Asian Journal of Chemistry Vol. 21, No. 9 (2009), 7316-7320

Electrochemical Reduction of *m*-Nitrophenol in Aqueous Methanol Medium at Various Electrodes

SANGITA GUPTA*, MANISH GUPTA† and P.S. VERMA
Department of Chemistry, University of Rajasthan, Jaipur-302 004, India
E-mail: sangita.uor@gmail.com

Voltammetric curves of *m*-nitrophenol in aqueous-methanol medium for acidic, basic and neutral ranges using B.R. Buffer for various concentrations (0.05, 0.1, 0.15 and 0.2 mM) and scan rates were obtained. The prominent three reduction peaks corresponding to $4e^-$ change of *m*-nitro phenol was characterized at 0.1 mM concentration in basic medium at scan rate 90 mV/s. The reversibility of the reaction was also studied by the cyclic voltammetry. Constant current electrolysis of 0.02 mM *m*-nitrophenol in basic medium gives *m*-hydroxy phenyl hydroxylamine at stainless steel (type 316) cathode and counter electrode of same size and material at constant current 1.9 A, respectively, as a major product which were confirmed by spectral and chemical analysis.

Key Words: Electrochemical reduction, *m*-Nitrophenol, Cyclic voltammetry, Constant current electrolysis.

INTRODUCTION

Numerous investigations have been made on the reduction of the aromatic nitro compounds. The nitro group is one of the best electrophores as regards to both ease of reduction and versatility of derived products. By the electroreduction[1] of nitrophenol isomer using stationary and rotating Cu electrodes and $Ti(SO_4)_2$ as additional agent, aminophenols were obtained in good yield. Depending on the electrolysis conditions, a great variety of products can be obtained by electroreduction of nitrophenols. Stainless steel electrode have been used widely in our laboratory for the electrochemical reduction of some nitro compounds[2-7].

In present work, the voltammetric studies of *m*-nitrophenol were carried out in acidic, neutral and basic medium and electrochemical reduction of *m*-nitrophenol at stainless steel electrode, products depending upon the conditions of the reduction. Under the basic condition the products *m*-nitrophenol is reduced to *m*-hydroxyl phenyl hydroxylamine (*m*-HPHA), which is further reduce to *m*-amino phenol.

---

†Deputy Director, RCEE, Shiksha Sankul, J.L.N. Marg, Jaipur-302 015, India.

EXPERIMENTAL

Solutions were prepared from A.R. methanol and double distilled water. Reagents such as acetic acid, phosphoric acid, boric acid, sodium hydroxide, oxalic acid, sodium acetate, potassium chloride and sodium chloride used were of A.R. grade. *m*-Nitrophenol was crystallized from methanol and the pale yellow, odourless crystals (m.p. 97 ºC) were used. The purity was checked by single spot TLC. IR spectra of *m*-nitrophenol and the product obtained, were recorded and studied to confirm the structure.

Cyclic voltammetric studies were carried out using a three electrode cell assembly having glassy carbon as the working electrode, Ag/AgCl as reference electrode and Pt wire as the counter electrode. Voltammograms of *m*-nitrophenol are recorded in 1:1 (v/v) water:methanol at 0.05, 0.1, 0.15 and 0.2 mM concentrations. B.R. Buffer was used to maintain desired pH *viz.* 3.9, 7.0, 9.1.

An Elico Model CL-95 Potentiostat cum Galvanostate coupled with a sweep generator were used for carrying out controlled current electrolysis. Stainless steel (SS316) electrode was used as cathode and counter electrode. The solution was stirred by a Remi 2LH hot plate stirrer throughout the electrolysis. H-cell was used as electrolysis cell to carried out constant current electrolysis. FT-IR spectra of *m*-nitro phenol and the product was obtained.

The preparative electrolysis of 100 mL of 0.02M *m*-nitrophenol were carried out at constant current of 1.9 A in basic medium (pH = 10) for 6 h. The thermometer was kept dipped under the surface of the catholyte. Stirring was done at the maximum speed of the magnetic stirrer. The potential was recorded at the start of the electrolysis and then after 15 min. The temperature was also recorded simultaneously at regular intervals. The electrolysis was terminated when the potential becomes constant with change in time.

Work-Up: After the electrolysis the catholyte was distilled under reduced pressure so that the volume of the catholyte was reduced to one third of it's original volume. No precipitate was obtained due to absence of azoxy and azo derivatives. The catholyte was then saturated with sodium chloride and cooled to less than 5 ºC and extracted with three lots of 15 mL each of benzene light petroleum. On evaporation solid *m*-hydroxyl phenyl hydroxylamine (*m*-HPHA) was obtained in 90 % yield. The purity of the compound was checked by single spot TLC.

RESULTS AND DISCUSSION

Cyclic voltammograms were recorded with an applied potential 0.0 V intial potential, 0.5 V and final potential -1.3 V at different, pH, concentrations and scan rates. Table-1 summarized the voltammetric data for *m*-nitrophenol in acidic, basic as well as in neutral medium.

TABLE-1
CURRENT-POTENTIAL MEASUREMENTS IN CYCLIC VOLTAMMETRY
X-axis = 0.1 V/cm, Scan rate = 90 mV/S, Applied E = 0.0 V,
+E = 0.5 V, -E = -1.5 V, Concentration = 0.1 mM

pH	Fig. No.	Cathodic wave			Anodic wave			Remark
		Wave No.	Potential (V)	Current (μA)	Wave No.	Potential (V)	Current (μA)	
3.9	1(a)	I	Not appeared		I	Not appeared		Cathodic wave is irreversible
		II	-0.52	0.62×10^3	II	Not appeared		
7.0	2(b)	I	Not appeared		I	Not appeared		cathodic wave is irreversible
		II	-0.61	0.43×10^3	II	0.33	0.18×10^3	
9.1	3(a)	I	-0.2	0.05×10^3	I	-0.53	0.02×10^3	II cathodic wave is reversible others are irreversible
		II	-0.65	0.19×10^3	II	0.22	0.13×10^3	
		III	-0.99	0.34×10^3	III	Not appeared		

Effect of the pH: Electrochemical reduction of *m*-nitrophenol is easier in basic medium because of these reasons. (i) In acidic medium (pH = 3.9) at concentration 0.1 mM, one cathodic wave (IInd) is appeared which is irreversible as shown in Fig. 1. (ii) In neutral medium (pH = 7.0) at concentration 0.1 mM one cathodic wave (IInd) is also appeared which is irreversible as shown in Fig. 2. (iii) In basic medium (pH = 9.1) at concentration 0.1 mM three cathodic waves are appeared, in which IInd wave is reversible as shown in Fig 3. Hence, in acidic and neutral medium less defined peaks obtained but in basic medium prominent peaks are appeared. (iv) Stainless Steel can be easily used as cathode in basic medium for constant current electrolysis due to its corrosive tendency in acidic media. (v) For constant current electrolysis the reduced product *m*-hydroxyl phenyl hydroxylamine (*m*-HPHA) was obtained in reasonably good yield (90 %) in basic medium.

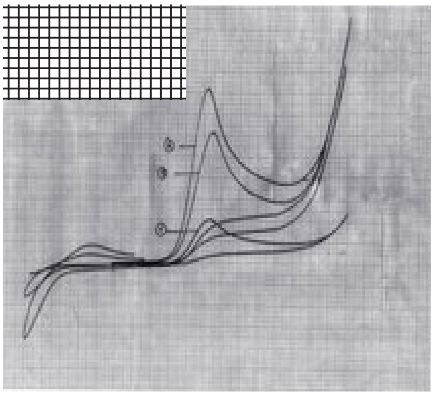

Fig. 1. Cyclic voltammograms of 0.1 mM *m*-nitrophenol at pH = 3.9, y axis (a) = 0.10 mA/cm, Gain = 0.01 mA/V

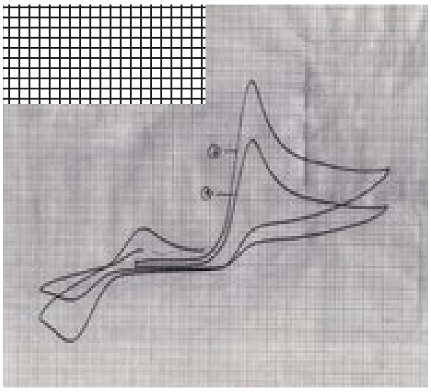

Fig. 2. Cyclic voltammograms of 0.1 mM *m*-nitrophenol at pH = 7, y axis (b) = 0.05 mA/cm, Gain = 0.01 mA/V

Effect of concentration: Three reduction waves are obtained for basic medium (pH = 9.1) as shown in Figs. 3-6. Out of these three waves second wave is reversible. When the concentration is increased from 0.05 to 0.15 mM, the peak current (I_p) also increases (for second peak). When the concentration increased further from 0.15 to 0.2 mM, I_p remains constant. This show that the reaction is adsorption control, as shown in Fig. 7. Table-2 summarized the voltammetric data for *m*-nitro phenol in basic medium (pH = 9.1) at different concentrations.

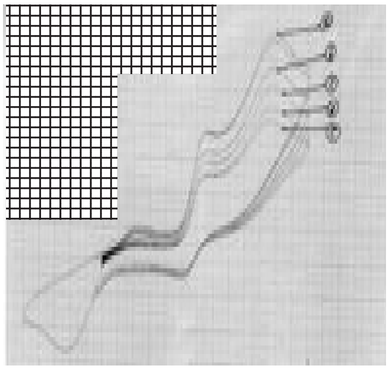

Fig. 3. Cyclic voltammograms of 0.1 mM *m*-nitrophenol at pH = 9.1, y axis (a) = 0.05 mA/cm, Gain = 0.01 mA/V

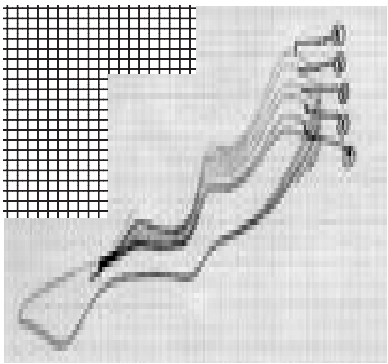

Fig 4. Cyclic voltammograms of 0.05 mM *m*-nitrophenol at pH = 9.1, y axis (a) = 0.05 mA/cm, Gain = 0.01 mA/V

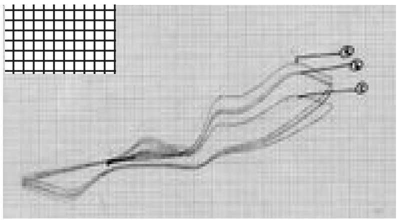

Fig. 5. Cyclic voltammograms of 0.15 mM *m*-nitrophenol at pH = 9.1, y axis (a) = 0.1 mA/cm, Gain = 0.01 mA/V

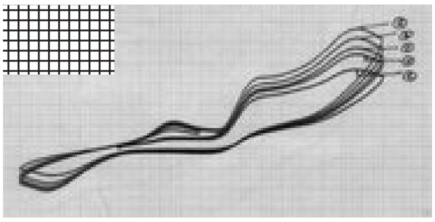

Fig. 6. Cyclic voltammograms of 0.2 mM *m*-nitrophenol at pH = 9.1, y axis (a) = 0.1 mA/cm, Gain = 0.01 mA/V, Scan rate (mV/s) (a) 90 (b) 80 (c) 70 (d) 60 (e) 50

TABLE-2
CURRENT MEASUREMENT WITH CONCENTRATION FOR PEAK II
X-axis = 0.1 V/cm, Scan rate = 90 mV/S, Applied E = 0.0 V,
+E = 0.5 V, -E = -1.3V, pH = 9.1

Concentration (mM)	I_P (μA)
0.05	0.14×10^3
0.10	0.19×10^3
0.15	0.32×10^3
0.20	0.33×10^3

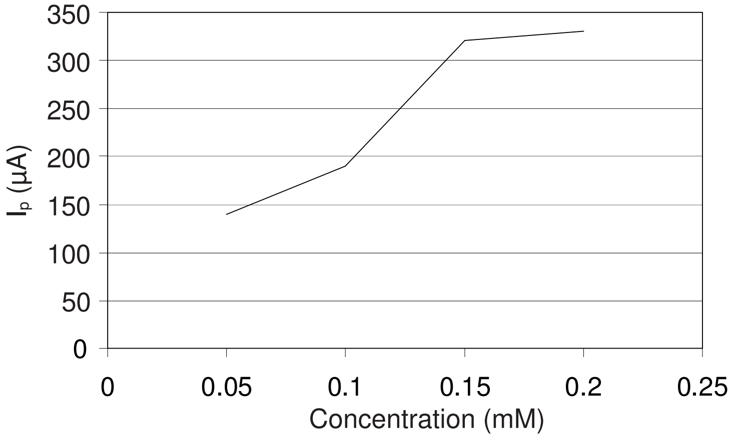

Fig. 7. Plot between concentration and I_p

Effect of scan rates: As the sweep rate was gradually increased to 50, 60, 70, 80, 90, mV/s (from bottom to up) peak current gradually shifted towards higher values as shown in Fig. 6.

The result of the preparative electrolysis at constant current of 1.9 A using stainless steel electrode led to the isolation of *m*-hydroxy phenyl hydroxylamine (*m*-HPHA). This is the 4-electron change process in basic conditions. Purity is checked by single spot TLC. The product is confirmed by the chemical and spectral analysis.

Chemical analysis: (1) The product reduced Tollen's reagent confirming that it was *m*-HPHA. (2) The product gives a precipitate with $FeCl_3$, which confirms the presence of m-HPHA. (3) The product did not respond to the dye test indicating the absence of primary amino group and thus there was no formation of *m*-aminophenol.

Spectral analysis: The peak due to the nitro group which were originally present in the starting material (*m*-nitrophenol) were no longer found in the products indicating that the reaction being completed. The hydroxyl amine derivative was confirmed by a broad band in the region 3600-3000 cm^{-1} and the primary amine salt had sharp peaks in the region 3000-2800 cm^{-1}.

REFERENCES

1. P.N. Anantharman and H.V.K. Udupa, *Trans. SAEST*, **15**, 41 (1980).
2. N. Singhal, I.K. Sharma and P.S. Verma, *Trans. SAEST*, **32**, 77 (1997).
3. S.R. Yadav, R. Yadav, A. Sharma, I.K. Sharma and P.S. Verma, *Bull. Electrochem.*, **18**, 87 (2002).
4. S.R. Yadav, P. Goyal, A. Sharma, I.K. Sharma and P.S. Verma, *J. Indian Chem. Soc.*, **79**, 695 (2002).
5. M. Vijay, A. Sharma, I.K. Sharma and P.S. Verma, *J. Electrochem. Soc. (India)*, **55**, 70 (2006).
6. M. Vijay, B. Sahay, M. Gupta, I.K. Sharma and P.S. Verma, *Asian J. Exp. Sci.*, **21**, 377 (2007).
7. M. Vijay, N. Kharia, S. Varshney and P.S. Verma, *J. Indian Chem. Soc.*, **46A**, 778 (2007).

(*Received*: 26 March 2009; *Accepted*: 24 August 2009) AJC-7769