

Reduction of vanadium(v) by oxalic acid in aqueous acid solutions

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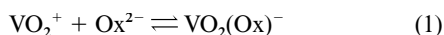
The reduction of vanadium(v) to vanadium(IV) by oxalate in acidic media proceeds at 50 °C via two parallel pathways that involve activated states of compositions $\{\text{VO}_2^+; 2\text{H}^+; 2\text{C}_2\text{O}_4^{2-}\}^*$ and $\{\text{VO}_2^+; 2\text{H}^+; 3\text{C}_2\text{O}_4^{2-}\}^*$, resulting in an apparent change in the partial order on oxalate as its concentration increases and a maximum in the rate/pH profiles. The best explanation for these results assumes outer sphere electron transfer as the rate determining step in both pathways, without formation of vanadium(III). The implications for the bioinorganic chemistry of vanadium are discussed.

Introduction

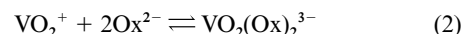
V(v) reduction by various organic and inorganic compounds was previously studied and reviewed; in most cases, V(IV) is formed and first-order kinetics in [V(v)] operate. Littler and Waters¹ have shown that most such reactions proceed via a free-radical mechanism, wherein V(v) undergoes a one-electron reduction. The reduction of V(v) by hydroquinone,² hypophosphorous acid³ and L-ascorbic acid⁴ proceeds through a complexation pre-equilibrium followed by an inner sphere one-electron transfer. The reaction with catechol has been studied in detail because of its relevance in bioinorganic chemistry (see below).^{5,6} In acidic media, catechol forms a complex with VO_2^+ that reacts with another VO_2^+ ion to generate V(IV) in the millisecond time range; this redox reaction becomes slower at higher pH.^{7,8} Another biologically important V(v) reductant is NADPH. The reaction of V(v) with NADPH in the presence of EDTA takes place readily in acidic media to produce V(IV).⁹

The driving force for these V(v) \rightarrow V(IV) reductions is highly dependent on pH; VO_2^+ is a strong oxidant in acid media. The value $E^\circ(\text{VO}_2^+/\text{VO}^{2+}) = 1.00 \text{ V}$ vs. SHE,^{10a} should be compared with the values $E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) = 0.77 \text{ V}$, and even $E^\circ(\text{O}_2/\text{H}_2\text{O}_2) = 0.68 \text{ V}$. The Nernst equation indicates a drop of 0.118 V per pH unit in $E(\text{V(v)}/\text{V(IV)})$ below pH 3.5,¹¹ and even higher drops in less acidic media. In near neutral media, aqueous V(IV) is unstable towards dismutation, but it may be stabilized by complexation. In these conditions, V(v) is a mild oxidant and V(IV) a mild reductant (and a very weak oxidant that may produce V(III)).

V(v) oxalate-complexes are well known.¹² Both $\text{VO}_2(\text{Ox})^-$ and $\text{VO}_2(\text{Ox})_2^{3-}$ have been characterized structurally in aqueous solution and in the solid phase, and their stabilities have been measured.^{13,14,15a,16} In acidic media, Voronova and Ivakin¹⁷ report $\log \beta_1 = 6.64$ and $\log \beta_2 = 10.20$ for the reactions shown in eqns. (1) and (2) at 20.0 °C. It has also been shown that the complexation equilibria are rapidly reached.¹⁸



[†] In what follows, Ox^{2-} denotes the dianion $\text{C}_2\text{O}_4^{2-}$ and $[\text{H}_2\text{Ox}]_{\text{T}}$ represents total (analytical) oxalate-containing species concentration.



V(IV)-oxalate complexes are also well known. Both $\text{VO}(\text{Ox})$ and $\text{VO}(\text{Ox})_2^{2-}$ have been described.^{19,20} The protonation state of the oxo groups in all these V(v) and V(IV) complexes may differ from that indicated in the above stoichiometries. For instance, at higher pH values, Tracey *et al.*¹⁴ describe the monooxalatovanadium(v) as $\text{VO}_2(\text{OH})_2(\text{Ox})^{3-}$. Vanadium is generally assumed to be hexa-coordinated in both oxidation states (although there is some controversy as to whether “ $\text{VO}_2(\text{Ox})^-$ ” is penta- or hexa-coordinated).^{14,21} If it is accepted that in acid media the moieties VO_2^+ and VO^{2+} remain unchanged upon oxalate substitution for water, the reduction of $\text{VO}_2(\text{Ox})_n^{1-2n}$ to $\text{VO}(\text{Ox})_n^{2-2n}$ involves probably the double protonation of one oxo group, without other appreciable changes in the coordination sphere. This facile interconversion may favor outer sphere reactions.

Due to the different stabilities of the V(v) and V(IV) complexes, V(v) becomes a more powerful oxidant in oxalate media ($E^\circ(\text{VO}_2(\text{Ox})^-/\text{VO}(\text{Ox})) = 1.13 \text{ V}$ and $E^\circ(\text{VO}_2(\text{Ox})_2^{3-}/\text{VO}(\text{Ox})_2^{2-}) = 1.22 \text{ V}$, calculated using stability constants from Table 1). This enhanced oxidation power is of importance, as recently a value of 1.41 V has been proposed for the one-electron standard redox potential of oxalate, $E^\circ(\text{Ox}^-/\text{Ox}^{2-})$.²³ Thus, $\text{Ox}^{\cdot-}$ radicals might be generated (in low concentrations) in acid media, in the course of a redox reaction leading to V(IV) and CO_2 . Thermodynamically, the oxidation of oxalate by V(v) in acidic solutions is assisted by a large driving force ($E^\circ(\text{HOx}^-/\text{CO}_2) = -0.511 \text{ V}$).^{10b,24} Indeed, it was observed earlier that aqueous solutions prepared by adding oxalic acid in excess under stirring to solid V_2O_5 suspended in boiling water¹⁹ or at room temperature²⁵ evolved to a V(IV) solution. The V(v) reduction by oxalate is used as a standard preparative procedure of V(IV) solutions.

This paper presents the results of an experimental study of the kinetics of V(v) reduction by oxalic acid. Kinetically, the process is governed by the first electron transfer (ET) and the participation of the radical anion $\text{Ox}^{\cdot-}$ as a true intermediate is discussed. A reaction scheme that accounts for the experimental results is proposed.

The important bioinorganic vanadium species are not only V(v) and V(IV). It is currently accepted that the blood of

Table 1 Solution equilibrium constants

Complex	log $K_{\text{formation}}^a$	Experimental conditions	Ref.
HOx ⁻	3.54 ^b	$I = 0.5 \text{ mol dm}^{-3} (\text{NaClO}_4) T = 25^\circ\text{C}$	15b
H ₂ Ox	4.57 ^c	$I = 0.5 \text{ mol dm}^{-3} (\text{NaClO}_4) T = 25^\circ\text{C}$	15b
VO(Ox)	6.45	$I = 1.0 \text{ mol dm}^{-3} (\text{NaClO}_4) T = 20^\circ\text{C}$	22
VO(Ox) ₂ ²⁻	11.77	$I = 1.0 \text{ mol dm}^{-3} (\text{NaClO}_4) T = 20^\circ\text{C}$	22
VO ₂ (Ox) ⁻	4.22	$I = 0.5 \text{ mol dm}^{-3} (\text{NaClO}_4)^d T = 20^\circ\text{C}$	15a
VO ₂ (Ox) ₂ ³⁻	7.99	$I = 0.5 \text{ mol dm}^{-3} (\text{NaClO}_4)^d T = 20^\circ\text{C}$	15a

^a Expressed as apparent formation constants from H⁺, Ox²⁻, VO₂⁺, VO²⁺. ^b $-\log K_{a2}$. ^c $-\log (K_{a1}K_{a2})$. ^d Interpolated from other I data.

ascidians (a major class of the *Tunicata*) contains V(III) as the aquo or sulfato complex in a medium of very low pH and strongly reducing conditions.^{26a,b,27} V(III) is generated from V(IV), that is produced by reduction of V(V) taken from sea water. It has been generally assumed that the so-called tunichromes (low molecular weight blood pigments that possess catechol-like functional groups) are the reductants,^{28,29} but recent papers suggest that NADPH is also a likely candidate.⁹ It is clear however that the reaction proceeds through the previous reduction to V(IV), and in this sense it has been indicated¹² that oxalate forms V(V) complexes with sufficiently large formation constants to be biologically significant. The results of this paper show that in acid media, reduction to V(IV) takes place upon complexation.

The way the reduction V(IV) → V(III) is achieved *in vivo* is still obscure. The value $E^\circ (\text{V(IV)/V(III)}) = 0.309 \text{ V}$,³⁰ and the pH dependence of reaction (3) justifies the requirement of low pH and highly reducing media to generate substantial amounts of V(III).



V(III) may also be generated in abiotic media; the V(V) reduction by benzaldehydes³¹ involves the formation of an intermediate compound with V(V) that evolves to benzoic acid and V(III). Rapid oxidation of the latter leads to V(IV). There are not many examples in which this V(V) reduction mechanism operates.

More strongly reducing conditions are required for the generation of V²⁺, $E^\circ (\text{V(III)/V(II)}) = -0.242 \text{ V}$.³⁰ In biological systems, this species becomes important only in V-nitrogenases.

Even though the total oxidation of oxalate could provide an adequate driving force for the reduction to proceed further to the V(IV) stage, there is no evidence of the formation of lower oxidation states in reaction media containing V(V) and oxalate.

Experimental

Reagents and equipment

All reagents, NH₄VO₃, H₂Ox·2H₂O and NaClO₄·H₂O, standard V(IV) and buffer solutions were of analytical grade (Merck) and were used as provided. Triply distilled water from a quartz apparatus was used to prepare solutions. Absorbance measurements and spectra were performed in a Hewlett-Packard 8453 diode-array spectrophotometer, using 5 cm cells.

Kinetic procedures and measurements

Kinetic measurements were carried out in a thermostatted ($T = 50.0 \pm 0.1^\circ\text{C}$) double-jacket cell with a perforated stopper fitted with pH and temperature sensors, gas inlet and outlet, and a sampling port. A typical experiment was started by adding 5 cm³ of $2.0 \times 10^{-2} \text{ mol dm}^{-3}$ V(V) to 95 cm³ of an oxalic acid solution of desired composition. V(IV) oxalate-complexes are reportedly light-sensitive,²⁴ and preliminary experiments performed under light demonstrated that the rate of reduction is sensitive to illumination. Therefore, all reported measurements

were performed in the dark under a stream of N₂ previously scrubbed through alkaline pyrogallol solution. Ionic strength (I) was fixed at 0.50 mol dm^{-3} (NaClO₄); the explored (total) oxalic acid concentration and pH ranges were $(0.5\text{--}2.5) \times 10^{-2} \text{ mol dm}^{-3}$ and 0.5–3.0, respectively.

The reaction progress was followed spectrophotometrically, by measuring the absorbance at 793.5 nm of aliquots withdrawn at different times. This is possible because V(V) species do not contribute appreciably to absorbance at this wavelength. Literature data^{15b,22,11} permit the calculation of the contribution of the (IV) species present in solution (VO²⁺, VO(Ox) and VO(Ox)₂²⁻) to the total V(IV) concentration, [V(IV)]_T (see Table 1). At a pH of about 0.5 the mono-oxalated species is predominant and is gradually converted to VO(Ox)₂²⁻ as the pH of the solution is raised. The cation VO²⁺ is only important at pH < 0.5. The measured absorbances were transformed into [V(IV)]_T values using eqn. (4), where l is the optical path, ϵ_i is the molar absorptivity and a_i the mole fraction of each V(IV) species.

$$A = (\epsilon_1 [\text{VO}^{2+}] + \epsilon_2 [\text{VO(Ox)}] + \epsilon_3 [\text{VO(Ox)}_2^{2-}]) l = (\epsilon_1 a_1 + \epsilon_2 a_2 + \epsilon_3 a_3) l [\text{V(IV)}]_T \quad (4)$$

The a_1 , a_2 and a_3 values were derived from equilibrium speciation calculations in V(IV)/NaClO₄/oxalic acid solutions as a function of pH.

The molar absorptivity of VO²⁺, $\epsilon_1 = 16 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ at 793.5 nm, was derived from the absorbance/concentration curve at pH = 1.0 in oxalate-free solutions and $I = 0.5 \text{ mol dm}^{-3}$ (NaClO₄). The molar absorptivity $\epsilon_3 = 27.0 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ (VO(Ox)₂²⁻) was obtained from measurements at pH > 2. The values found for both ϵ_1 and ϵ_3 were coincident with those reported in the literature.³² The molar absorptivity of VO(Ox) (ϵ_2) was derived from absorbance measurements of solutions containing variable oxalic acid/V(IV) molar relationships at pH 2.0 and $I = 0.50 \text{ mol dm}^{-3}$. The absorbance data at 793.5 nm were fitted using ϵ_1 , ϵ_3 and the apparent stability constants to yield $\epsilon_2 = 21 \pm 2 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$.

Fig. 1 presents the speciation diagram as a function of pH for

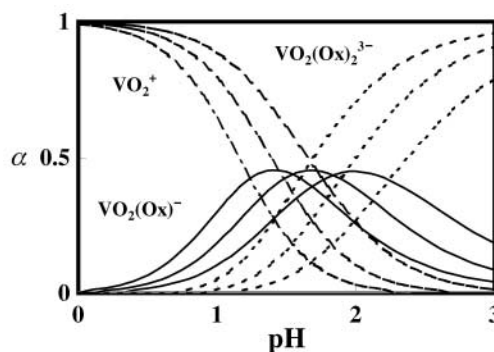


Fig. 1 Distribution of V(V) species in oxalic acid α as a function of pH at 50.0°C for $[\text{V(V)}]_T = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{H}_2\text{Ox}]_T = (0.5, 1.0 \text{ and } 2.0) \times 10^{-2} \text{ mol dm}^{-3}$ and $I = 0.50 \text{ mol dm}^{-3}$. Total oxalic acid concentration increases to the left.

$[V(v)]_T = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$, (total) oxalic acid concentrations ranging between $(0.5\text{--}2.0) \times 10^{-2} \text{ mol dm}^{-3}$ and $T = 50.0^\circ \text{C}$, calculated using the constants listed in Table 1. ‡ Hydrolysis equilibrium constants involved in these calculations were taken from the literature.¹¹ At $\text{pH} < 1$ the cation VO_2^+ predominates even at high oxalate concentrations, whereas at $\text{pH} > 2$ it becomes negligible at the highest oxalate concentrations explored. Decavanadates and $\text{VO}(\text{OH})_3$ are not significant in the pH range 0–3 (Corrections for temperature and ionic strength on apparent constants were performed in those cases where enthalpies or ionic strength dependence were available).

Results and discussion

Figs. 2–4 show the results presented as typical first-order plots in

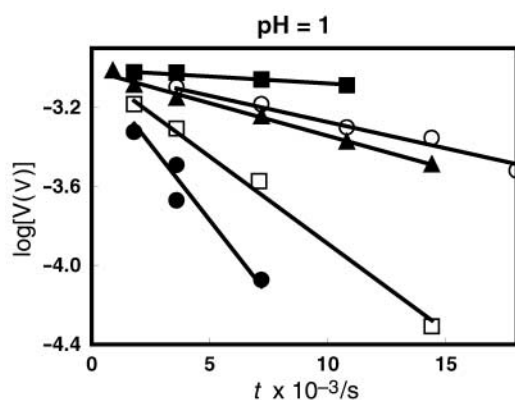


Fig. 2 First-order plot for the reduction of $1.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ V(v)}$ by $[\text{H}_2\text{Ox}]_T (\times 10^2 \text{ mol dm}^{-3})$ (■) 0.5, (○) 0.75, (▲) 1.0, (□) 1.5, (●) 2.0, pH 1.0, 50°C and $I = 0.50 \text{ mol dm}^{-3}$.

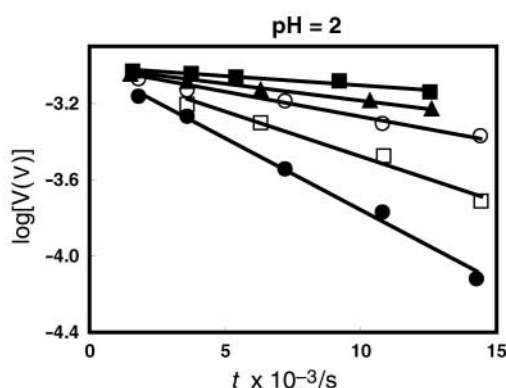


Fig. 3 First-order plot for the reduction of $1.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ V(v)}$ by $[\text{H}_2\text{Ox}]_T (\times 10^2 \text{ mol dm}^{-3})$ (■) 0.5, (○) 0.75, (▲) 1.0, (□) 1.5, (●) 2.0, pH 2.0, 50°C and $I = 0.50 \text{ mol dm}^{-3}$.

V(v) for different (total) oxalic acid concentrations at $\text{pH} = 1, 2$ and 3 , respectively. Pseudo first-order rate constants k_p , calculated as $-1/2 \times \text{slope}$ (see below, eqn. (14)) are collected in Table 2 and plotted as a function of $[\text{H}_2\text{Ox}]_T$ in Fig. 5 and against pH in Fig. 6.

A reaction mechanism that accounts for these results is given by eqns. (5)–(13).

‡ Tracey *et al.*¹⁴ have reported stability constants for mono- and bis-oxalato complexes of V(v) at higher pH (> 7). For the mono-oxalato species, the complex contains one proton less than the species assumed by Voronova and Ivakin.¹⁷ Both data are compatible if the acidity constant for $\text{VO}_2(\text{Ox})^-$ (to yield $\text{VO}(\text{OH})_3(\text{Ox})^{2-}$) is of the order of $10^{-4} \text{ mol dm}^{-3}$. For the bis-oxalato complex, the link between the constants reported by Tracey and Voronova is the acidity constant of VO_2^+ (to yield $\text{H}_2\text{VO}_4^- + 2\text{H}^+$). Using the reported value (10^7) for this constant,¹¹ there is a discrepancy between the two sets of data of *ca.* 2 units in $\text{p}K_a$. We have used Voronova and Ivakin's data, which were measured in conditions closer to our own.

Table 2 Pseudo first-order rate constants (k_p) of V(v) reduction in $[\text{H}_2\text{Ox}]_T = (0.5\text{--}2.5) \times 10^{-2} \text{ mol dm}^{-3}$ for $[\text{V(v)}] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$, $\text{pH} = 1\text{--}3$ at 50°C and $I = 0.50 \text{ mol dm}^{-3}$

$10^2 [\text{H}_2\text{Ox}]_T / \text{mol dm}^{-3}$	$10^5 k_p / \text{s}^{-1}$		
	$\text{pH} = 1.0$	$\text{pH} = 2.0$	$\text{pH} = 3.0$
0.50	0.354	0.487	—
0.75	1.33	1.16	—
1.00	1.65	0.886	—
1.50	4.41	2.21	0.117
2.00	7.53	3.59	0.139
2.50	—	—	0.197

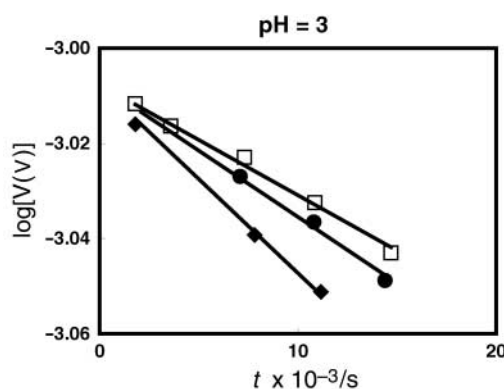


Fig. 4 First-order plot for the reduction of $1.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ V(v)}$ by $[\text{H}_2\text{Ox}]_T (\times 10^2 \text{ mol dm}^{-3})$ (□) 1.5, (●) 2.0, (◆) 2.5, pH 3.0, 50°C and $I = 0.50 \text{ mol dm}^{-3}$.

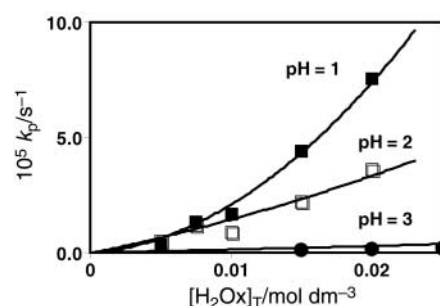


Fig. 5 Pseudo first-order rate constants k_p of V(v) reduction as a function of $[\text{H}_2\text{Ox}]_T$ for $[\text{V(v)}]_T = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ at 50.0°C and $I = 0.50 \text{ mol dm}^{-3}$. The points represent experimental data and the solid lines were calculated using eqn. (15).

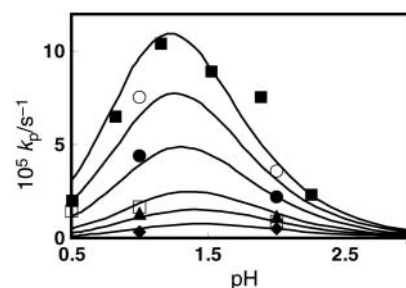
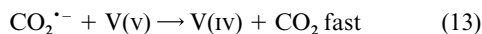
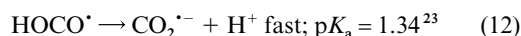
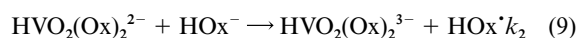


Fig. 6 Pseudo first-order rate constants k_p of V(v) reduction as a function of pH for $[\text{V(v)}]_T = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ at 50.0°C and $I = 0.50 \text{ mol dm}^{-3}$ by $[\text{H}_2\text{Ox}]_T (\times 10^2 \text{ mol dm}^{-3})$ (◆) 0.5, (▲) 0.75, (□) 1.0, (○) 1.5, (●) 2.0 and (■) 2.5. The points represent experimental data and the solid lines were calculated using eqn. (15).





According to this mechanism, the rate of V(v) reduction is given by eqn. (14), and eqn. (15) shows the dependence of k_p on $[\text{HOx}^-]$ and $[\text{H}^+]$. K_{a1} and K_{a2} are the acidity constants of oxalic acid, and K_{f1} and K_{f2} the stability constants of the mono- and bis-oxalatovanadium(v) complexes, respectively. In eqn. (15), $k_1' = k_1 K_1$ and $k_2' = k_2 K_2$.

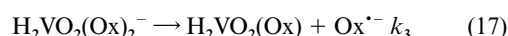
$$-(1/2)d[\text{V(v)}]/dt = k_p [\text{V(v)}] = \frac{k_1 K_{f1} [\text{VO}_2(\text{Ox})_2^{3-}] [\text{HOx}^-] [\text{H}^+] + k_2 K_{f2} [\text{VO}_2(\text{Ox})_2^{3-}] [\text{HOx}^-] [\text{H}^+]}{1 + (K_{f1} K_{a2} [\text{HOx}^-] / [\text{H}^+]) + (K_{f2} K_{a2}^2 [\text{HOx}^-]^2 / [\text{H}^+]^2)} \quad (14)$$

$$k_p = \frac{\{k_1' [\text{HOx}^-]^2 K_{f1} K_{a2} + (k_2' [\text{HOx}^-]^3 K_{f2} K_{a2}^2 / [\text{H}^+])\}}{\{1 + (K_{f1} K_{a2} [\text{HOx}^-] / [\text{H}^+]) + (K_{f2} K_{a2}^2 [\text{HOx}^-]^2 / [\text{H}^+]^2)\}} \quad (15)$$

The best fitting values for the rate constants are $k_1' = (2.16 \pm 0.01) \times 10^{-1} \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$ and $k_2' = (2.09 \pm 0.01) \times 10^{-1} \text{ mol}^{-1} \text{ dm}^6 \text{ s}^{-1}$ and were calculated using eqn. (15). K values from Table 1 and a linear multiple regression routine.³³ The lines represented in Figs. 5 and 6 illustrate that a good fit is obtained in spite of the scatter of the data at pH = 2 and low $[\text{H}_2\text{Ox}]_{\text{T}}$, and the use of some K values uncorrected for T and/or I effects. The standard deviation of experimental points with respect to the fitted curves are 0.89×10^{-7} , 1.1×10^{-7} and $0.62 \times 10^{-7} \text{ s}^{-1}$ respectively for pH = 1, 2 and 3.

The mechanism explains the increase in the partial order of reaction in $[\text{H}_2\text{Ox}]_{\text{T}}$ as pH decreases from 3.0 to 1.0 (see Fig. 5) and the maximum observed in the rate/pH profiles, especially at higher $[\text{H}_2\text{Ox}]_{\text{T}}$. The pH dependence can be rationalized only if both HOx^- and H^+ (or $\text{Ox}^{2-} + 2\text{H}^+$) are assumed to participate in the activated state (together with either the mono- or the bis-oxalatovanadium(v) complex).

Essentially, this mechanism accepts that two activated states lead to the reaction products; their compositions are $\{\text{VO}_2^+; 2\text{H}^+; 2\text{Ox}^{2-}\}^*$ and $\{\text{VO}_2^+; 2\text{H}^+; 3\text{Ox}^{2-}\}^*$. The proton requirement clearly highlights the need to protonate one of the two oxo bonds before the redox process takes place. As written, eqns. (6)–(7) and (9)–(10) probably represent a sequence of a rate-determining electron transfer step followed by the rapid acid–base equilibration of V(iv). Decomposition of HOx^* (eqn. (11)) and acid–base equilibration of HOCO^* (eqn. (12)) are also fast processes. Eqn. (6) probably represents a simple outer sphere ET reaction with non-coordinated HOx^- , although alternative inner sphere processes may also account for the data. A reaction scheme composed of eqns. (16) and (17) is kinetically indistinguishable from that formed by eqns. (5)–(7). Note that $\text{H}_2\text{VO}_2(\text{Ox})$ and $\text{VO}(\text{Ox})$ are the same species.



§ The data fitting procedure demonstrates that a further term, representing the reduction of VO_2^+ , makes a negligible contribution to the rate.

It is also possible to write equations for the second pathway assuming an inner-sphere mechanism. In this case however, it would be required that the reacting species is $\text{VO}(\text{Ox})_3^{3-}$, which should be either hepta-coordinated or should contain two monodentate oxalate groups.

Oxalate reacts very slowly with another oxometallate, MnO_4^- , in spite of its high oxidation power.³⁴ Substitution on V(v) is much faster than substitution on Mn(vii), and this fact seems to determine the increased rate of reaction, although the final process is outer sphere. Oxalate complexation seems to be crucial in determining a decrease in the reorganization energy around vanadium, and an increase in the driving force. In agreement, upon addition of Mn^{2+} , the reaction $\text{MnO}_4^- + \text{Ox}^{2-}$ proceeds smoothly, with participation of oxalato complexes of Mn^{3+} .^{35a,b} Well documented electron transfer from bound oxalate to a metal ion depend on photochemical activation (*e.g.* tris-oxalatoferrate(III)),³⁶ demonstrating the existence of a large reorganization barrier. Oxalate is a ubiquitous bridging ligand in electron transfers between two metal centers, in the course of which it remains unchanged. Again, this fact demonstrates a large kinetic inertia of oxalate for one-electron oxidation.

It is clear that the high reorganization energy involved in the evolution $\text{HOx}^- \rightarrow \text{HOx}^*$ limits kinetically the reducing power of oxalate. Kanoufi and Bard²³ found that oxalate dianion is oxidized *via* outer sphere ET by electrogenerated tris-(2,2'-bipyridine)ruthenium(III), $\text{Ru}(\text{bipy})_3^{3+}$. They have addressed the problem of the very limited stability of $\text{Ox}^{\cdot-}$, fragmentation taking place very readily (eqn. (11)). Although a very short lifetime is proposed for $\text{Ox}^{\cdot-}$, their results suggest that outer sphere reactions of oxalate may be described by the Marcus theory. In our case, we cannot proceed in this direction because of the unknown values of the protonation pre-equilibrium constants for the mono- and bis-oxalato complexes. The higher expected K_2 value ($K_2 \gg K_1$) is largely cancelled out by the unfavourable work term associated with k_2 , yielding $k_1 K_1 \cong k_2 K_2$. The lack of stable ion pairs in the ET reaction may favour also the time separation of ET proper and the fragmentation reaction (eqn. (11)). Thus, the main reaction pathway at pH = 3 is through k_2 , whereas at pH = 1 (and not too high oxalate concentrations), k_1 predominates.

V(iv) does not inhibit the reaction; thus, V(iv) does not scavenge the radical ion $\text{CO}_2^{\cdot-}$. This radical is a strong reductant ($E^\circ = -1.9 \text{ V}$),³⁷ able in principle to reduce both V(v) and V(iv). The absence of a barrier in the diffusion away of the products of the outer sphere reactions favours the reaction with another V(v) (eqn. (13)) rather than a further reduction of V(iv).

The lack of detection of V(III) is not experimental proof of this contention, because the comproportionation reaction $\text{V(III)} + \text{V(v)} \rightarrow 2\text{V(iv)}$ is fast enough to preclude V(III) detection. Direct two-electron reduction of V(v) rarely operates in other cases (*e.g.* benzaldehyde)³¹ and there is no indication either that V(III) is involved in the present system.

In spite of the similarities in pH and the presence of highly reducing species, the acid oxalate medium fails to generate and/or stabilize V(III), as observed in the blood of ascidians. Although the higher temperatures used in this work might be responsible for this difference, the formation of V(III) in biological media is more likely due to the influence of an adequate coordination environment around vanadium. An adequate coordination sphere may prevent the diffusion away of the radical species formed in the first ET step and may stabilize V(III), making the second ET more facile. Of course, a more efficient reductant may also explain the formation of V(III).

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