Searching for the Mechanism of the Electrocatalytic Oxidation of Mercaptopropionic Acid by an Amavadine Model

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Abstract

By cyclic voltammetry (CV) in aqueous solutions of KCl, the *Amavadine* models $[NBu_4]_2[VL_2]$ (L = $HIDPA^{3-}$ — N-hydroxy-α,α'-iminodipropionate — or $HIDA^{3-}$ — N-hydroxy-α,α'-iminodiacetate) undergo a single-electron reversible oxidation. The anodically generated V^V species acts as an electron-transfer mediator in the electrocatalytic oxidation of some thiols and evidence is presented for the involvement of an interaction between the substrate (mercaptopropionic acid) and the vanadium complex. The mechanism has been investigated by CV simulation and a preliminary account is now being discussed.

Introduction

Amavadine is a natural vanadium complex present in the mushrooms *Amanita muscaria*, whose biological role has not been clarified yet, but there is considerable circumstantial evidence suggesting that it can be involved in some kind of electron transfer process [1]. Therefore, the electrochemical investigation of vanadium complexes

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which may be considered as inorganic models of *Amavadine* has been a matter of current interest [2-4].

The inorganic models of *Amavadine* under study include the complexes with $HIDPA^{3-}$ and $HIDA^{3-}$, since it appears [5] that *Amavadine* contains the octacoordinated vanadium(IV) centre $[V(HIDPA)_2]^{2-}$ rather than the previously proposed five-coordinated oxovanadium(IV) species $[VO(HIDPA)_2]$ [6]. The results presented were obtained from cyclic voltammetric and controlled potential electrolysis experiments.

Results and Discussion

By cyclic voltammetry in 0.2 mol dm^{-3} KCl aqueous solutions and at a platinum disc (ϕ = 0.5 mm) working electrode, $[NBu_4]_2[VL_2]$ (L = $HIDPA^{3-}$ or $HIDA^{3-}$) undergo a single-electron reversible oxidation at $E_{1/2}^{ox}$ = 0.49 V or 0.52 V *vs.* SCE, respectively, the former corresponding to a less anodic value in agreement with the expected stronger electron releasing ability of $HIDPA^{3-}$ relatively to $HIDA^{3-}$. The observed electrode process corresponds to the $V^{iv} \rightleftharpoons V^{v}$ interconversion.

The vanadium systems of this study are involved in the electrocatalytic oxidation of biological thiols, in particular cysteine ($HSCH_2CHNH_2COOH$) , cysteine methyl ester and penicillamine [7], as well as mercaptoacetic and mercaptopropionic acids [$HS(CH_2)_2COOH$ and $HS(CH_2)_3COOH$, respectively]. In the absence of the V system, no direct anodic oxidation of these substrates has been detected. Moreover, their electrocatalytic preparative oxidation afforded the products resulting from loss of H^+ and S-S coupling.

The catalytic nature of the anodic wave is evident from the enhancement of the anodic peak current upon the addition of increasing amounts of thiol. However, a simple outer-sphere EC type mechanism between the substrate and the mediator does not seem to occur. Indeed, some additional interaction appears to lead to a limit of the velocity of the catalytic reaction upon increasing the substrate concentration. This effect is clearly shown in Figure 1 for the vanadium-HIDA complex/mercaptopropionic acid system which shows the suppression of the increase of the catalytic effect for excess factors γ (defined as the ratio between the substrate and the catalyst concentrations) higher than 4.

These results led us to consider a Michaelis-Menten type mechanism, as described in the Scheme, which was investigated by using a CV simulation programme [8]. For each scan rate (v) and each value of the excess factor (γ), the simulated and experimental cyclic voltammograms were analysed in terms of plots of the ratio i_c/i_o *vs.* -log(v) (an example is depicted in Fig. 2). A good fitting was obtained for k_1 and k_2 values of 1.2×10^3 $M^{-1}s^{-1}$ and 2.5 s^{-1}.

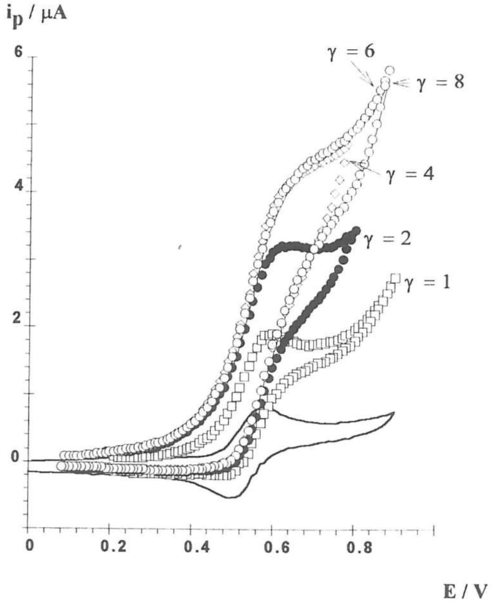
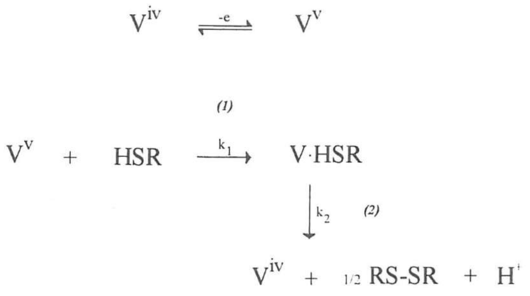


Figure 1. Cyclic voltammograms for $[V(HIDA)_2]^{2-}$ (—) and the mercaptopropionic acid/vanadium complex system (concentration ratios given by γ), run at 200 mV s^{-1} at a platinum disc electrode and in 0.2 mol dm^{-3} KCl / H_2O. Potentials in Volts *vs.* SCE.



Scheme

To our knowledge, this study provides the first example of a redox catalysis process involving a Michaelis-Menten type mechanism, a result with evident biological significance.

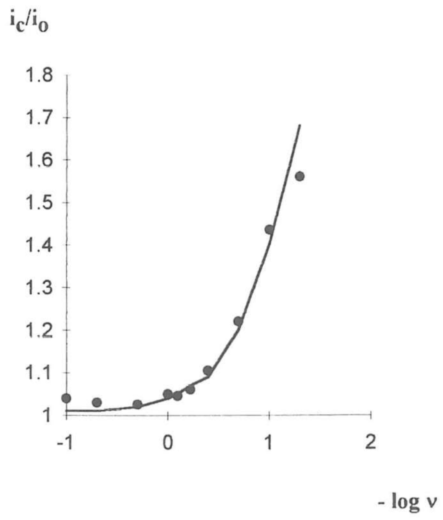


Figure 2. Plot of experimental (•) and simulated (—) i_c/i_o *vs* -log(ν) (ν = scan rate in V s^{-1}), for $\gamma = 1$. Simulated values were obtained by considering k_1 and k_2 values of 1.2×10^3 $M^{-1}s^{-1}$ and 2.5 s^{-1}, respectively.

Acknowledgements

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Redox Properties of Carbene Complexes of Chromium and Tungsten

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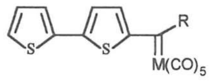
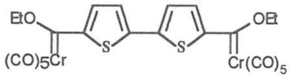
Abstract

The electrochemical behaviour of the following carbene complexes of chromium and tungsten (**1-4**), was investigated by cyclic voltammetry (CV) and controlled-potential electrolysis (CPE), in 0.2 M $[NBu_4][BF_4]$/MeCN, thf or CH_2Cl_2, at Pt-electrodes.



1 M = Cr R = OEt
2 M = Cr R = NC_4H_8
4 M = W R = OEt



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They all show a single anodic wave with $E_{p/2}^{ox}$ in the range +0.88 V to +1.12 V (*vs.* S.C.E.). For the chromium compounds (**1-3**) this wave presents a partially reversible character, whereas the oxidation wave of the tungsten compound (**4**) is irreversible at all the scan rates investigated. These processes correspond to the expected $M^0 \rightarrow M^I$ oxidations. However, CPE carried out for complexes **1**, **2** and **4** indicate the participation of more than one electron in the overall anodic process. For the chromium compounds (**1-3**), the values of the ligand P_L parameter were estimated for the carbene ligands, as follows: -0.62 V (**1**), -0.56 V (**2**) and -0.38 V (**3**). The complexes also present cathodic waves and the first one is reversible for **1**, **3** and **4** [$E_{1/2}^{red}$ in the range from -0.70 V to -1.02 V (*vs.* S.C.E.)]. CPE carried out for **1** and **3** show that only a single electron is involved in this process. However, compound **2** shows an irreversible cathodic wave at a

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