mathrm{Hg^{0} + Hg^{II} \xrightarrow{\text{fast}} (Hg^{I})_2} \qquad (3)$$

The two-electron path proceeds with the formation of vanadium(IV) ($\mathrm{VO^{2+}}$) and mercury(0) atoms,

$$\mathrm{V^{II} + Hg^{II} \xrightarrow{k_2/k_3} V^{IV} + Hg^{0}} \qquad (4)$$

where the $\mathrm{Hg^{0}}$ reacts subsequently as in (3). It is possible to measure final concentrations of vanadium(III) (400 nm) and vanadium(IV) (760 nm). Hence the ratio of rate constants for the one- and two-electron processes (a and b respectively) can be obtained, (5)

$$\frac{[\mathrm{V^{III}}]_\infty}{[\mathrm{V^{IV}}]_\infty} = \frac{2a}{b} \qquad (5)$$

The kinetics of the two-electron step were determined by studying the rate of formation of vanadium(IV) at 760 nm. On varying the concentration of hydrogen ions the rate constant b shows an inverse [H$^+$]-dependence. Assuming $\mathrm{HgOH^{+}}$ is a reactant, this dependence may be expressed as in (6)

$$b = k_2 + k_3K_a[\mathrm{H^+}]^{-1} \qquad (6)$$

where K_a is the acid dissociation constant for $\mathrm{Hg^{2+}}$. From the variations of both $[\mathrm{V^{III}}]/[\mathrm{V^{IV}}]$ and b with [H$^+$] it can be concluded that the rate constant a for the one-electron path is independent of [H$^+$], ($a = k_1$). Stopped-flow oscillograph traces of absorbance changes in the 425nm region indicate the formation and decay of a further species. The spectrum and rate of decay (380—480 nm) were in reasonable agreement with those observed for $\mathrm{VOV^{4+}}$ in (7)[10]

$$\mathrm{VOV^{4+} + H^{+} \rightarrow V^{3+} + VOH^{2+}} \qquad (7)$$

Since at 25° and $[\mathrm{H^+}] = 1{\cdot}0\mathrm{M}$ the rate constant for the reaction of $\mathrm{V^{2+}}$ with $\mathrm{Hg^{2+}}$ (10·7 l mole^{-1} sec^{-1}) is greater than that for the reaction of $\mathrm{V^{2+}}$ with $\mathrm{VO^{2+}}$ (0·97 l mole^{-1}

sec^{-1}), and the mercury(II) is always in at least ten-fold excess, it can be concluded that <1% of the vanadium(III) is formed from the reaction of V^{2+} with VO^{2+}, *i e via* VOV^{4+} Even when the mercury(II) solution contains an equivalent amount of vanadium(IV) the contribution from this path remains small and can be neglected The maximum concentration of VOV^{4+} ($\epsilon = 6800$) observed in a run with $[V^{2+}] = 4\ 4 \times 10^{-3}$M, $[Hg^{2+}] = 4\ 7 \times 10^{-2}$M, and $[H^+] = 1{\cdot}0$ M, was 8×10^{-6}M It is possible that some of the VOV^{4+} is formed from the reaction of V^{2+} with traces of oxygen remaining in the system

Activation parameters for k_1, k_2, and k_3 are shown in the Table Before making a direct comparison of these quantities it is important to consider whether the reactions are inner- or outer-sphere Thus in the reaction of chromium(II) with hexachloroiridium(IV) it has been shown that $\Delta H^{\ddagger}_{is} - \Delta H^{\ddagger}_{os} = 5\ 7$ kcal mole^{-1} and $\Delta S^{\ddagger}_{is} - \Delta S^{\ddagger}_{os} = 19\ 0$ e u[11] While we believe that the two electron paths in (4) are inner-sphere,[12] the mechanism of the one-electron path seems less certain The higher $\Delta H^{\ddagger}$ value for the one-electron path may (in part) reflect energy requirements for the formation of Hg^{I} ions

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