The Acid Promoted Disproportionation of a Vanadium(IV) Phenolate: Implications for Vanadium Uptake in Tunicates

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Under anaerobic conditions $V^{IV}O$(salen) (salen = *N,N'*-ethylenebis-salicylideneaminato) undergoes an acid promoted disproportionation to yield a V^{III}(salen) species and $V^{V}O(salen)^+$ which upon addition of chloride ion react *via* back electron transfer to yield $V^{IV}O$(salen) and $V^{IV}Cl_2$(salen).

The ability of certain sessile marine organisms known as tunicates to accumulate vanadium from seawater by over a million fold has fascinated scientists for over 50 years.[1,2] While the function of the vanadium in these organisms remains obscure, some recent progress has been made towards an understanding of the mechanism of its accumulation. It is now known that the vanadium is initially transported across the membrane as vanadium(V). Inside the cell this is reduced to a mixture of vanadium(III) and vanadium(IV) presumably by pigments known as tunichromes.[2] The precise mechanism of this reduction, however, is still unclear. Since the newly isolated and characterized tunichromes are polyphenolic compounds[3] we have begun studying vanadium phenolate co-ordination chemistry[4—6] and some of our recent results suggest a possible mechanism for the formation of vanadium(III) and vanadium(IV) from vanadium(V).

In air, the addition of nonco-ordinating acids, such as $HClO_4$ (or HBF_4) to an acetonitrile solution of the vanadium(IV) species, vanadyl(salene) (salen = *N,N'*-ethylenebis-salicylideneaminato) produces the dark blue oxidized product, $V^{V}O(salen)^+$. Oxygen is not the primary oxidant however, as when the above reaction is run under anaerobic conditions a dark green–brown solution is produced.† This solution has been shown by cyclic voltammetry and rotating platinum electrode voltammetry to consist of 50% of the *oxidized* $V^{V}O(salen)^+$ and 50% of a *reduced* species, '$V^{III}(H_2salen)$' (the exact nature of this product is uncertain) (Figure 1). The valence state of the reduced product has been confirmed by solution magnetic measurements. The observation that after the reaction is complete half the vanadium is in the trivalent state and half in the pentavalent state, coupled with the fact that vanadium(V) is formed even in the absence of an external oxidant (*i.e.* O_2), indicates that a disproportionation [reaction (1)] has occurred.

$$2V^{IV}O(\text{salen}) + 4H^+ \rightarrow V^{V}O(\text{salen})^+ + \text{'}V^{III}(H_2\text{salen})\text{'} + H_2O \quad (1)$$

If the reactions outlined above are run in the presence of a co-ordinating acid such as HCl, no redox chemistry is observed. Rather the V=O oxygen is protonated and lost to produce the deep blue $V^{IV}Cl_2$(salen) as determined by electrochemistry, analysis, and mass spectrometry.[7] The difference in reaction between $HClO_4$ and HCl indicated that the co-ordinating anion had an effect on the reaction path. This hypothesis was confirmed by the addition of chloride ion to an anaerobic solution of vanadyl(salen) in the presence of two equivalents of $HClO_4$. Upon addition of the chloride, the green–brown solution instantly turned a dark blue. Electrochemical analysis of this solution revealed that it contained

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† In air oxygen does function as an oxidant in this system, in that it oxidises the vanadium(III) complex formed in the disproportionation (*vide infra*).

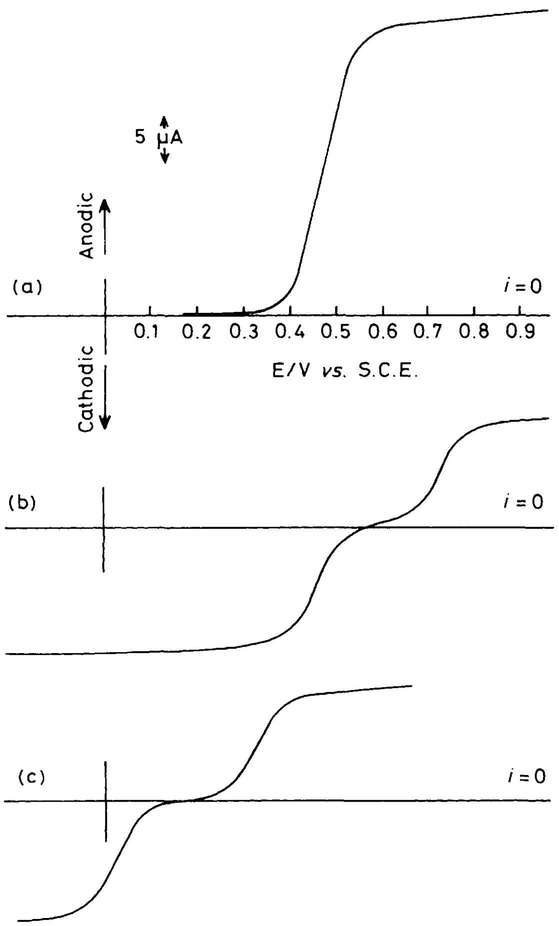

Figure 1. (a) The oxidation of $V^{IV}O(salen)$ in acetonitrile containing 0.1 M $Bu^n{}_4PF_6$ on a rotating platinum electrode. All potentials are *vs.* the standard calomel electrode (S.C.E.). (b) After anaerobic addition of $HClO_4$. The wave at 0.47 V represents the reduction of $V^VO(salen)^+$ and the wave at +0.73 V the oxidation of '$V^{III}(H_2salen)$'. (c) After anaerobic addition of $HClO_4$ followed by Et_4NCl (final Cl-concentration ~0.05 M). The wave at +0.02 V represents the reduction of $V^VCl_2(salen)$ and the wave at +0.34 V the oxidation of $V^{IV}O(salen)$. The shift in the $E_{1/2}$ for the $V^{IV/V}(salen)$ couple from that seen in (a) and (b) is due to the presence of chloride ion.

only $V^{IV}O(salen)$ and $V^{IV}Cl_2(salen)$ (Figure 1). Thus, in the presence of chloride ion the vanadium(III), initially produced by disproportionation, is unstable towards oxidation by the vanadium(V). It is therefore oxidized to form $V^{IV}Cl_2(salen)$ with the concomitant reduction of the $V^VO(salen)^+$ back to vanadyl(salen) [reaction (2)].

$$V^VO(salen)^+ + V^{III}(H_2salen) + 4Cl^- \rightarrow V^{IV}O(salen) + V^{IV}Cl_2(salen) + 2HCl \quad (2)$$

The mechanism in the tunicates that reduces the initially transported vanadium(V) to a mixture of vanadium(III) and vanadium(IV) remains uncertain. The most likely reductant, *i.e.* one of the tunichromes, appears *in vitro* at least only to reduce vanadium(V) to vanadium(IV).[8] Our work suggests a means within this context that could produce vanadium(III) using tunichromes as reductants. Vanadium(IV) produced by tunichrome reduction could undergo a disproportionation to produce vanadium(III) and vanadium(V). The vanadium(V) could then undergo further reduction by the tunichromes. Whether disproportionation of vanadium(IV) is a viable mechanism will depend on a variety of factors including its ligation, the acidity, and the presence or absence of coordinating anions. It is clear however that the relative stabilities of the various oxidation states of vanadium phenolate complexes can be varied over a wide range by a number of factors and that these must be taken into account in any attempt to formulate a mechanism.

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References

1 N. D. Chasteen, *Struct. Bonding (Berlin)*, 1983, **53**, 107.
2 K. Kustin and G. C. McLeod, *Struct. Bonding (Berlin)*, 1983, **53**, 140.
3 R. C. Bruening, E. M. Oltz, J. Furukawa, N. Nakanishi, and K. Kustin, *J. Am. Chem. Soc.*, 1985, **107**, 5298.
4 J. A. Bonadies and C. J. Carrano, *J. Am. Chem. Soc.*, 1986, in the press.
5 V. Pecoraro, J. A. Bonadies, C. A. Marrese, and C. J. Carrano, *J. Am. Chem. Soc.*, 1984, **106**, 3360.
6 P. E. Riley, V. L. Pecoraro, J. A. Bonadies, C. J. Carrano, and K. N. Raymond, *Inorg. Chem.*, 1986, **25**, 154.
7 M. Pasquali, F. Marchetti, and C. Floriani, *Inorg. Chem.*, 1979, **18**, 2401.
8 I. G. Macara, G. C. McLeod, and K. Kustin, *Biochem. J.*, 1979, **181**, 457.