

**ELECTROCATALYTIC OXIDATION OF PYROGALLOL
BY AN AMAVADIN MODEL – A PRELIMINARY STUDY**

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Abstract

By cyclic voltammetry in a methanolic solution, the amavadin model [Bu₄N]₂[V(HIDA)₂] (HIDA= tribasic form of the N-hydroxy- α,α' iminodiacetic acid) acts as an electron-transfer mediator in the electrocatalytic oxidation of pyrogallol (1,2,3-trihydroxybenzene). The mechanism of this anodic process is being investigated by digital simulation of cyclic voltammograms and a preliminary result is presented.

Key words: Amavadin, Pyrogallol, Electrocatalysis, Cyclic voltammetry, Digital simulation of cyclic voltammograms

Introduction

The study of the amavadin mediated oxidation of biological thiols in aqueous medium has already been described [1], showing that such a process proceeds via an unprecedented type of electrocatalysis involving a Michaelis-Menten type mechanism where an interaction between the substrate (thiol) and the oxidized form of the mediator takes place.

In the search of other potential substrates for such a novel type of electrocatalytic oxidation process, we found that polyphenols, which are present in diverse groups of organisms and are involved in a variety of physiological processes [2,3], appear to be good candidates.

The results presented herein concern pyrogallol, *i.e.* 1,2,3-trihydroxybenzene, that is known to be a substrate for some enzymes which catalyse its oxidation [4,5], and were obtained from cyclic voltammetric and controlled potential electrolysis experiments.

Results and discussion

By cyclic voltammetry in a 0.2 mol dm^{-3} $[\text{NBu}_4][\text{BF}_4]$ methanolic solution and at a platinum disc ($\phi = 0.5 \text{ mm}$) working electrode, $[\text{Bu}_4\text{N}]_2[\text{V}(\text{HIDA})_2]$ undergoes a single-electron reversible oxidation at $E^\circ = 0.41 \text{ V vs. SCE}$, corresponding to the $\text{V}^{\text{IV}} \leftrightarrow \text{V}^{\text{V}}$ interconversion. This vanadium system is involved in the electrocatalytic oxidation of pyrogallol which, in the absence of the vanadium system, presents an anodic process at a considerably higher oxidation potential value ($E_{\text{p}}^{\text{ox}} = 0.72 \text{ V}$). The cyclic voltammetric study has been performed for different values of scan rate and substrate concentrations.

The catalytic nature of the anodic wave of the vanadium complex, in the presence of pyrogallol, is accounted for by the enhancement of the anodic peak current upon addition of increasing amounts of the phenol derivative (Fig. 1, as indicated by the different values of the excess factor γ defined as the ratio between the pyrogallol and the vanadium complex concentration).

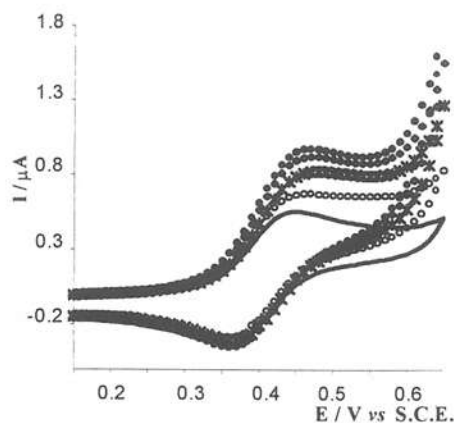


Fig 1. Cyclic voltammograms for the $[\text{V}(\text{HIDA})_2]^{2-}$ complex ($c = 0.41 \text{ mM}$) in the absence (solid line) and in the presence of pyrogallol (symbols), in $0.2 \text{ M } [\text{NBu}_4][\text{BF}_4]/\text{CH}_3\text{OH}$, at a platinum disc working electrode ($\phi = 0.5 \text{ mm}$) for a scan rate of 1 V s^{-1} . γ values of 4.3 (O); 8.3 (+); 10.5 (◊) and 13.3 (●).

However, the overall process cannot be described by means of a classical redox catalysis mechanism. In fact, a saturation effect of the catalytic activity with both the increase of the substrate concentration and the decrease of the scan rate and was observed. The former observation is illustrated in Figure 2, in which i_0 and i_c represent the anodic peak current of the mediator before and after the addition of pyrogallol, respectively.

In addition, a catalytic process simply involving a progressive quenching of the mediator by formation of a stable product with the oxidized substrate could not be considered because it would not explain the preservation of the reversible character of the wave upon increasing the substrate concentration (Fig. 1).

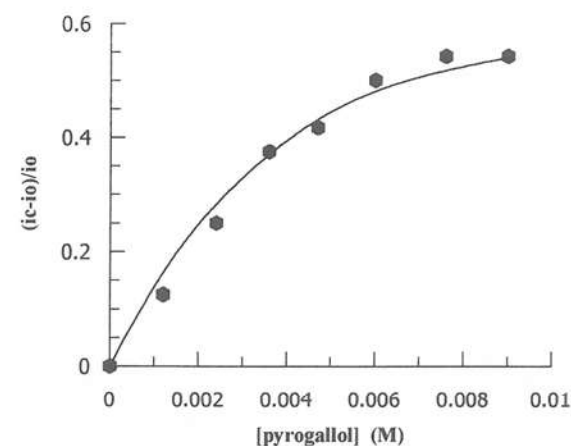
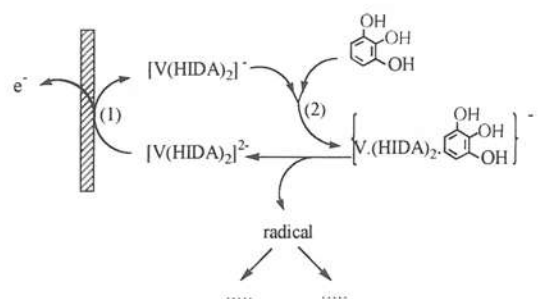


Fig 2. Plot of experimental (symbol) and simulated (line) normalised peak current $(i_c - i_0)/i_0$ vs. the pyrogallol concentration. Concentration of the vanadium complex, $c = 0.41 \text{ mM}$. Scan rate of 0.2 Vs^{-1} .

These results led us to consider a more complex mechanism which is being investigated by digital simulation of the cyclic voltammograms. It involves the formation of an adduct between the V^{IV} species and pyrogallol, similar to a Michaelis-Menten type kinetics (scheme, reactions 1 and 2), followed by dissociation of the adduct to give a reactive radical which then i) oxidizes the mediator, thus accounting for the experimentally observed reversible character of its catalytic wave and for the saturation of its catalytic activity for low scan rates, or ii) undergoes H^+ loss followed by coupling.



Scheme

For the scan rate of 0.2 Vs^{-1} , the simulated and experimental cyclic voltammograms are in good agreement (Fig 2., solid line and symbols, respectively). However, an acceptable fitting has not yet been achieved for the entire range of scan rates under study.

Preparative scale electrolysis has also been performed in the presence of a 4 molar excess of pyrogallol leading to the consumption of 5 Faradays/mol of the vanadium complex. Attempts to isolate the products from the electrolysed solution have not yet been successful.

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Acknowledgements

This work has been partially supported by the Foundation for Science and Technology (FCT) and the PRAXIS XXI programme (Portugal). We also thank Dr. C. Nervi for the simulation programme.

ESTIMATE of ELECTROCHEMICAL LIGAND PARAMETERS in IRON(II) ADDUCTS of $[\text{FeH}(\text{CN})(\text{dppe})_2]$

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Abstract

The cyclic voltammetric study of the following isocyanide complexes derived from *trans*- $[\text{FeH}(\text{CN})(\text{dppe})_2]$ **1** (dppe = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) enabled the estimate of the values of the electrochemical Pickett P_L and Lever E_L ligand parameters for the corresponding cyano-derived ligands: *trans*- $[\text{FeH}(\text{CNR})(\text{dppe})_2]\text{A}$ **2** [R = H (**2a**) or Et (**2c**), $\text{A}^- = \text{BF}_4^-$; R = Me (**2b**), $\text{A}^- = \text{I}^-$; R = C(O)Ph (**2d**), $\text{A}^- = \text{Cl}^-$] or *trans*- $[\text{FeH}(\text{CN}\rightarrow\text{X})(\text{dppe})_2]$ **3** [X = BPh_3 (**3a**), $\text{VCl}_3(\text{thf})_2$ (**3b**) or BF_3 (**3c**)].

Keywords: Iron complexes; Cyclic voltammetry; Cyano-derived ligands; Isocyanides; Ligand parameters.

Results and discussion

All the cyano-derived iron complexes exhibit, at 200 mV s^{-1} (Table), a reversible (or irreversible, compounds **2a** and **2d**) anodic wave at $E_{1/2}^{\text{ox}}$ (or $E_{p/2}^{\text{ox}}$) in the 0.30 – 1.24 V vs. SCE range. As expected, the oxidation wave of the neutral complexes **1** and **3** are shown at lower potentials, in the 0.30 – 0.80 V vs. SCE range, in comparison with those of the cationic complexes **2**.

Within the neutral complexes, the iron compound **2a**, derived from protonation of the parent complex **1**, presents an anomalously low oxidation potential suggesting that CNH is involved in hydrogen bonding with the BF_4^- counter-ion, *i.e.*

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