

Table 1. Cyclic voltammetry data for cytochrome *c*₃ *D. vulgaris* Hildenborough at a doped tin oxide electrode. Same conditions as in Figure 1.

v (Vs ⁻¹)	i _p (μA)	E (V)
0.02	10.2	0.09
0.05	19.	0.105
0.10	28.	0.108
0.20	36.	0.165
0.30	43.5	0.195
0.40	47.	0.205
0.50	40.	0.222

It is clear that further conclusions should only be drawn after coulometric measurements.

The cyclic voltammograms and the plot of peak current vs square root of scan rate obtained for *D. gigas* cytochrome *c*₃ at a pyrolytic

graphite electrode are shown in Figure 2. Two cathodic and two anodic peaks are observed at potentials close to -0.465, -0.55, -0.49 and -0.435 V vs SCE. These peaks are probably related to the transfer of four electrons and further studies including deconvolution procedures are necessary in order to determine the standard potentials.

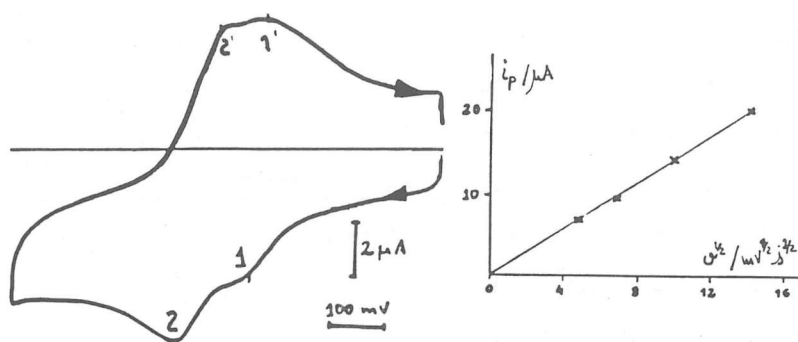


Figure 2. Cyclic voltammogram and plot of *i_p* vs *v*^{1/2} for a 0.63 mM solution of cytochrome *c*₃ *D. gigas* in phosphate buffer 0.1 M pH 7, at a pyrolytic graphite "edge" cleaved electrode. Potential limits -0.3 -0.9 V, scan rate 0.02 Vs⁻¹.

(1) F.A.Armstrong, H.A.O.Hill and N.J.Walton, Quarterly Review of Biophysics 18,3(1986)261.

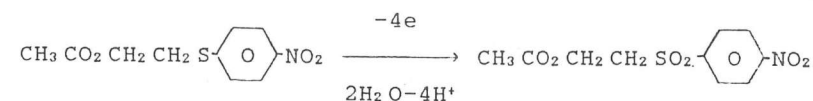
ELECTROCHEMICAL BEHAVIOUR OF ARYLTHIOETHYL GROUPS IN CARBOXYL PROTECTION

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Electrolysis can provide an appropriate way to cleave protecting groups of interest in synthesis⁽¹⁾. Arylthioethyl groups are suitable for the protection of the carboxyl function and are conventionally removed by treatment with alkali after conversion into the corresponding sulphone by catalytic oxidation⁽²⁾. This paper reports the investigation of an alternative route to the oxidation of the sulphide to sulphone by electrolysis. The model compound selected for study was the p-nitrophenylthioethyl ester of acetic acid and the desired reaction was



For these studies the anode was Pt or vitreous C and the medium CH₃CN or CH₃CN with small additions of water containing NaClO₄ or Bu₄NBF₄ (TBAB)

Cyclic voltammograms for the compound in CH₃CN/TBAB is shown in figure 1. Two well formed but totally irreversible oxidation peaks at + 1.8V and + 2.2V vs SCE can be seen.

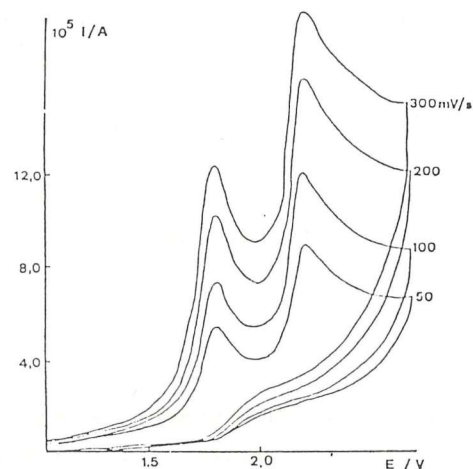


Figure 1 : Cyclic voltammograms for the oxidation of 2×10^{-3} mol dm^{-3} $\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_2\text{S}-\text{O}-\text{NO}_2$ in $\text{CH}_3\text{CN}/\text{TBAB}$ ($0,1 \text{ mol dm}^{-3}$) at a vitreous carbon electrode and at different sweep rates as indicated.

Comparison of the cyclic voltammetry characteristics of the first peak with those of ferrocene indicates that 2e per substrate molecule are involved in the first oxidation step. This is confirmed by results obtained with the potential step method which also suggested that the second peak in the cyclic voltammogram also corresponds to a process involving the transfer of 2e per substrate molecule. In fact, the slope for the I vs $t^{-1/2}$ plot for a potential step to a potential after the second peak doubles the value for the same plot obtained at the first peak.

Constant potential electrolyses also confirm the number of electrons involved in each process. When the potential was set just after the first oxidation peak, coulometry shows that $n=2$ and product analysis by HPLC suggested the formation of sulphoxide in good yields. When

the potential was set beyond the second peak, coulometry showed $n=4$ and the corresponding sulphone was detected but the maximum yield was only 49%. The presence of other peaks in the chromatogram indicated that side reactions take place. The yields in sulphone are reported in table 1 for several electrolyses carried out under slightly different conditions.

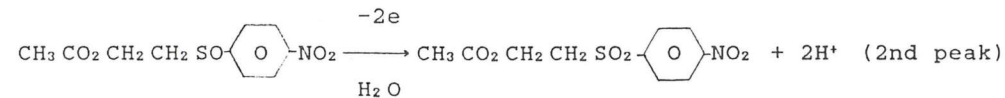
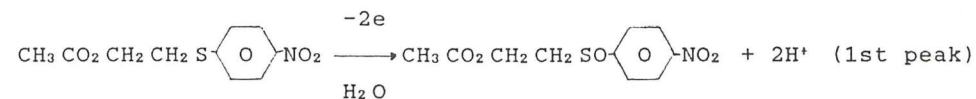
TABLE 1

Medium	E/V vs SCE	n	yield(%)
$\text{CH}_3\text{CN}/\text{Bu}_4\text{NBF}_4$	+ 2.28	4	33
$\text{CH}_3\text{CN}/\text{Bu}_4\text{NBF}_4 + 0,2\% \text{H}_2\text{O}$	+ 2.28	4	25
$\text{CH}_3\text{CN}/\text{Bu}_4\text{NBF}_4 + 2\% \text{H}_2\text{O}$	+ 2.28	4	traces
$\text{CH}_3\text{CN}/\text{NaClO}_4$	+ 2.30	3	49
$\text{CH}_3\text{CN}/\text{NaClO}_4$	+ 2.30	3	44

Data on constant potential electrolysis for 2×10^{-4} moles of $\text{CH}_3\text{COOCH}_2\text{CH}_2\text{S}-\text{O}-\text{NO}_2$ in different media.

Hence, it can be concluded that the oxidation of the acetic acid derivative occurs in two steps according to the scheme below, although parallel reactions also occur.

A more complete understanding of the mechanism needs further work mainly with regard to the identification of the other reaction products



References

1. M.I. Montenegro, *Electrochim. Acta*, 31 (1986) 607
2. M.J. Amaral, G.C. Barrett, H.N. Rydon and J.E. Willett, *J. Chem. Soc., (C)*, (1966) 806

STABILITY CONSTANTS OF BIS-CROWN ETHER - METAL ION COMPLEXES

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INTRODUCTION

Crown ether derivatives (macrocyclic polyethers) have been used as components in liquid membrane electrodes exhibiting potassium ion sensitivity (1). Nevertheless, the performance characteristics of such crown compound based electrodes, especially the selectivity data were found inferior to those of the antibiotic valinomycin based sensor (2).

Synthetic urethane linked bis-crown ether ligands were designed as ionophores for potassium ion-selective membranes at the Technical University of Budapest (3,4). The analytically important properties of these synthetic ligand based electrodes exceed the relevant characteristics of other macrocyclic polyether based sensors and are comparable with those of the valinomycin based electrode, the ion-selectivity of such sensors being advantageously affected not only by the ring size of the crown ethers and its substituents, but also by the