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Electrochemical Reduction of *M*-Nitro Benzoic Acid at Various Electrode and pH

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ABSTRACT

Electrochemical Behaviour of *m*-nitro benzoic acid has been studied with the help of cyclic voltammetry at various scan rates and pH. Information obtained from cyclic voltammetric studies was used for establishing optimum condition for electrochemical reduction of *m*-nitro benzoic acid at macro scale. Reduction was carried out by economically viable stainless steel (SS-316) electrode using galvanostat process in aqueous basic medium. The obtained product was isolated and characterized by combined application of chromatographic and spectroscopic techniques.

Keywords: Electrochemical reduction, Stainless Steel (SS-316) electrode, *m*-nitro benzoic acid, Cyclic Voltammetry and Galvanostat.

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INTRODUCTION

Electro-organic synthesis has now become a viable method for synthesis. It is a green and less polluting method and product in good yield [1]. The electrochemical reduction of nitro group is extremely sensitive to a number of variables thus by simply changing the pH of the reaction medium or the nature of electrode different products are obtained in good yield [2-5]. The present work deals with the electrochemical studies (cyclic voltammetry and constant current electrolysis at SS-316 electrode) of *m*-nitro benzoic acid in acidic, neutral and basic media, which elucidate the mechanism, kinetics and products of electrode processes.

Constant current electrolysis at stainless steel (SS-316) electrode *m*-nitro benzoic acid gave different products in different media. Economically viable stainless steel (SS-316) electrode, which has been used successfully in our laboratory [6-10]. was used in the present work also.

MATERIALS AND METHODS

All the reagents KCl, NaOH, CH₃COONa, *m*- nitro benzoic acid, methanol and acetic acid etc.used were of AR grade.

Cyclic voltammograms were recorded on a fully computer controlled Basic Electrochemistry System ECDA 001 (Conserve Enterprises, Mumbai, India) , using 3- electrode cell assembly with 1mm diameter glassy carbon as working electrode, Ag/AgCl as reference electrode and Pt wire as the auxiliary electrode. In aqueous media,1.0mM concentration of depolarizer and KCl were used as supporting electrolyte to maintain the ionic strength of the solution at 0.1 M. BR buffer was used to maintain desired pH viz.5.0, 9.0.

Galvanostat, designed and made by CDPE (Center for Development of Physics Education, University of Rajasthan, Jaipur) was used for carrying out constant current electrolysis for which stainless steel (SS-316) electrode was used as cathode as well as anode. The solution was stirred by a Remi 2LH hot plate cum stirrer throughout the electrolysis.

Experimental

The preparative electrolysis of 200 ml 0.1M *m*-nitro benzoic acid was carried out at constant current (1 amp.) in alkaline solution (pH=9) containing (1MCH₃COONa +0.5M NaOH) as well as in acidic media (pH=5) containing (1M CH₃COOH + 1M CH₃COONa) in 1:1 CH₃OH:H₂O.After electrolysis the methanol was removed from the solution by distillation .The catholyte was then extracted repeatedly with ether layer. The ether layer was collected in watch glass and allowed to evaporate. After evaporation product was recrystallized with alcohol and pure crystals were obtained.

RESULTS AND DISCUSSION

Most cyclic voltammograms were recorded with an initial potential E_i of 1300 mV and switching potential E_s of -1200 mV at different scan rates viz. 50, 100, 200, 300, 400 and 500 mV/sec (Fig. 1,2). *m*-nitro benzoic acid at scan rate of 50 mV/sec and pH 5,9 appeared at -353 mV and -280 mV, respectively. As the sweep rate was gradually increased to 200, 300, 400 and 500 mV/sec, peak gradually shifted towards higher values as is expected for an irreversible electron transfer processes.

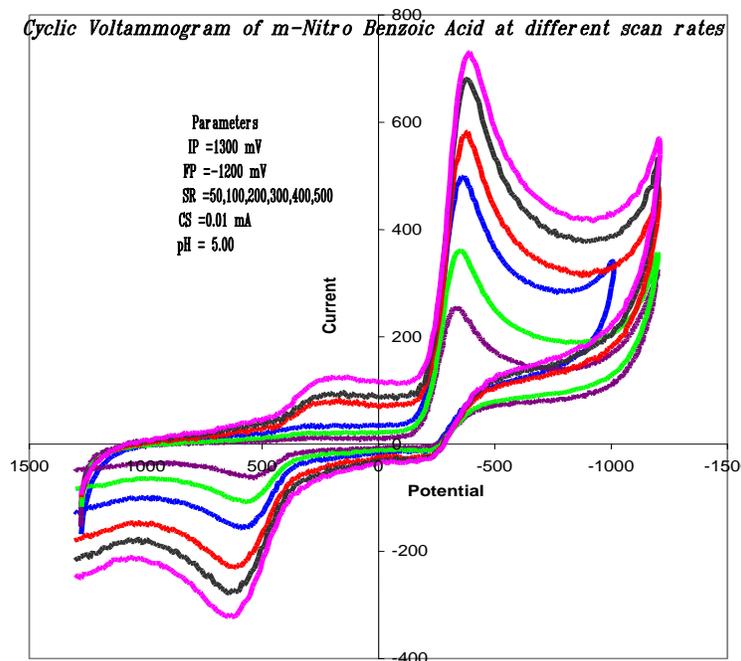


Fig: 1 Cyclic Voltammogram of *m*-Nitro Benzoic Acid at 5.0 pH

Table1: (Effect of scan rate on voltammetric parameters of *m*-nitro benzoic acid (1mM methanolic solution containing BR buffer))

S.N.	pH	Scan Rate (mV\sec)	E_p (mV/s)	$E_{p1/2}$ (mV/s)	I_{pc} (mA)	αna	$I_{pc}/v^{1/2}$	Effect of scan rate	Remark
1	5	50	-353	-261	61	0.00051859	8.626	Peak potential shift towards negative side of potential with increasing scan rates	Irreversible
2	5	100	-373	-275	83	0.00048684	8.300		
3	5	300	-392	-291	159	0.00047238	9.180		
4	5	400	-395	-300	170	0.00050221	8.500		
5	5	500	-401	-307	221	0.00050755	9.883		
6	9	50	-280	-186	76	0.00050755	10.248	With increasing scan rates potential shift towards	Irreversible
7	9	100	-294	-196	92	0.00048684	10.345		
8	9	300	-302	-204	187	0.00040092	10.796		
9	9	500	-320	-210	236	0.00048789	10.854		

								negative side of potential	
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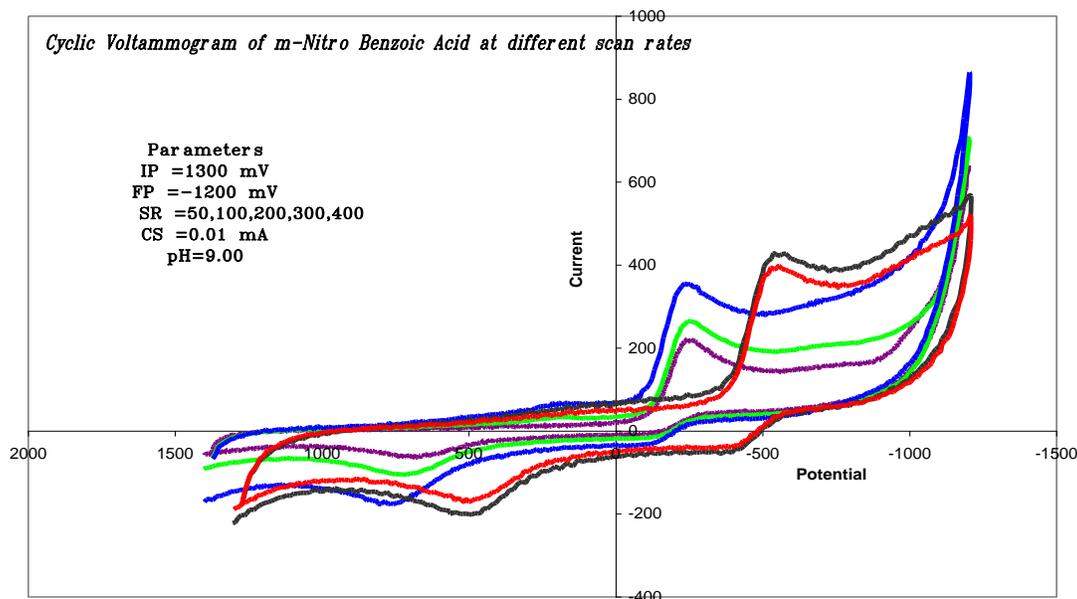


Fig: 2 Cyclic Voltammogram of *m*-Nitro Benzoic Acid at 9.0 pH

Table-1 summarizes the voltammetric data for *m*-nitro benzoic acid in acidic and basic media. Constant values of $I_{pc}/v^{1/2}$ and linear nature of I_{pc} vs. $v^{1/2}$ plots indicates that the reduction of *m*-nitro benzoic acid is a diffusion-controlled process.

m-aminobenzoic acid and 3,3-dicarboxy azobenzene electrolytically reduced products were obtained in reasonably good yields. Single spot TLC checked the purity of compounds. The identities of products were further confirmed on the basis of IR and NMR data have been given in table 2 and 3.

On the basis of kinetic parameters, number of total electrons change during reduction and product of bulk electrolysis the probable mechanism for the reduction of *o*-nitro benzoic acid is given as follows:

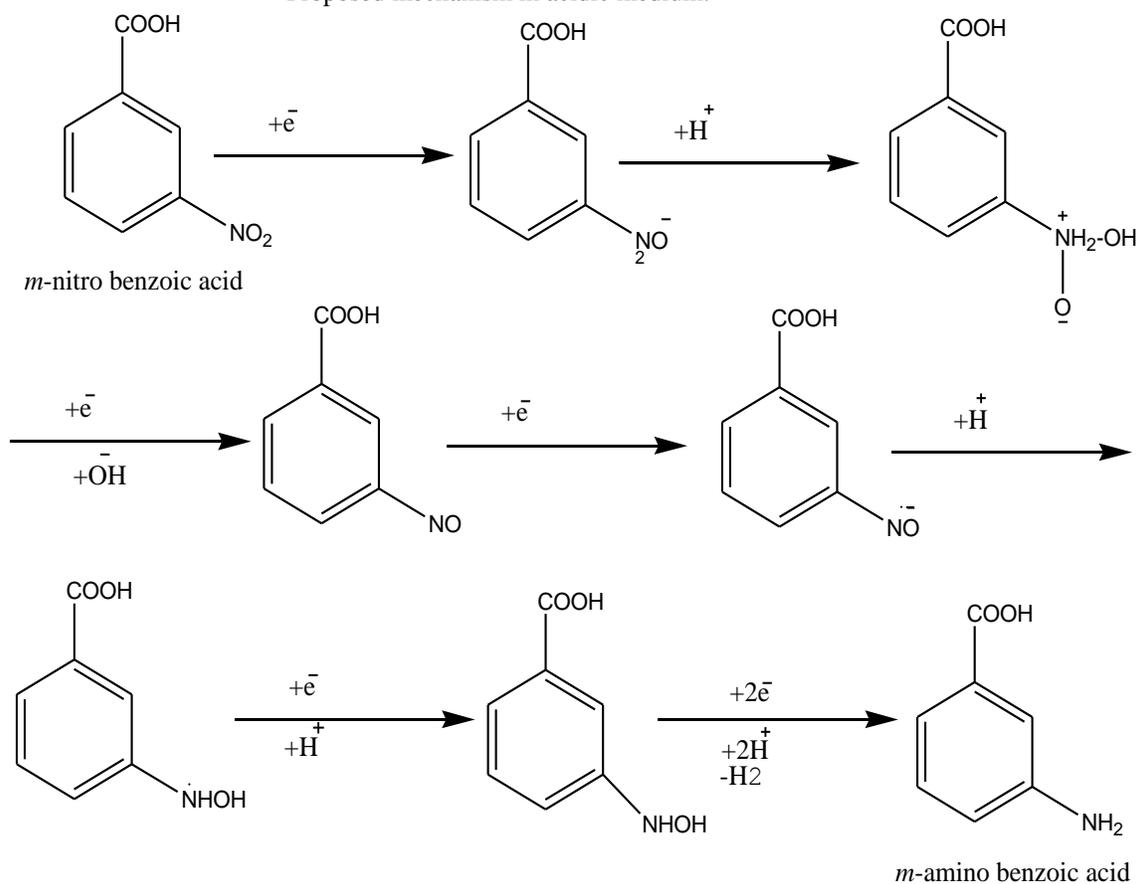
Table 2: (Characterization table for synthesis in basic media)

Starting material	NMR data (δ)	IR data (cm^{-1})	Product confirmed
<i>m</i> -nitro benzoic acid	4H, $\delta=6.0-8.4$ (aromatic proton) 1H, $\delta=9.0-11.0$ (carboxyl proton)	1650-1440 b,s (aromatic ring) 2880-2950 s (C-H stretching) 1510-1420 w	3,3'-dicarboxy azobenzene

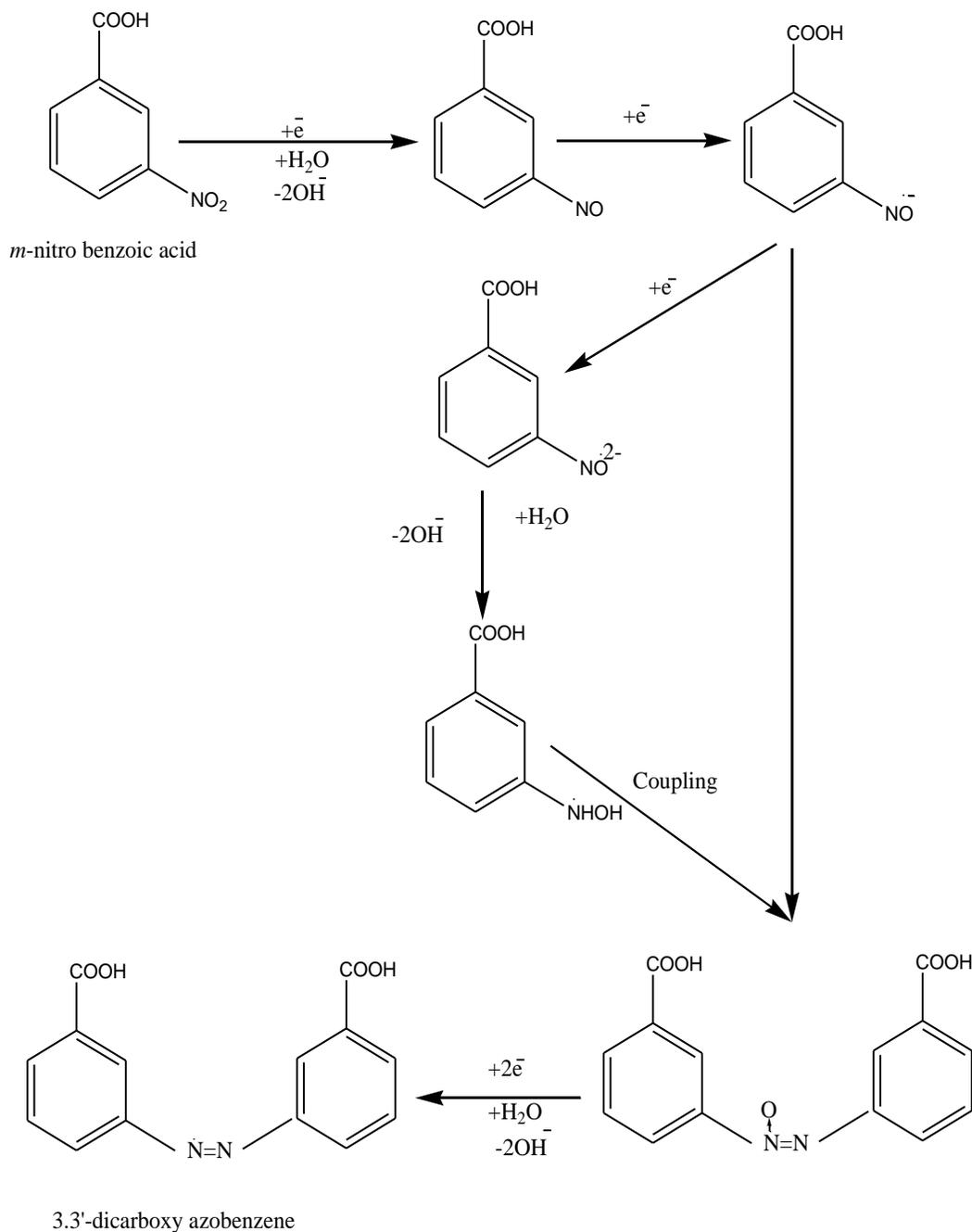
Table 3: (Characterization table for synthesis in acidic media)

Starting material	NMR data (δ)	IR data (cm^{-1})	Product confirmed
<i>m</i> -nitro benzoic acid	4H, δ =6.6-8.4 (aromatic ring) 1H, δ =9.0-11.0 (COOH) 2H, δ =3.8 (NH ₂)	3030s (Ar-H stretching) 2950 s (C-H stretching) 3420s (N-H symm.stretch) 1640b (N-H bending) 1290 s (C-N stretching) 3500-2500 s (O-H stretching) 1760 s (-C=O stretching) 1220 s (-C-O stretching) 920 b (O-H bending)	<i>m</i> -amino benzoic acid

Proposed mechanism in acidic medium:-



Proposed mechanism in basic medium:-



CONCLUSIONS

Electrochemical reduction of *m*-nitro benzoic acid was carried out at macro scale by economically viable stainless steel (SS-316) electrode using galvanostat process in aqueous acidic and basic medium. The obtained product *m*-aminobenzoic acid and 3,3-dicarboxy



azobenzene were isolated and characterized by combined application of chromatographic and spectroscopic techniques.

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