# Kinetics of the Oxidation of Vanadium(III) by Bromine in Aqueous Solutions

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The reaction of $2V^{3+} + Br_2 + 2H_2O \longrightarrow 2VO^{2+} + 2Br^- + 4H^+$ obeys the rate expression $-d[V^{III}]/dt = k'[V^{III}][Br_2][H^+]^{-1}$ with $k' = 4.57 \pm 0.44\ s^{-1}$, $E_a = 63.6 \pm 2.9$ kJ mol$^{-1}$ and $\Delta S^{\ddagger} = -38.1 \pm 7$J mol$^{-1}$ K$^{-1}$ at 25 °C and ionic strength, $\mu = 2.0$M. $V^{3+}$ Therefore reacts with $Br_2$ at a negligible rate compared with that of $VOH^{2+}$. Added chloride ion enhances the rate of the reaction while bromide decreases it.

THE oxidations of vanadium(III) by halogens are examples of non-complementary reactions, $2V^{3+} + X_2 + 2H_2O \longrightarrow 2VO^{2+} + 2X^- + 4H^+$, and could in principle proceed initially *via* either one- or two-electron paths [(1) and (2)]:

$$V^{III} + X_2 \rightleftharpoons V^{IV} + X_2^-,\ V^{III} + X_2^- \longrightarrow V^{IV} + 2X^- \quad (1)$$

$$V^{III} + X_2 \rightleftharpoons V^{V} + 2X^-,\ V^{III} + V^{V} \longrightarrow 2V^{IV} \quad (2)$$

In other reactions vanadium has been shown to react by both types of mechanism, *e.g.* the non-complementary reaction $2V^{III} + Tl^{III} \longrightarrow 2V^{IV} + Tl^{I}$ has been shown[1] to proceed *via* a one-electron path while the complementary reaction $V^{V} + Sn^{II} \longrightarrow V^{III} + Sn^{IV}$ is probably[2] a direct two-electron transfer.

Early work[3] on the oxidation of vanadium(III) by iodine in the presence of an excess of iodide showed that the reaction obeyed the rate expression $-d[I_2]/dt = k'[V^{3+}][I_3^-][H^+]^{-1}[I^-]^{-1}$ with $k'$ *ca.* $1.7 \times 10^{-5}$ mol l$^{-1}$ s$^{-1}$. It was shown that the addition of $V^{IV}$ had no effect on the rate of reaction, there was no path involving HOI, and the only path for the reaction was $VOH^{2+} + I_2 \longrightarrow$.

## EXPERIMENTAL

Vanadium(III) solutions were prepared as follows. Ammonium metavanadate was dissolved in dilute perchloric acid, reduced to vanadium(IV) with sodium sulphite, and sodium carbonate solution added to precipitate hydrated $V_2O_4$. The latter was then washed to remove sulphate ions, dissolved in perchloric acid, and the vanadium(IV) reduced to vanadium(III) electrolytically in a nitrogen atmosphere at a mercury cathode at 0 °C. Vanadium(III) concentrations were estimated after oxidation to vanadium(IV) with an excess of $KIO_3$ by titration of the liberated $I_2$ with standard thiosulphate solution.[4] Sodium perchlorate solutions were prepared by neutralising a slurry of sodium carbonate with perchloric acid (both AnalaR), and their concentrations were determined by evaporating a known volume of solution to dryness and weighing the resulting solid. Bromine solutions were prepared by dissolving AnalaR bromine in distilled water and their concentrations estimated iodometrically by addition of an excess of potassium iodide and titration of the liberated iodine with standard thiosulphate solution.

Spectra were measured using Unicam SP 800 (qualitatively) and SP 500 (quantitatively) spectrophotometers. The course of the reaction between vanadium(III) and bromine was followed by monitoring the bromine concentration at 395 nm. The measured values of the extinction coefficients used were: $\varepsilon_{Br_2} = 180.0 \pm 0.1$ and $\varepsilon_{VIII} = 9.79 \pm 0.05$ l mol$^{-1}$ cm$^{-1}$. Most kinetic measurements were made manually using 4-cm quartz cells in a thermostatted cell compartment of a Unicam SP 500 spectrophotometer, but the fastest reactions (those at low acid concentration) were followed using a home-made stopped-flow apparatus.[5] The reaction of vanadium(IV) with bromine is much slower than that of vanadium(III), but to avoid complications due to this further reaction all runs were performed with $2[V^{III}] = [Br_2]$. The ionic strength was maintained at $\mu = 2.0$M using sodium perchlorate as the 'inert' electrolyte.

## RESULTS

*Stoicheiometry.*—Solutions of bromine and vanadium(III) of known concentration were mixed in volumetric flasks and kept in a thermostat for about 30 min. The excess $V^{III}$ or $Br_2$ was then estimated volumetrically (Table 1). The average value obtained for the ratio $[V^{III}]_{consumed} : [Br_2]_{consumed}$ was 2·08 : 1, thus confirming that the overall reaction can be written as $2V^{III} + Br_2 \longrightarrow 2V^{IV} + 2Br^-$ and that oxidation of vanadium(III) to vanadium(V) is negligible under these conditions (it would have led to a stoicheiometric ratio $<2$). Thus $-2d[Br_2]/dt = -d[V^{III}]/dt = +d[V^{IV}]/dt$.

TABLE 1

The stoicheiometry of the reaction between vanadium(III) and bromine. $\mu = 1.0$M; $[H^+] = 1.0$M; Temp. = 25 °C

| $10^2[V^{III}]_0$ M | $10^2[V^{III}]_\infty$ M | $10^2[Br_2]_0$ M | $10^2[Br_2]_\infty$ M | $[V^{III}]_{consumed}/[Br_2]_{consumed}$ |
|---|---|---|---|---|
| 5·97 | 1·01 | 2·37 | 0·00 | 2·09 |
| 6·43 | 1·48 | 2·37 | 0·00 | 2·09 |
| 7·34 | 2·46 | 2·37 | 0·00 | 2·06 |
| 1·32 | 0·00 | 2·24 | 1·62 | 2·10 |
| 0·88 | 0·00 | 2·24 | 1·84 | 2·10 |

Average = 2·08 ± 0·02

*Kinetics.*—We assumed that the reaction obeyed second-order kinetics, with $-d[V^{III}]/dt = k[V^{III}][Br_2]$ and always used $2[Br_2]_0 = [V^{III}]_0$. Plots were made of $1/O.D._t$ against time, where the slope is equal to $k/(2\varepsilon_{VIII} + \varepsilon_{Br_2})l$. ($O.D._t$ is the optical density at time $t$, $\varepsilon_{VIII}$ and $\varepsilon_{Br_2}$ are the molar extinction coefficients of the two species, and $l$ is the path length.) Good straight line graphs were

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

[2] E. A. M. Wetton and W. C. E. Higginson, *J. Chem. Soc.*, 1965, 5890.

[3] J. B. Ramsay and M. J. Heldman, *J. Amer. Chem. Soc.*, 1936, **58**, 1153.

[4] W. C. E. Higginson and A. G. Sykes, *J. Chem. Soc.*, 1962, 2841.

[5] J. H. Rawsthorne, D.Phil. Thesis, University of Sussex, 1967.

obtained for up to about 80% reaction (Figure 1) and this, together with the constancy of the rate constants obtained (Table 2), confirms that the reaction is second order.

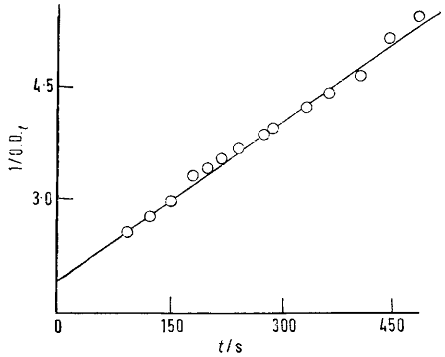

FIGURE 1 Second-order plot for the vanadium(III)–bromine reaction: $[\mathrm{V^{III}}]_0 = 1{\cdot}6 \times 10^{-3}\,\mathrm{M}$; $[\mathrm{Br_2}]_0 = 8{\cdot}0 \times 10^{-4}\,\mathrm{M}$; $[\mathrm{H^+}] = 1{\cdot}0\,\mathrm{M}$; $\mu = 2{\cdot}0\,\mathrm{M}$; Temp. = 25 °C

The results in Table 2 show that the rate constant decreases with increasing $[\mathrm{H^+}]$. A plot of $\log k$ against $\log\,[\mathrm{H^+}]$ gave a good straight line of slope $-0{\cdot}98 \pm 0{\cdot}03$, the order with respect to $[\mathrm{H^+}]$. The rate expression can therefore be written as in equation (3). Values of $k'$ calculated using this expression are listed in Table 2 and give an average value of $4{\cdot}57 \pm 0{\cdot}44\ \mathrm{s^{-1}}$.

TABLE 2

Rate constants for the vanadium(III)–bromine reaction at various acid concentrations. Temp. = 25 °C; $\mu = 2{\cdot}0\,\mathrm{M}$

| Number of runs | $10^3[\mathrm{V^{III}}]$ (M) | $10^3[\mathrm{Br_2}]$ (M) | $[\mathrm{H^+}]$ (M) | $k/\mathrm{mol^{-1}\ s^{-1}}$ | | $k'/\mathrm{s^{-1}}$ |
|---|---|---|---|---|---|---|
| 1 | 1·6 | 0·8 | 1·0 | 5·04 | | 5·04 |
| 1 | 1·6 | 0·8 | 1·0 | 5·21 | 4·66 | 5·21 |
| 1 | 2·4 | 1·2 | 1·0 | 4·01 | ± 0·23 | 4·01 |
| 1 | 3·2 | 1·6 | 1·0 | 4·38 | | 4·38 |
| 1 | 2·4 | 1·2 | 2·0 | 1·75 | | 3·50 |
| 1 | 2·4 | 1·2 | 1·7 | 2·48 | | 4·21 |
| 1 | 2·4 | 1·2 | 1·5 | 3·14 | | 4·71 |
| 1 | 2·4 | 1·2 | 0·8 | 5·90 | | 4·72 |
| 1 | 2·4 | 1·2 | 0·65 | 7·45 | | 4·84 |
| 1 | 2·4 | 1·2 | 0·50 | 10·08 | | 5·04 |
| 4 [a] | 20·0 | 10·0 | 0·243 | 20·3 ± 1·1 | | 4·93 |
| 4 [a] | 20·0 | 10·0 | 0·193 | 23·0 ± 2·3 | | 4·45 |
| 4 [a] | 20·0 | 10·0 | 0·143 | 32·7 ± 3·4 | | 4·67 |
| | | | | | Average = | 4·56 ± 0·44 |

[a] Runs performed using the stopped-flow apparatus.

$$-\mathrm{d}[\mathrm{V^{III}}]/\mathrm{d}t = k'[\mathrm{V^{III}}][\mathrm{Br_2}][\mathrm{H^+}]^{-1} \qquad (3)$$

The second-order rate constant $k$ was also measured at four different temperatures (Table 3). A plot of $\log k$ against $1/T$ was a good straight line yielding the Arrhenius parameters $E_a = 63{\cdot}6 \pm 2{\cdot}9\ \mathrm{kJ\ mol^{-1}}$ and $\Delta S^\ddagger = -38{\cdot}1 \pm 1{\cdot}7\ \mathrm{J\ mol^{-1}\ K^{-1}}$ from the absolute rate equation (4)

$$k = \frac{\mathrm{e}kT}{h}\,\mathrm{e}^{\Delta S^\ddagger/R}\,\mathrm{e}^{-E_a/RT} \qquad (4)$$

The effect of adding chloride and bromide ions to the reaction mixture was investigated. The rate constants obtained are listed in Table 4. It will be seen that bromide slows down the reaction while chloride accelerates it. These results are discussed later.

TABLE 3

Rate constants for the vanadium(III)–bromine reaction as a function of temperature. $\mu = 2{\cdot}0\,\mathrm{M}$; $[\mathrm{V^{III}}]_0 = 2{\cdot}4 \times 10^{-3}\,\mathrm{M}$; $[\mathrm{Br_2}]_0 = 1{\cdot}2 \times 10^{-3}\,\mathrm{M}$; $[\mathrm{H^+}] = 1{\cdot}0\,\mathrm{M}$

| Temp./°C | $k/\mathrm{l\ mol^{-1}\ s^{-1}}$ | Temp./°C | $k/\mathrm{l\ mol^{-1}\ s^{-1}}$ |
|---|---|---|---|
| 35 | 11·6 | 15 | 2·44 |
| 35 | 11·4 | 15 | 2·08 |
| 35 | 11·1 | 5 | 0·97 |
| 15 | 2·80 | | |

TABLE 4

Rate constants for the vanadium(III)–bromine reaction as a function of added chloride and bromide ions. $\mu = 2{\cdot}0\,\mathrm{M}$; $[\mathrm{V^{III}}]_0 = 2{\cdot}4 \times 10^{-3}\,\mathrm{M}$; $[\mathrm{Br_2}]_0 = 1{\cdot}2 \times 10^{-3}\,\mathrm{M}$; $[\mathrm{H^+}] = 1{\cdot}0\,\mathrm{M}$. Temp. = 25 °C

| $[\mathrm{Cl^-}]$(M) | $[\mathrm{Br^-}]$(M) | $k/\mathrm{l\ mol^{-1}\ s^{-1}}$ |
|---|---|---|
| 0·002 | | 5·75 |
| 0·004 | | 7·55 |
| 0·006 | | 8·90 |
| 0·008 | | 9·44 |
| 0·010 | | 9·97 |
| | 0·01 | 2·73 [a] |
| | 0·03 | 2·12 |
| | 0·04 | 1·84 |
| | 0·10 | 1·35 |
| | 0·20 | 0·86 |

[a] $[\mathrm{V^{III}}]_0 = 1{\cdot}6 \times 10^{-3}\,\mathrm{M}$; $[\mathrm{Br_2}]_0 = 8{\cdot}0 \times 10^{-4}\,\mathrm{M}$.

## DISCUSSION

The acid-dependence data fit the rate expression (3). The most probable mechanism to account for this is as in equations (5)—(8), with $k_2$, $k_3 \gg k_1$ and $2k_1K_1 = k'$.

$$\mathrm{V^{3+} + H_2O \overset{K_1}{\rightleftharpoons} VOH^{2+} + H^+} \qquad (5)$$

$$\mathrm{VOH^{2+} + Br_2 \xrightarrow{k_1} VOH^+ + Br_2^-} \qquad (6)$$

$$\mathrm{VOH^{2+} + Br_2^- \xrightarrow{k_2} VOH^+ + 2Br^-} \qquad (7)$$

$$\mathrm{2VOH^+ \xrightarrow{k_3} 2VO^{2+} + 2H^+} \qquad (8)$$

Taking $K_1 = 1{\cdot}3 \times 10^{-3}\ \mathrm{mol\ l^{-1}}$,[6] this gives $k_1 = 1{\cdot}8 \times 10^3\ \mathrm{l\ mol^{-1}\ s^{-1}}$. The approximate values $\Delta H = 42\ \mathrm{kJ\ mol^{-1}}$ and $\Delta S = +84\ \mathrm{J\ mol^{-1}\ K^{-1}}$ have been reported[7] for reaction (5), and using these together with our measured Arrhenius parameters for $k'$ we obtain the following approximate Arrhenius parameters for $k_1$: $\Delta H^\ddagger = 19{\cdot}7\ \mathrm{kJ\ mol^{-1}}$ and $\Delta S^\ddagger = -121\ \mathrm{J\ mol^{-1}\ K^{-1}}$. The reactions of vanadium(III) with bromine and iodine are identical in that $\mathrm{V^{3+}}$ reacts at a rate negligible compared with that of $\mathrm{VOH^{2+}}$.

The catalysis of the vanadium(III)–bromine reaction by added chloride ions can be qualitatively attributed to chloride complexes of $\mathrm{V^{III}}$ and/or $\mathrm{Br_2}$ reacting more

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[6] 'Stability Constants of Metal-Ion Complexes,' Chem. Soc. Special Publ. No. 17, 2nd edn., 1964; Suppl. 1, 1971.

[7] S. C. Furman and C. S. Garner, *J. Amer. Chem. Soc.*, 1950, **72**, 1785.

rapidly than the uncomplexed species. No quantitative data have been published concerning $V^{III}$–$Cl^-$ complexes but $Br_2Cl^-$ is well known, with $K_3 = 1{\cdot}4$ l mol$^{-1}$. It seems likely that hydrolysis of $V^{3+}$ would

$$H_2O + V^{3+} + Br_2 \xrightleftharpoons{k} VO^{2+} + Br_2^- + 2H^+ \quad (9)$$

$$V^{3+} + Cl^- \xrightleftharpoons{K_2} VCl^{2+} \quad (10)$$

$$Br_2 + Cl^- \xrightleftharpoons{K_3} Br_2Cl^- \quad (11)$$

$$VCl^{2+} + Br_2 \xrightarrow{k_4} VCl^{3+} + Br_2^- \quad (12)$$

$$H_2O + V^{3+} + Br_2Cl^- \xrightarrow{k_5} VO^{2+} + Br_2^- + Cl^- + 2H^+ \quad (13)$$

still be a precondition for reaction but we have not investigated the acid dependence of the catalysed reaction so the unhydrolysed species have been given in reactions (9)—(13). The two paths for the catalysed reaction (10), (12) and (11), (13) are kinetically indistinguishable. If only small fractions of $V^{III}$ and $Br_2$ are present as the complexed ions (an assumption which is correct for $Br_2$ since $K_3 = 1{\cdot}4$ l mol$^{-1}$ and therefore only about 1% of the total bromine is present as $Br_2Cl^-$ at the highest $[Cl^-]$ used, and is probably correct for $V^{3+}$ by analogy with $Fe^{3+}$), then a plot of $k$ against $[Cl^-]$ should be linear. The plot (Figure 2) is indeed linear within the limits of experimental error, with an intercept of $4{\cdot}93 \pm 0{\cdot}36$ l mol$^{-1}$ s$^{-1}$ (to be compared with the value of $k = 4{\cdot}66 \pm 0{\cdot}23$ l mol$^{-1}$ s$^{-1}$ obtained in the absence of added chloride) and slope of $(5{\cdot}55 \pm 0{\cdot}59) \times 10^2$ l$^2$ mol$^{-2}$ s$^{-1}$.

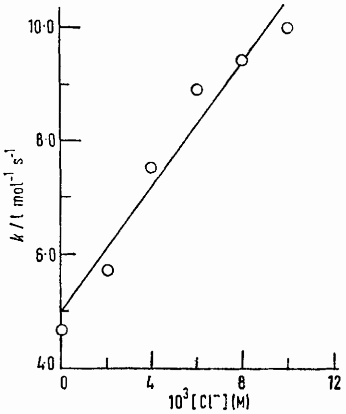

FIGURE 2 The catalysis of the vanadium(III)–bromine reaction by chloride ions; $\mu = 2{\cdot}0$M: Temp. = 25 °C

Writing,

$$\begin{aligned}\text{Rate} &= k[V^{3+}][Br_2] + k_4[VCl^{2+}][Br_2] + k_5[V^{3+}][Br_2Cl^-]\\ &= [V^{3+}][Br_2]\{k + (k_4K_2 + k_5K_3)[Cl^-]\} \quad (14)\end{aligned}$$

it can be seen that $(k_4K_2 + k_5K_3) = 5{\cdot}55 \times 10^2$ l$^2$ mol$^{-2}$ s$^{-1}$. In the absence of information concerning $K_2$, we attribute all the catalysis to $Br_2Cl^-$ and from $k_5K_3 = 5{\cdot}55 \times 10^2$ l$^2$ mol$^{-2}$ s$^{-1}$ obtain the result $k_5 = 4 \times 10^2$ l mol$^{-1}$ s$^{-1}$.

Added $Br^-$, unlike $Cl^-$, decreases the rate of the reaction. Although $Br^-$ is generated during the course of the reaction the second-order plots did not show retardation effects, but $[Br^-]$ used to obtain the data in Table 4 were 5—50 times greater than those generated during a run. Quantitative treatment of the data is not possible because of the lack of published data concerning $V^{III}$–$Br^-$ complexes, but it can be shown that the formation of $Br_3^-$, the decrease in [HOBr], and the formation of $VBr^{2+}$ with increasing $[Br^-]$, cannot individually account for the observed decrease in rate [unless the formation constant for $VBr^{2+}$ is taken to be improbably large ($K > 40$ l mol$^{-1}$)]. This suggests that the first step in the mechanism may consist of one of the reversible reactions $V^{III} + Br_2 \rightleftharpoons V^V + 2Br^-$ or $V^{III} + Br_2 \rightleftharpoons V^{IV} + Br + Br^-$.

The value of $k_1 = 1{\cdot}8 \times 10^3$ l mol$^{-1}$ s$^{-1}$ for the $VOH^{2+}$–$Br_2$ reaction might be thought to be evidence that the reaction proceeds by an outer-sphere mechanism since substitution into the inner-co-ordination sphere of $V^{3+}$ appears to be a relatively slow process, with the second-order rate constant for $V^{3+} + NCS^- \longrightarrow VNCS^{2+}$ having the value[8] of 63 l mol$^{-1}$ s$^{-1}$. However, if the relative rates of substitution at $VOH^{2+}$ and $V^{3+}$ are similar to those of $FeOH^{2+}$ and $Fe^{3+}$ (*ca.* 100 : 1—1000 : 1), $k_1$ for the oxidation reaction will be considerably less than the rate constant for substitution at $VOH^{2+}$.

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[1/2196 *Received, 19th November,* 1971]

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[8] M. Eigen and R. G. Wilkins, 'Mechanisms of Inorganic Reactions,' Advances in Chemistry Series 49, Amer. Chem. Soc., 1965.