

The Electrochemical Behaviour of Novel Multifunctional α -Hydroxymethylated Nitroalkenes at Glassy Carbon and Wax Impregnated Carbon Paste Electrodes

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The electrochemical behaviour of novel multifunctional α -hydroxymethylated nitroalkenes was studied with respect to oxidation of –OH moiety and reduction of nitro group using the cyclic voltammetric technique at glassy carbon and wax impregnated carbon paste electrodes with sulphuric acid as the supporting electrolyte. The –OH moiety attached to the nitroalkene side chain was found to undergo irreversible four electrons electrochemical oxidation to form an acid at the glassy carbon electrode but no oxidation was observed at the wax impregnated carbon paste electrode. Oxidation in sulphuric acid medium becomes easier with increasing the sulphuric acid concentration. This unusual behaviour is attributed to the formation of a six-membered cyclic structure at lower concentrations of sulphuric acid due to intramolecular hydrogen bonding. Going to the lower potential range, reduction of nitro group was observed in sulphuric acid medium both at the glassy carbon and wax impregnated carbon paste electrodes. A comparative study indicated easier reduction at the glassy carbon electrode. Non hydroxymethylated beta nitroalkenes undergo reduction at a lower negative potential compared to the corresponding α -hydroxymethylated nitroalkenes.

Keywords

- α -hydroxymethylated nitroalkenes
- wax impregnated carbon paste electrode
- electrochemical investigation
- electroreduction

INTRODUCTION

The α -hydroxymethylated nitroalkenes are known to be electron deficient allylic alcohols. These compounds find versatile applications in the preparation of different compounds, which is reflected in the ability of the alpha hydroxymethyl group to undergo chemical transformation into ethers, alkyl halides, aldehydes, carboxylates, *etc.* In addition, the reactive nitro group could be converted

into important compounds such as oximes, hydroxylamines and amines.¹ Nitro compounds can be introduced into living organisms either as drugs or toxins and their fate there often involves an oxidation-reduction process.² The biological activity of several nitro compounds is dependent on the nitro group reduction process due to the formation of active intermediate species^{3–5} that interact with DNA to produce biochemical damage. The reduction

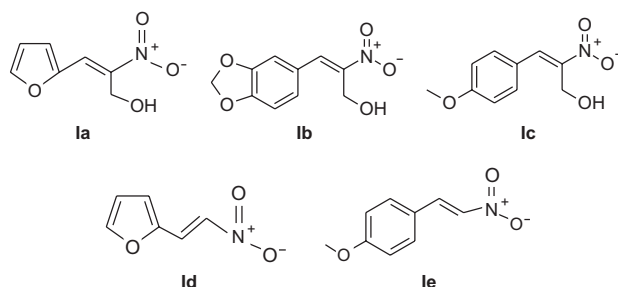
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properties of the nitro group are therefore of prime importance and have received considerable attention. They have been mainly investigated by using pulse radiolysis,⁶ ESR spectroscopy^{7,8} and also electrochemical techniques.^{9–11} Though biological electron transfer reactions are complicated, the biological and electrochemical electron transfer reactions have many things in common. Both involve essentially heterogeneous electron transfer processes, pH and temperature dependent, and occur at the electrode/electrolyte interface or at the membrane/solution interface. Hence, explanations based on electrochemistry have played an important role in interpreting and understanding the biological phenomena.

There are no reports in the literature on electrochemical investigations of these multifunctional α -hydroxymethylated nitroalkenes though there are a few papers on electrochemical reduction of nitroalkenes. To the best of our knowledge, there are no reports on electrochemical investigations of these compounds at the wax impregnated carbon paste electrode. We have investigated not only the anodic oxidation of the –OH group attached to the conjugated nitroalkene but also the reduction using sulphuric acid as supporting electrolyte at the glassy carbon and wax impregnated carbon paste electrodes.

Despite the attractive properties of carbon paste electrodes, they suffer substantially from the presence of oxygen entrapped¹² in the paste brought in by carbon particles, resulting in background currents and hence decreased sensitivity. This is solved by removing adsorbed electroactive species, mainly oxygen, by heating at high temperature with subsequent impregnation of the pores by ceresin wax.¹³ Carbon paste electrode impregnated with ceresin wax was first introduced¹⁴ into use in all common solvents in electrochemistry not only due to its low background currents over a wide range of potentials but also owing to its increased positive potential range.

In order to investigate the electrochemical characteristics and to study the redox path, we synthesized the following compounds (Scheme 1): (2*E*)-3-(2-furyl)-2-nitroprop-2-en-1-ol [**Ia**], (2*E*)-3-(1,3-benzodioxol-5-yl)-2-nitroprop-2-en-1-ol [**Ib**], (2*E*)-3-(4-methoxyphenyl)-2-nitroprop-2-en-1-ol [**Ic**], 2-[2-furyl]-1-nitroethene [**Id**] and 2-[4-methoxyphenyl]-1-nitroethene [**Ie**].



Scheme 1.

Compounds **Ia**, **Ib** and **Ic** were synthesized via a one-pot multicomponent and atom economical reaction that takes place at room temperature. Such a simple and efficient method using nitroalkenes was unknown in the literature until Irishi *et al.*¹ published their results. These compounds also exhibit interesting biological (anticancer) properties. Nitrostyrene derivatives are found to be potent inhibitors of human telomerase.¹⁵ These observations prompted us to undertake their electrochemical investigation.

EXPERIMENTAL

Reagents and Chemicals

The compounds used in our study, α -hydroxymethylated nitroalkenes and the non hydroxymethylated nitroalkenes were prepared in the laboratory and purified according to the procedures given in the previously published results.^{1,16} The prepared compounds were of very high purity, which was confirmed by spectral data. The solvents used, acetonitrile, methanol (Merck) and the supporting electrolyte sulphuric acid, were of A.R. grade. Carbon powder of spectroscopic grade and ceresin wax (Merck) with a congealing point 60 °C were used. All solutions were prepared with doubly distilled deionized water.

Instrumentation and Apparatus

Electrochemical experiments were carried out using a potentiostat provided with the data acquisition PC interface card fabricated at the Analytical Chemistry Division, Bhabha Atomic Research Centre, Mumbai, compatible with an IBM personal computer. Experiments were performed using a one-compartment three electrode system, in which wax impregnated carbon paste electrode (WICPE)/glassy carbon electrode (GCE) were used as working electrodes, saturated calomel electrode (SCE) as reference and platinum wire as an auxiliary electrode. Cyclic voltammetry was the main tool in the investigation.

Preparation of the Wax Impregnated Carbon Paste Electrode

Wax impregnated carbon powder^{13,14} prepared was mixed with the binder, silicone oil, in the mass ratio 5:3 in an agate mortar and homogenized with a pestle. The electrode consists of a Teflon well, which is mounted at the end of a Teflon tube. The prepared paste was filled into the Teflon well. A copper wire fixed to a graphite rod and inserted into the Teflon tube served to establish electrical contact with the external circuit.

Pretreatment of the Glassy Carbon Electrode

Before each measurement, the glassy carbon surface was polished with alumina (BAS CF-1050) on an alumina polishing pad (BAS MF-1040) for 50 s and then rinsed with doubly distilled water.

Procedure

If not mentioned otherwise, before voltammetric measurements, the solution was purged with nitrogen for 20 minutes to remove dissolved oxygen and a stream of nitrogen gas was blanketed over the solution. The cell was thermostated for the required temperature. The WICPE electrode surface was renewed mechanically by smoothing off some paste and then polishing it on a piece of transparent paper before conducting each experiment whereas the surface of GCE was subjected to the above mentioned pretreatment. The experiments were performed in unstirred solutions.

Determination of the Number of Electrons

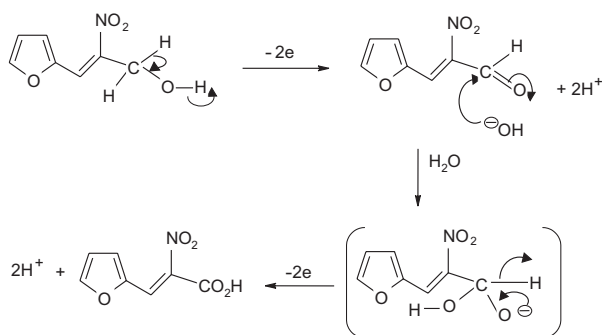
This was carried out by controlled potential coulometry using $2.0 \times 10^{-2} \text{ mol dm}^{-3}$ compound **1a** in sulphuric acid medium. The net charge was obtained by subtracting the charge of the blank from the total charge of **1a** solution. Cyclic voltammetry and spectrophotometry were employed for monitoring the coulometric experiments.

Infrared spectroscopy was used to characterize the products obtained.

RESULTS AND DISCUSSION

The Nature of Cyclic Voltamograms

Voltamograms of the blank were recorded in supporting electrolyte $4 \times 10^{-2} \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ in methanol medium at a scan rate of 0.05 V s^{-1} at GCE and WICPE. All compounds were studied at GCE and WICPE. Compounds **1a**, **1b** and **1c** underwent oxidation at GCE. Figure 1 represents the cyclic voltamogram of **1a** recorded at a concentration of $2 \times 10^{-3} \text{ mol dm}^{-3}$ in H_2SO_4 as supporting electrolyte in methanol medium at GCE. The voltamogram showed only one peak in the anodic region. This corresponds to the oxidation of the $-\text{OH}$ group to the corresponding acid by a four electron electrochemical oxidation process. This was confirmed by controlled potential coulometry experiments. Absence of the cathodic wave in the reverse scan confirms the irreversible nature of the electron transfer process. The electrochemical process can be represented by the following mechanism:



Scheme 2.

The IR spectrum (KBr) of the oxidized product of **1b** by bulk electrolysis at GCE, recorded using a JASCO

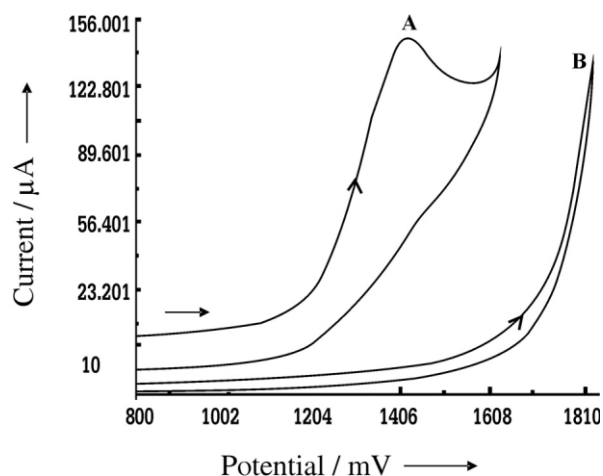


Figure 1. Cyclic voltamogram of pure electrolyte in methanol (B) and that of oxidation of $2 \times 10^{-3} \text{ mol dm}^{-3}$ compound **1a** in supporting electrolyte $4 \times 10^{-2} \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ (A) at a scan rate of 0.05 V s^{-1} at GCE.

FTIR 430 spectrophotometer, provides further evidence for the product formed. The absorption frequency at 1512 cm^{-1} is due to $-\text{NO}_2$, at 1610 cm^{-1} to $\text{C}=\text{C}$ of the nitroalkene, at 1645 cm^{-1} to the carbonyl group of carboxylic acid, at $3140\text{--}3159 \text{ cm}^{-1}$ to $\text{C}\text{--}\text{H}$ and at $3200\text{--}3500 \text{ cm}^{-1}$ to the $-\text{OH}$ group of carboxylic acid. The IR spectra of compound **1b** before oxidation showed adsorption frequencies at 1505.7 cm^{-1} corresponding to the $-\text{NO}_2$ group, at 1604.2 cm^{-1} due to $\text{C}=\text{C}$ and at 3559 cm^{-1} due to the $-\text{OH}$ group of allylic alcohol.

1b was found to undergo oxidation at a lower potential with an oxidation potential of 1.385 V as compared to **1a** or **1c** which undergo oxidation at 1.419 V and 1.603 V , respectively, at GCE under the same conditions. Electrochemical oxidation of compounds **1a**, **1b** and **1c** was also studied at a concentration of $2 \times 10^{-3} \text{ mol dm}^{-3}$ in supporting electrolyte H_2SO_4 ($4 \times 10^{-2} \text{ mol dm}^{-3}$) at WICPE. No peak was observed in the anodic region at WICPE. No electrochemical oxidation of these compounds takes place at this electrode.

Going towards lower potentials, the nitro group was found to undergo reduction at both electrodes. It is well known that nitro groups undergo reduction to hydroxylamine at GCE.¹⁷ However, the reduction to hydroxylamine was observed at a much higher potential at GCE compared to WICPE. This implies easier reduction at GCE. This could be due to the presence of the pasting liquid at the WICPE surface, which decreases the electron transfer rate (slower kinetics), causing a higher over-potential compared to homogeneous electrodes. The increasing lipophilicity of the pasting liquid enhances the electrode over-potential (irreversibility). This is due to the marked hydrophobicity of the liquid, which hinders the access of the analyte to the surface. Cyclic voltamograms were also recorded at a wider scale, $+1.6 \text{ V}$ to -1.1 V , using both electrodes. At GCE, both the oxidation peak correspond-

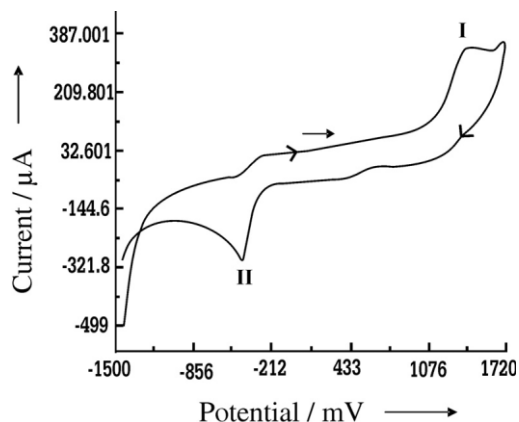


Figure 2. Cyclic voltammogram of 2×10^{-3} mol dm $^{-3}$ compound **Ib** in supporting electrolyte 4×10^{-2} mol dm $^{-3}$ H $_2$ SO $_4$ at a scan rate of 0.05 V s $^{-1}$ at GCE in a wide potential range. Peak I corresponds to the oxidation of -OH moiety and peak II corresponds to the reduction of nitro group.

ing to the oxidation of -OH moiety and the reduction peak corresponding to the reduction of nitro group were observed. A typical voltammogram recorded at GCE for **Ib** is depicted in Figure 2.

While studying the electrochemical reduction of nitro group alone at GCE, only **Ia** and **Id** showed second waves at -0.975 V and -0.905 V, respectively, whereas **Ib** and **Ic** did not show a second wave in the potential range employed. The second wave observed in the above potential range has been reported for the reduction of oximes.¹⁸ As reported, the hydroxylamine formed subsequently tautomerizes to form an oxime, which undergoes reduction at these potentials. At WICPE, though the oxidation peak was not observed, the reduction peak corresponding to the nitro group was present in the same cathodic region as observed while recording the cyclic voltammogram in the wider potential range. Reductions of **Ia**, **Ib** and **Ic** were compared with **Id** and **Ie** in the same medium at GCE and WICPE. The reduction of **Ia**, **Ib** and

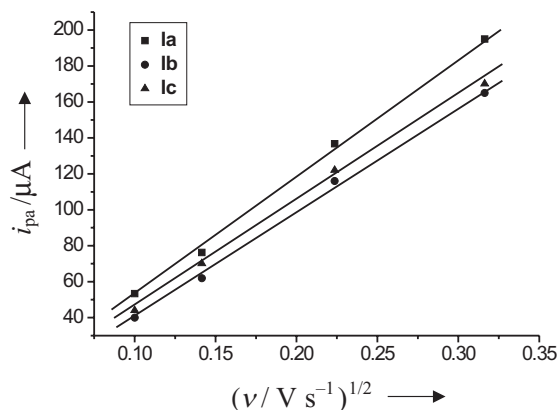


Figure 3. Plot of variation of oxidation peak currents of 2×10^{-3} mol dm $^{-3}$ compounds **Ia**, **Ib** and **Ic** with the square root of the scan rate in 4×10^{-2} mol dm $^{-3}$ H $_2$ SO $_4$ at GCE.

Ic took place at a lower potential compared to the non hydroxymethylated compounds. Reduction potentials were -0.433 V, -0.455 V and -0.489 V, respectively, for **Ia**, **Ib** and **Ic** at GCE. At WICPE; **Ia**, **Ib** and **Ic** got reduced at -0.452 V, -0.470 V and -0.512 V, respectively. **Id** got reduced at -0.372 V and -0.402 V at GCE and WICPE, respectively, whereas **Ie** showed reduction at -0.402 V and -0.425 V at GCE and WICPE, respectively. The substituent plays an important role in the electrochemical reduction as it is evident in the case of electrochemical reduction of **Ie**. The methoxy group donates electrons by resonance, *i.e.*, +R (or +M) effect, and the dipole associated with it operates in the opposite direction, *i.e.* -I effect. The -I effect of methoxy substantially decreases with distance but its +M effect is strongly felt by the aryl ring in conjugation with it. Therefore, the methoxy group increases electron density. Hence, it will be more difficult to reduce the methoxy substituted compound, as it is evident from the reduction potentials of these compounds.

Effect of the Scan Rate

The positive shift in potential observed for a fixed concentration (2×10^{-3} mol dm $^{-3}$ in each case) of **Ia**, **Ib** and **Ic** at the scan rate confirms the irreversible nature of the electron transfer process. The oxidation peak current increased linearly with the square root of the scan rate over the range 0.01 V to 0.1 V s $^{-1}$ (Figure 3). The linearity indicates that the reaction rate is controlled by semi-infinite linear diffusion¹⁹⁻²⁰ and can be also reflected in an uncomplicated redox reaction.

The effect of the scan rate variation corresponding to the reduction of the nitro group was also studied in the sulphuric acid medium at both electrodes. The plots (Figure 4) of the peak current of all the compounds investigated, α -hydroxymethylated as well as non-hydroxymethylated nitroalkenes against the square root of the scan rate, show a linear relationship that satisfies the condition for the diffusion controlled electrochemical process.

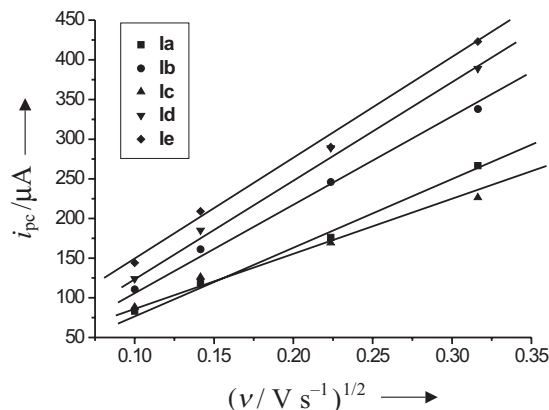


Figure 4. Plot of variation of reduction peak currents of 2×10^{-3} mol dm $^{-3}$ compounds **Ia**, **Ib**, **Ic**, **Id** and **Ie** at a scan rate of 0.05 V s $^{-1}$ at GCE in 4×10^{-2} mol dm $^{-3}$ H $_2$ SO $_4$ supporting electrolyte.

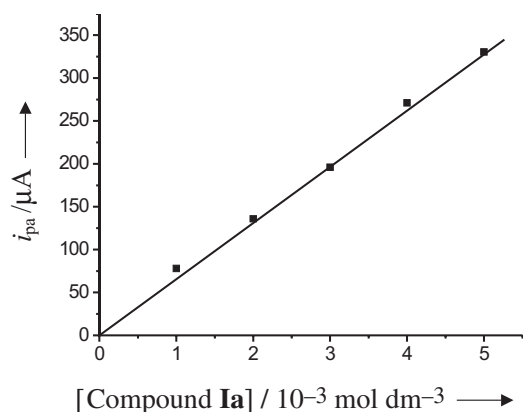


Figure 5. Influence of variation of compound **Ia** concentration on its peak currents in 4×10^{-2} mol dm⁻³ H₂SO₄ as supporting electrolyte at a scan rate of 0.05 V s⁻¹ at GCE.

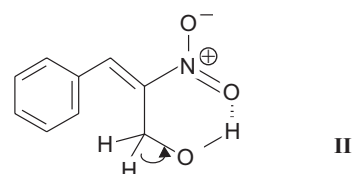
Effect of Concentration Variation

As the concentration of **Ia** was increased from 1.0×10^{-3} mol dm⁻³ to 5×10^{-3} mol dm⁻³, the anodic peak current increased linearly as the concentration with $R^2 = 0.9981$ at GCE, as shown in Figure 5, which indicates that the process was diffusion-controlled.^{21–22}

Dependence of Cyclic Voltammograms on Sulphuric Acid Concentration

Keeping the concentration of **Ia** constant (2.0×10^{-3} mol dm⁻³), the concentration of sulphuric acid was increased from 1.2×10^{-2} mol dm⁻³ to 4.8×10^{-2} mol dm⁻³ and the cyclic voltammograms were recorded at GCE. With an increase in the sulphuric acid concentration, the anodic peak potential shifts towards less a positive value, implying easier oxidation of **Ia**, as represented in Table I.

The molecule should undergo easy oxidation due to the formation of more stable conjugated aldehydes, which on further oxidation yield carboxylic acid. In the present study, we report unusual behaviour in the oxidation of **Ia**, **Ib** and **Ic**. The unusual behaviour observed in this case could be attributed to the formation of a six membered cyclic structure (**II**, Scheme 3) due to intramolecular hydrogen bonding. There is competition between intramo-



Scheme 3.

lecular and intermolecular (due to the hydrogen from sulphuric acid) hydrogen bonding.

Intramolecular hydrogen bonding favours cyclization and hence more potential is required to break this structure in the oxidation process whereas intermolecular hydrogen bonding does not favour such a structure due to the presence of excess sulphuric acid. The values of D_0 and k_0 were evaluated using equations (1) and (2), respectively.^{19,23}

$$D_0 = \{i_{pa} \div 2.99 \times 10^5 n (an_a)^{1/2} AC^* v\}^2 \quad (1)$$

$$k_0 = i_{pa} \div 0.227 nFA C^* \exp\{-an_a f (E_p - E^f)\} \quad (2)$$

The apparent diffusion coefficient values and k_0 for the oxidation of $-OH$ moiety (Table I) reveal an unusual trend with an increase in H₂SO₄ concentration. Diffusion arises due to the depletion of the electroactive species near the electrode surface and this depletion is only due to the charge transfer occurring at the electrode surface. The diffusion coefficient values increase with the concentration of sulphuric acid, indicating a favourable reaction at higher concentrations. The kinetics of charge transfer may be of great use in understanding biological redox processes. The values of k_0 also imply easier charge transfer with increased concentrations of H₂SO₄. The different behaviour observed in the case of oxidation of hydroxymethylated nitroalkenes accounts for the formation of a cyclic structure at lower concentration of H₂SO₄, as shown in structure **II**.

The effect of variation of sulphuric acid on the electro-reduction was also studied at both electrodes by keeping the concentration of compound **Ia** constant at 2×10^{-3} mol dm⁻³ and increasing the concentration of H₂SO₄ from 0.8×10^{-2} mol dm⁻³ to 4.0×10^{-2} mol dm⁻³. The reduction peak potential was found to shift to less negative values (Table II) with an increase in sulphuric acid concentration at both electrodes, which is an indication of the involvement of proton in the electrochemical reduction process.

Effect of Variation of Solvents Composition

In aqueous acetonitrile and aqueous methanol, oxidation becomes difficult at GCE with the increase of organic solvent fraction as the oxidation potential shifts from 1.385 V, 1.391 V in aqueous methanol (volume ratio, $\psi = 20:80$) and aqueous acetonitrile ($\psi = 20:80$) to 1.432 V, 1.448 V

TABLE I. The influence of variation of sulphuric acid concentration on the electrochemical oxidation of compound **Ia** at a scan rate of 0.05 V s⁻¹ at GCE

[H ₂ SO ₄] 10 ⁻² mol dm ⁻³	E _{pa} V	-i _{pa} μA	D ₀ 10 ⁻⁵ cm ² s ⁻¹	k ₀ 10 ⁻⁴ cm s ⁻¹
1.2	1.484	34.1	0.8229	0.4983
2.4	1.450	88.0	4.6311	1.286
3.2	1.441	100.1	5.9922	1.463
4.0	1.419	137.8	7.3480	2.014
4.8	1.375	160.2	8.7882	2.341

TABLE II. The influence of variation of sulphuric acid concentration on the electrochemical reduction of **la** at a scan rate of 0.05 V s⁻¹ at GCE and WICPE

[H ₂ SO ₄] 10 ⁻² mol dm ⁻³	GCE			WICPE		
	-E _{p1} / V	i _{p1} / μA	-E _{p2} / V	i _{p2} / μA	-E _{p1} / V	i _{p1} / μA
0.8	0.528	197.0	1.026	125.5	0.547	18.8
2.0	0.493	233.3	0.955	159.8	0.508	27.6
2.8	0.468	252.5	0.939	173.9	0.476	33.4
4.0	0.407	280.0	0.913	185.2	0.445	40.1

in aqueous methanol ($\psi = 44:56$) and aqueous acetonitrile ($\psi = 44:56$), respectively. This could be due to the decrease in conductivity as the organic content increased. A drop in peak current was observed due to slower charge transfer. There were no significant differences in oxidation potential in methanol and acetonitrile.

Temperature Dependence of Voltamograms

The oxidation peak potential increased from 1.419 V to 1.478 V as the temperature was increased from 300 K to 319 K. Oxidation is more favoured at lower temperature.

CONCLUSION

The hydroxymethylated nitroalkenes undergo irreversible four electron charge transfer at GCE but no oxidation takes place at WICPE. Electrochemical reduction of the nitro group takes place at both GCE and WICPE. Higher reduction potentials indicate much easier reduction at GCE compared to WICPE due to marked hydrophobicity of the pasting liquid as well as wax, which hinders the access of analyte towards the surface in the case of WICPE. Reduction of hydroxymethylated compounds is difficult, as it is evident from the lower reduction potential compared to the non-hydroxymethylated compounds. Easier oxidation with increased concentration of sulphuric acid is due to the formation of a six membered cyclic structure formed as a result of intramolecular hydrogen bonding at lower concentrations of sulphuric acid.

REFERENCES

1. N. Rastogi, I. N. N. Namboothiri, and M. Cojocar, *Tetrahedron Lett.* **45** (2004) 4745–4748.
2. C. Karakus and P. Zuman, *J. Electroanal. Chem.* **396** (1995) 499–505.
3. P. J. Declerck and C. J. de Ranter, *Biochem. Pharmacol.* **35** (1986) 59–61.
4. P. J. Declerck and C. J. de Ranter, *J. Chem. Soc., Faraday Trans.1* **83** (1987) 257–265.
5. J. H. Tocher and D. I. Edwards, *Biochem. Pharmacol.* **48** (1994) 1089–1094.
6. L. Sjöberg and T. E. Eriksen, *J. Chem. Soc., Faraday Trans.1* **76** (1980) 1402–1408.
7. C. Corvaja, O. Farnia, and E. Vianello, *Electrochim. Acta.* **11** (1966) 919–929.
8. Ya. Stradyn, R. Gavar, L. Baumane, B. Vigante, and B. Dubur, *Chem. Heterocycl. Compd.* **33** (1997) 184–189.
9. J. Y. David, J. P. Hurvois, and A. T. L. Toupet, *Tetrahedron* **51** (1995) 3181–3196.
10. L. J. Núñez-Vergara, S. Bollo, C. Olea-Azar, P. A. Navarrete-Encina, and J. A. Squella, *J. Electroanal. Chem.* **436** (1997) 227–238.
11. M. M. Ellaihy and P. Zuman, *J. Pharm. Sci.* **81** (1992) 191–196.
12. I. Svancara, M. Pravda, M. Hvizdalova, K. Vytras, and K. Kalcher, *Electroanalysis* **6** (1994) 663–671.
13. J. Lindquist, *Anal. Chem.* **45** (1973) 1006–1008.
14. S. S. Atuma and J. Lindquist, *Analyst* **98** (1973) 886–894.
15. J. H. Kim, J. Hyun Kim, G. E. Lee, J. E. Lee, and I. K. Chung, *Mol. Pharmacol.* **63** (2003) 1117–1124.
16. A. I. Vogel, A. R. Tatchell, B. S. Furnis, and A. J. Hannaford, *Vogels Text Book of Practical Organic Chemistry*, Addison Wesley, Longman Ltd, Essex, 1996, p. 1035.
17. J. A. Squella, J. C. Sturm, B. W. Lopez, M. Bontá, and L. J. Núñez-Vergara, *J. Electroanal. Chem.* **466** (1999) 90–98.
18. M. Wessling and H. J. Schäfer, *Chem. Ber.* **124** (1991) 2303–2306.
19. A. J. Bard and L. R. Faulkner, *Electrochemical Methods – Fundamentals and Applications*, John Wiley and Sons, New York, 1980, pp. 219–223.
20. R. S. Nicholason and I. Shain, *Anal. Chem.* **36** (1964) 706–723.
21. E. Ramanathan, P. S. M. Kannan, S. Thangavelu, and K. S. Udupa, *Bull. Electrochem.* **4** (1988) 365–370.
22. B. Eswarappa, B. S. Sherigara, and B. E. Kumara Swamy, *Bull. Electrochem.* **20** (2004) 1–4.
23. M. Noel and K. I. Vasu, *Cyclic Voltammetry and the Frontiers in Electrochemistry*, Oxford and IBH Publishing Co. Pvt. Ltd., New Delhi, 1990, p. 174.

SAŽETAK**Elektrokemijsko ponašanje novih višefunkcionalnih α -hidroksimetiliranih nitroalkena na elektrodama od staklastog ugljika i voskom impregnirane ugljikove paste****Ronald J. Mascarenhas, Irishi N. Namboothiri, Bailure S. Sherigara i
Kittappa M. Mahadevan**

Istražena je oksidacija –OH grupe i redukcija nitro grupe novih višefunkcionalnih α -hidroksimetiliranih nitroalkena koristeći cikličku voltometriju na elektrodama od staklastog ugljika i voskom impregnirane ugljikove paste u otopini sumporne kiseline kao osnovnom elektrolitu. Na staklastom ugljiku –OH grupa koja se nalazi na pokrajnom lancu nitroalkena ireverzibilno se oksidira do kiseline u elektrodnoj reakciji koja uključuje prijenos četiri elektrona, ali se oksidacija ne vidi na elektrodi od ugljikove paste. Povećanje koncentracije sumporne kiseline olakšava oksidaciju. Ovo neobično ponašanje objašnjeno je šesteročlanom cikličkom strukturom stabiliziranom vodikovim vezama koja se stvara pri nižim koncentracijama kiseline. Kod nižih potencijala uočena je redukcija nitro grupe na obje elektrode, ali je na staklastom ugljiku redukcija olakšana. Beta nitroalkeni koji nisu hidroksimetilirani reduciraju se kod nižih potencijala nego odgovarajući α -hidroksimetilirani nitroalkeni.