One- and Two-equivalent Paths in the Reaction of Vanadium(II) with Mercury(II). A Recalculation of Kinetic Parameters

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Kinetic parameters for the one- and two-electron paths in the reaction of vanadium(II) with mercury(II) have been recalculated. The one-electron path ($a = k_a$) is independent of [H+]; at 25° $k_a = 1.04 \pm 0.11$ l mol^{-1} s^{-1}, $\Delta H_a^{\ddagger} = 15.8 \pm 0.8$ kcal mol^{-1}, and $\Delta S_a^{\ddagger} = -5.6 \pm 2.7$ e.u. There is now no detectable contribution from an [H+]-independent path for the two-electron reaction ($b = k_b$[H+]$^{-1}$), and at 25° $k_b = 8.69 \pm 0.02$ s^{-1}, $\Delta H_b^{\ddagger} = 14.8 \pm 0.2$ kcal mol^{-1}, and $\Delta S_b^{\ddagger} = -4.6 \pm 0.8$ e.u.

WE wish to rectify an error which has been made in evaluating kinetic data for the reaction of vanadium(II) and mercury(II).[1] Rate constants associated with the one- and two-equivalent paths for this reaction (a and b respectively) are as defined in equation (1), where

$$[V^{III}]_{\infty}/[V^{IV}]_{\infty} = 2a/b \qquad (1)$$

$[V^{III}]_{\infty}$ and $[V^{IV}]_{\infty}$ are the final concentrations of the two products. Kinetic measurements on the rate of formation of vanadium(IV) at 760 nm do not, in fact, give b directly as was previously supposed. For runs under pseudo-first-order conditions with a large excess of the mercury(II) reactant the rate law (2) is obtained, which

$$-d[V^{II}]/dt = (2a + b)[V^{II}][Hg^{II}] \qquad (2)$$

on integration gives (3), where $[V^{II}]_0$ is the initial

$$[V^{II}] = [V^{II}]_0 \exp\{-(2a + b)[Hg^{II}]t\} \qquad (3)$$

concentration of vanadium(II). The rate law for the formation of vanadium(IV) is given by equation (4).

$$d[V^{IV}]/dt = b[V^{II}][Hg^{II}] \qquad (4)$$

This can only be integrated after substituting for $[V^{II}]$ as in (3). Hence equation (5) is obtained,

$$[V^{IV}] = \frac{b}{(2a + b)} [V^{II}]_0(1 - \exp\{-(2a + b)[Hg^{II}]t\}) \quad (5)$$

Graphs of log (OD$_{\infty}$ − OD$_t$) against time, t, at 760 nm ($\varepsilon = 17.2$ l mol^{-1} cm^{-1} for V^{IV}) therefore give $(2a + b)$ and not solely b. Rate constants b in Table 1 (and Table 5) of reference 1 should read $(2a + b)$, and values of a in Table 2 are incorrect. Correct values are given in Table 1 of this paper. Although b exhibits an [H+]$^{-1}$ dependence there is now no measurable [H+]-independent term. Thus we can write $a = k_a$† and $b = k_b$[H+]$^{-1}$. Revised rate constants and activation parameters for k_a and k_b are given in Tables 2 and 3. Comments regarding the effect of Cl$^-$ and SO$_4^{2-}$ remain unchanged.

TABLE 1

Product analyses and second-order rate constants for the reaction of vanadium(II) with mercury(II), $\mu = 2.0$M (LiClO$_4$)

Temp. (°C)	[H+] (M)	[V^{IV}]$_\infty$/[V^{III}]$_\infty$	$(2a + b)$ * (l mol^{-1} s^{-1})	a (l mol^{-1} s^{-1})	b † (l mol^{-1} s^{-1})
10.0	0.25	15.6	9.34	0.280	8.78
	0.50	8.1	5.00	0.275	4.45
	1.12	5.25	2.60	0.208	2.18
	1.37	4.0	2.24	0.224	1.79
	1.91	2.45	1.80	0.261	1.28
15.0	0.50	8.1	7.86	0.432	7.00
	1.12	4.56	4.04	0.363	3.31
	1.37	3.35	3.48	0.400	2.68
	1.91	2.70	2.77	0.374	2.02
20.0	0.50	8.1	13.0	0.715	11.7
	1.12	3.76	6.58	0.691	5.20
	1.37	3.00	5.64	0.705	4.23
	1.91	2.33	4.44	0.667	3.11
25.0	0.27	13.3	34.6	1.21	32.2
	0.29	13.3	32.3	1.13	30.1
	0.50	7.33	19.5	1.17	17.2
	0.50	7.33	19.5	1.17	17.2
	0.92	4.26	11.5	1.09	9.27
	1.00	3.76	10.7	1.12	8.44
	1.00	4.00	10.7	1.07	8.54
	1.17	3.55	9.40	1.03	7.33
	1.37	2.85	8.29	1.08	6.14
	1.57	3.00	7.47	0.93	5.60
	1.57	3.17	7.47	0.90	5.68
	1.82	2.57	6.70	0.94	4.82
	1.82	2.70	6.70	0.91	4.89
	1.91	2.57	6.47	0.91	4.66
	1.91	2.33	6.47	0.97	4.53
	1.91	2.33	6.47	0.97	4.53

* From computed data in Table 3 of ref. 1. † Calculated using a values for individual runs. Alternatively b can be determined using an averaged value of a at each temperature. The latter method has been used in computing activation parameters for b.

TABLE 2

Values of k_a and k_b for the one- and two-electron paths in the reaction of vanadium(II) with mercury(II), $\mu = 2.0$M (LiClO$_4$)

Temp. (°C)	k_a (l mol^{-1} s^{-1})	k_b (s^{-1})
10	0.250 ± 0.032	2.23 ± 0.02
15	0.392 ± 0.031	3.58 ± 0.04
20	0.695 ± 0.021	5.80 ± 0.01
25	1.04 ± 0.11	8.69 ± 0.02

TABLE 3

A summary of kinetic data (revised) for the reaction of vanadium(II) with mercury(II), $\mu = 2.0$M (LiClO$_4$)

Rate constants (25°)	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (e.u.)
k_a (1 electron)* = 1.04 ± 0.11 (1 mol^{-1} s^{-1})	15.8 ± 0.8	−5.6 ± 2.7
k_b (2 electrons) = 8.69 ± 0.02 (s^{-1})	14.8 ± 0.2	−4.6 ± 0.8

* Alternatively, and possibly less precisely, k_a can be evaluated by plotting $(2a + b)$ against [H+]$^{-1}$ (see Figure 1 of ref. 1) and measuring the intercepts ($2a$). This gives $k_a = 0.92 \pm 0.03$ at 25°, $\Delta H^{\ddagger} = 10.9 \pm 0.7$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -20.8 \pm 2.2$ e.u. If all k_a values are taken into account, and the activation parameters re-computed, these are $\Delta H^{\ddagger} = 13.9 \pm 1.3$ kcal mol^{-1} and $\Delta S^{\ddagger} = -11.8 \pm 4.4$.

† At 25° a small (decreasing) trend in a values with increasing [H+] is noted. Since a is determined indirectly we are uncertain as to whether this ($\pm 10\%$) effect is meaningful and have, therefore, averaged a values.

[1] M. Green and A. G. Sykes, *J. Chem. Soc. (A),* 1970, 3221.

The mechanistic implications are (i) that the one-electron path $V^{II} + Hg^{II} \longrightarrow V^{III} + Hg^{I}$ is possibly V^{2+}-substitution controlled [2-4] and (ii) that the two-electron path, $V^{II} + Hg^{II} \longrightarrow V^{IV} + Hg^0$, proceeds *via* a hydroxy-bridged activated complex. The presence of a hydroxide group in the activated complex is important since the vanadium(IV) product is the vanadyl ion VO^{2+}. The reaction of vanadium(II) with vanadium(IV) is too slow to be effective.[5] An inner-sphere mechanism seems likely for a path involving transfer of two electrons.[1] If the reactants are V^{2+} and $HgOH^+$ then the bimolecular rate constant for this path will be $3 \cdot 2 \times 10^4$ l mol^{-1} s^{-1} at 25°,[6] and it is necessary to invoke proton transfer between the two co-ordination spheres and loss of an H_2O ligand from the Hg^{2+} reactant prior to formation of an inner-sphere activated complex. Alternatively loss of a proton from the H_2O-bridged precursor complex VH_2OHg^{4+} is a possible mechanism. We note that the activation parameters for k_a and k_b (the latter a composite term) are remarkably similar.

[2] H. J. Price and H. Taube, *Inorg. Chem.*, 1968, **7**, 1.
[3] N. Sutin, *Acc. Chem. Res.*, 1968, **1**, 228.
[4] M. Green, R. S. Taylor, and A. G. Sykes, *J. Chem. Soc. (A)*, 1971, 509.

[5] T. W. Newton and F. B. Baker, *Inorg. Chem.*, 1964, **3**, 569.
[6] R. Arnek and W. Kakolowicz, *Acta Chem. Scand.*, 1967, **21**, 1449, give a value $2 \cdot 75 \times 10^{-4}$ mol l^{-1} for the acid dissociation constant of Hg^{2+} at 25°, $\mu = 3 \cdot 0$M (NaClO$_4$).