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Electrochemical Reduction of *m*-nitrotoluene at Glassy Carbon and Stainless Steel Electrode at Different pH

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Abstract : The voltammograms of *m*-nitrotoluene (aqueous-methanol solution) in BR buffer at different pH 4.0, 7.0, 9.0 exhibits the one reduction peak; effect of scan rate on cathodic peak potential indicates that these reactions are irreversible. Constant current electrolysis in acidic and basic media of *m*-nitrotoluene gives *m*-toluidine and 3,3' dimethyl azo benzene respectively as a major products which were confirmed by TLC, NMR, IR spectrum analyses.

Keywords : Electrochemical Reduction, *m*-nitro toluene SS cathode, Cyclic Voltammetry and Constant Current Electrolysis.

Introduction

Numerous investigations have been made on the reduction of aromatic nitro compounds and number of different products has been obtained under various conditions (Zuman and Rupp, 1995). This is caused more by differences in the chemical follow-up reactions rather than by the electrochemical reactions. It is well known that the reduction of Nitro compounds has played a vital role in the development of organic-electrochemistry (Fichter, 1942).

The present work deals with the electrochemical studies (cyclic voltametry and constant current electrolysis at SS-(316) electrode) of *m*-nitro toluene (Swan, 1956; Malik *et al*., 1999) in acidic, neutral and basic media.

Constant current electrolysis at SS cathode *m*-nitro toluene gave different products in different media, which have been studied in detail by means of various techniques (Nicholson *et al*., 1985; Yadav *et al*., 2002a). Economically viable stainless steel electrode (SS-316) has been used successfully in our laboratory (Yadav *et al*., 2002b).

Materials and Methods

All the reagents, NaOH, CH_3COONa, KNO_3, *m*-nitro toluene, methanol and acetic acid, etc. used were of AR grade. The solutions were prepared in double distilled water. Nitro toluene re-crystallized from methanol was used for reduction purpose. Prior to electrolysis, TLC, which gave single spot, was used to check the purity of the compound.

Cyclic voltammograms were recorded on a fully computer controlled Basic Electrochemistry System-ECDA 001 (Conserved, Mumbai, India), using 3-electrode cell assembly with 1mm diameter glassy carbon as working electrode, Ag/AgCl as reference electrode and Pt wire as counter electrode. In aqueous media, 1.0 mM concentration of depolarizer and KNO_3 were used as supporting electrolyte to maintain the

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ionic strength of the solution at 0.1 M. BR buffer was used to maintain desired pH *viz.* 4.0, 7.0, and 9.0. Galvanostat, designed and made by CDPE (Centre for Development of Physics Education, Univ. of Rajasthan, Jaipur), was used for carrying out controlled current electrolysis. Stainless steel (SS-316) electrode was used as cathode. The solution was stirred by a Remi 2LH hot plate cum stirrer throughout the electrolysis. FT-IR spectra of *m*-nitro toluene and the products were obtained and compared for analysis, identification and characterization.

The preparative electrolysis of 200 ml 0.1M *m*-nitro toluene was carried out at constant current (at 1 amp.) in alkaline solution containing (1M CH_3COONa + 0.5MNaOH) as well as in acidic media containing (1M CH_3COONa + 1M CH_3-COOH pH=4) in 1:1 CH_3OH: H_2O.

After electrolysis the methanol was removed from the solution by distillation at reduced pressure (30 mm Hg). The catholyte was then extracted repeatedly with ether layer. The ether layer was collected in watch glass and was allowed to evaporate. After evaporation product was then recrystallized with absolute alcohol and pure crystals were obtained.

Results and Discussion

Most cyclic voltammograms were recorded with an initial potential E_i of 700 mV and final (switching) potential E_s of -1400 mV at different scan rates viz. 30, 60, 100, 200, 400 and 500 mV/sec (Fig. 1, 2 and 3). *m*-nitro toluene at scan rate of 30mV/sec and pH=7, 4 and 9 appeared at -839 mV, -824mV and -890 mV, respectively. As the sweep rate was gradually increased to 60, 100, 200, 400 and 500 mV/sec, peak gradually shifted towards higher values as is expected for an irreversible electron transfer processes.

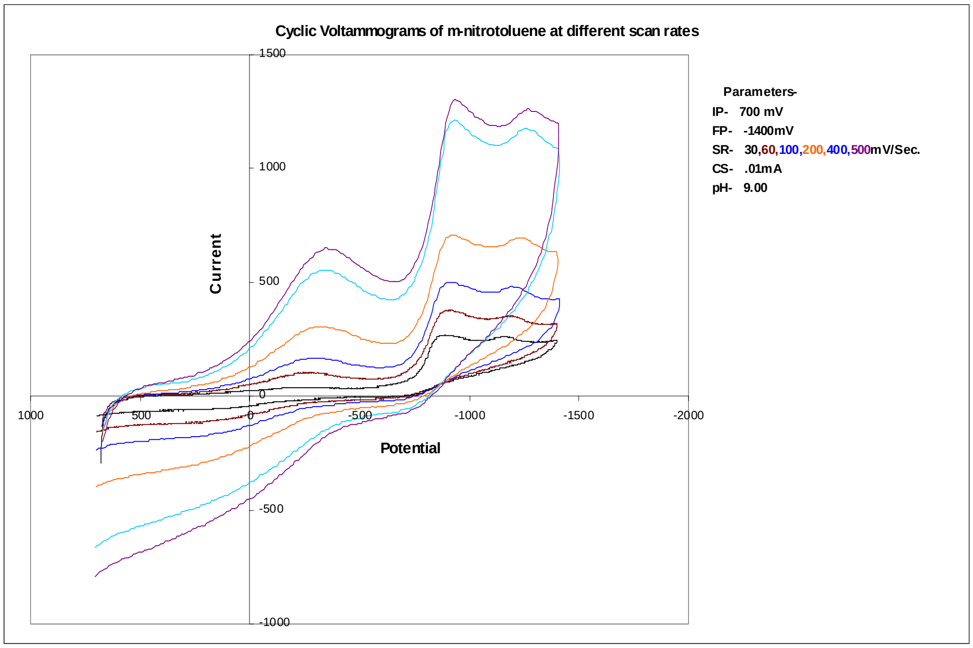


Fig. 1 : Cyclic Voltammograms of *m*-nitrotoluene at different scan rates

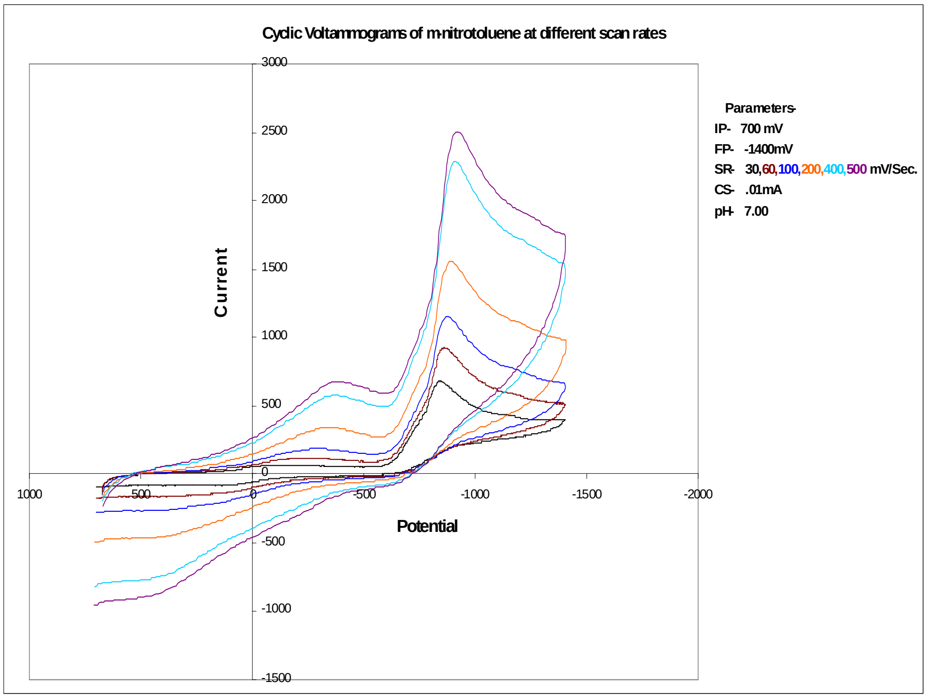


Fig. 2 : Cyclic Voltammograms of *m*-nitrotoluene at different scan rates

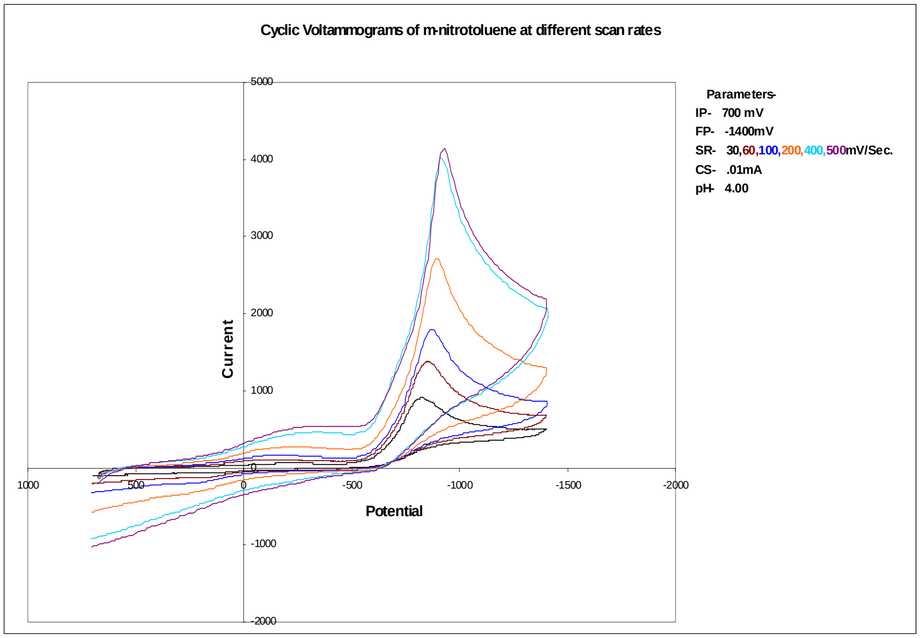


Fig. 3 : Cyclic Voltammograms of *m*-nitrotoluene at different scan rates

Table-1 summarizes current potential measurements by cyclic voltammetry for *m*-nitro toluene in acidic, basic as well as in neutral media, which confirms irreversible nature of the reduction process of *m*-nitro toluene.

Above mentioned electrolytically reduced produced was obtained in reasonably good yield. Single spot TLC checked the purity of compounds. The identity of products was further confirmed on the basis of melting point spectroscopic analysis. IR and NMR data have been given below in table 2 and 3.

Table 1: Current potential measurements by Cyclic Voltammetry for *m*-nitrotoluene

Condition applied :
Initial potential E_i : 700 mV
Switching potential E_s : -1400 mV

Electrodes applied :
Working Electrode : Glassy Carbon
Reference Electrode : Ag/AgCl
Auxilliary Electrode : Platinum

S.N	Medium	Scan rate	Cathodic Wave				Effect of scan rate	Remark (Cathodic wave)
	pH	(mV/s)	E_{pc}(mV)		I_{pc}(μA)			
			I^{st} peak	II^{nd} peak	I^{st} peak	II^{nd} peak		
1	4.0	30	-824	-	907	-	With increasing scan rates peak potential shifts towards negative side of potential	Irreversible
2	4.0	60	-857	-	1377	-		Irreversible
3	4.0	100	-873	-	1796	-		Irreversible
4	4.0	200	-902	-	2701	-		Irreversible
5	4.0	400	-918	-	4026	-		Irreversible
6	4.0	500	-931	-	4133	-		Irreversible
7	7.0	30	-839	-	680	-	Peak potential show considerable cathodic shift of potential with increasing scan rates.	Irreversible
8	7.0	60	-864	-	927	-		Irreversible
9	7.0	100	-878	-	1155	-		Irreversible
10	7.0	200	-890	-	1558	-		Irreversible
11	7.0	400	-907	-	2282	-		Irreversible
12	7.0	500	-924	-	2509	-		Irreversible
13	9.0	30	-890	-1166	270	260	Peak potential shifts towards negative side of potential with increasing scan rates.	Irreversible
14	9.0	60	-894	-1197	379	351		Irreversible
15	9.0	100	-897	-1213	500	481		Irreversible
16	9.0	200	-935	-1237	707	696		Irreversible

Table 2 : Characterization table for synthesis in basic media

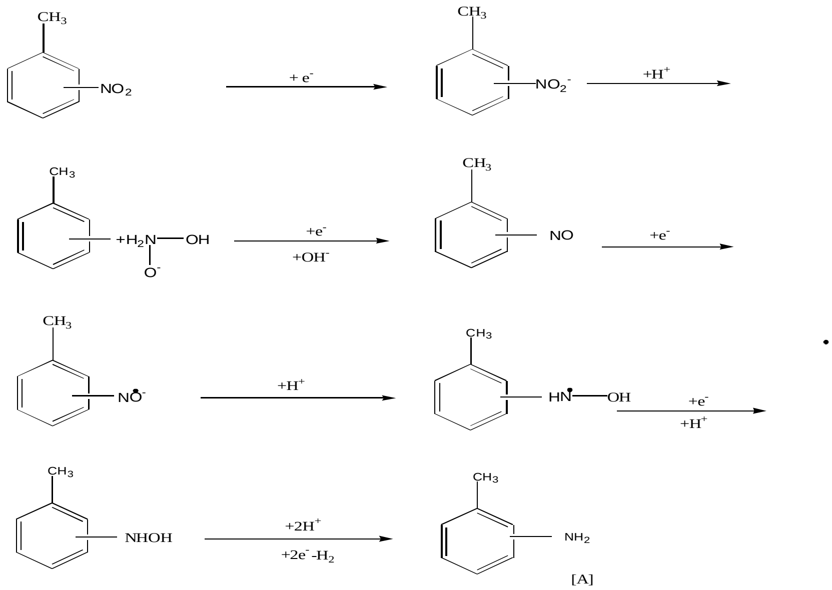
Starting material	M.Pt. (°C)	NMR data (δ)	IR data (cm^{-1})	Product
m -nitrotoluene	46	8H, δ = 6.0-8.8 unsymmetrical pattern (aromatic	1650-1440 b,s (aromatic ring), 2880 s (C-H stretching), 1510-1420 w	*m* - azotoluene (3-3' dimethyl azobenzene)

Table 3 : Characterization table for synthesis in acidic media

Starting material	B.Pt. (°C)	NMR data (δ)	IR data (cm^{-1})	Product confirmed
m - nitrotoluene	204	4H, δ = 6.6-8.2, unsymmetrical pattern (aromatic proton), 3H, s, δ=2.4 (-C$\underline{H}_3$), 2H, s, δ= 3.8 (-N$\underline{H}_2$)	3030 s (Ar-H- stretching), 2950 s (C-H stretching),1650-1440 b,s (aromatic ring),3420 s(symmetric stretching N-H), 3500 s (asymmetric stretching N-H),1640 b (bending N-H), 1290 s(C-N stretching), 710 and770 m (m-substitution)	*m* - toluidine (3-methyl aniline)

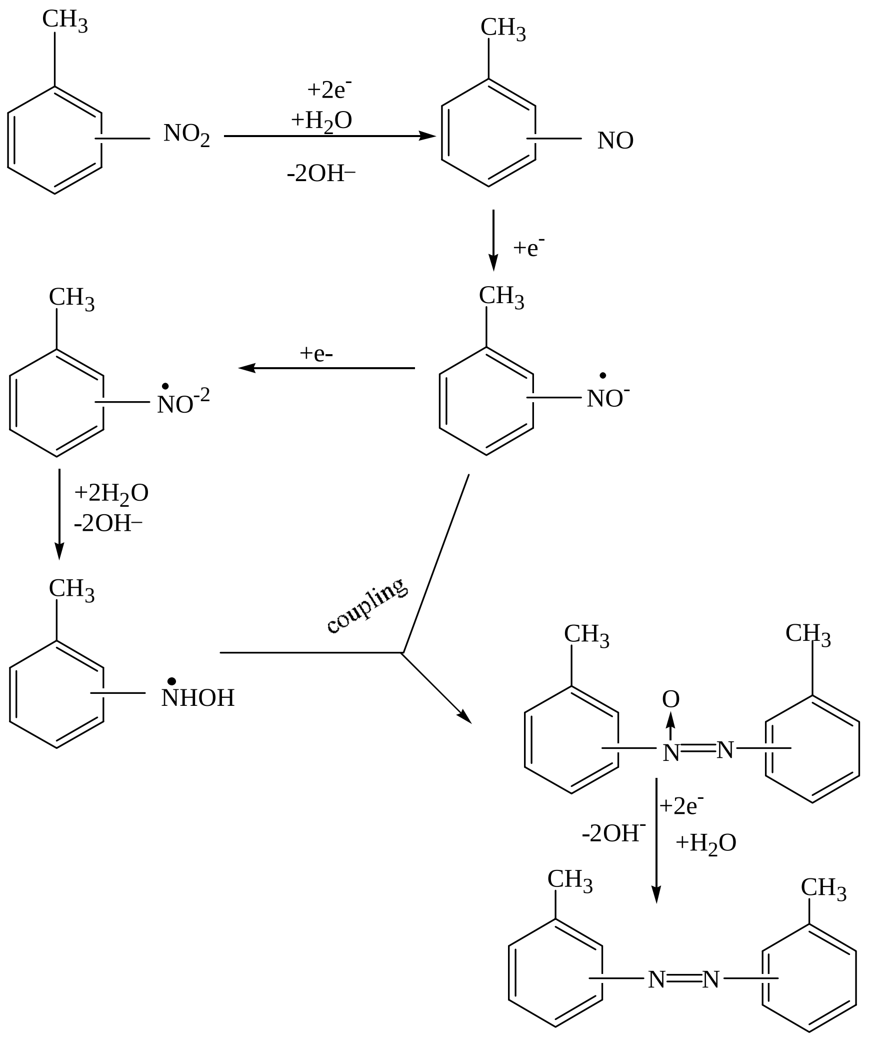
On the basis of all above studies a scheme for reduction of nitrotoluene (*o*, - *m*- and *p*-) have been suggested that has the basis of proton availability is suggested.

Scheme (1). That occurring under condition of high proton availability (acidic condition).



Here [A] is (*o*, - *m*-and *p*-) –toluidine of their respective nitrotoluene.

Scheme (2). That occurring under condition of low proton availability (basic and neutral condition).



[B]

Here [B] is (2, 2’ – 3, 3’ – 4, 4’ –) – dimethyl azobenzene of their respective nitrotoluene.

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