

Electrochemical Reduction of *p*-Nitro benzoic acid at Glassy Carbon and Stainless Steel (SS-316) Electrode at Different pH

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Cyclic voltammogram of *p*-nitro benzoic acid (aqueous-methanol solution) in BR Buffer at different pH 5 and 9 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 *p*-nitro benzoic acid gives *p*-amino benzoic acid and 4,4'-dicarboxy azobenzene, respectively. TLC, NMR and IR spectrum analyses confirmed the products.

Key Words: Cyclic voltammetry, Constant current electrolysis, *p*-Nitro benzoic acid, Stainless steel (SS-316) electrode.

INTRODUCTION

The 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 yield¹⁻⁴. It is well known that the reduction of nitro compounds has played a vital role in the development of organic-electro-chemistry⁵.

The present work deals with the electrochemical studies (cyclic voltammetry and constant current electrolysis at SS-316 electrode) of *p*-nitro benzoic acid in acidic and basic media.

Constant current electrolysis at stainless steel (SS-316) electrode *p*-nitro benzoic acid gave different products in different media. Economically viable stainless steel (SS-316) electrode has been used successfully in our laboratory⁶⁻¹⁰, was used in the present work also.

EXPERIMENTAL

All the reagents KCl, NaOH, CH₃COONa, *p*-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,

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Ag/AgCl as reference electrode and Pt wire as the auxiliary electrode. In aqueous media, 1.0 mM 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 Center for Development of Physics Education (CDPE), University of Rajasthan, Jaipur was used for carrying out constant current electrolysis. For constant current electrolysis stainless steel (SS-316) electrode was used as a cathode as well as anode. The solution was stirred by a Remi 2LH hot plate cum stirrer throughout the electrolysis.

Experimental procedure: The preparative electrolysis of 200 mL 0.1M *p*-nitro benzoic acid was carried out at constant current (1 amp.) in alkaline solution (pH = 9.0) containing (1 M CH₃COONa + 0.5 M NaOH) as well as in acidic media (pH = 5.0) containing (1 M CH₃COOH + 1 M 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 1400 mV and final potential E_s of -1000 mV at different scan rates *viz.*, 10, 50, 100, 200 and 500 mV/s (Figs. 1 and 2).

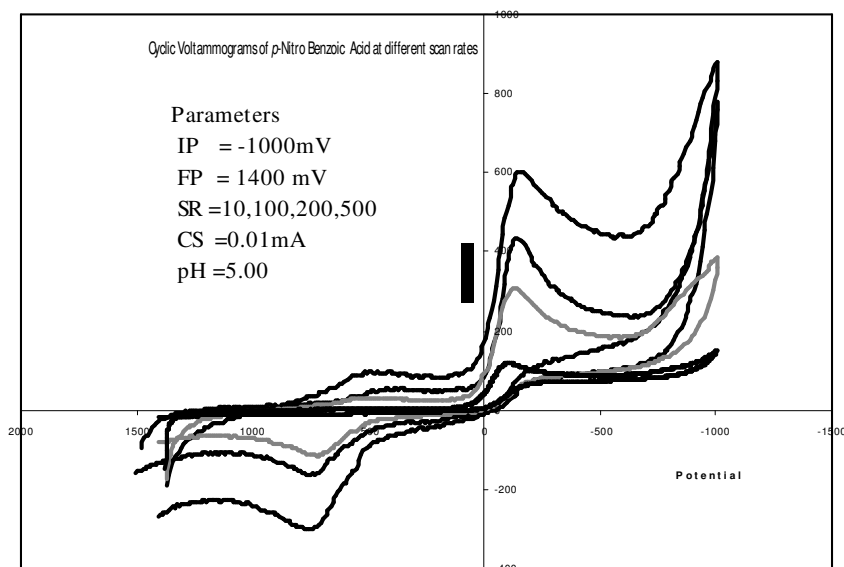
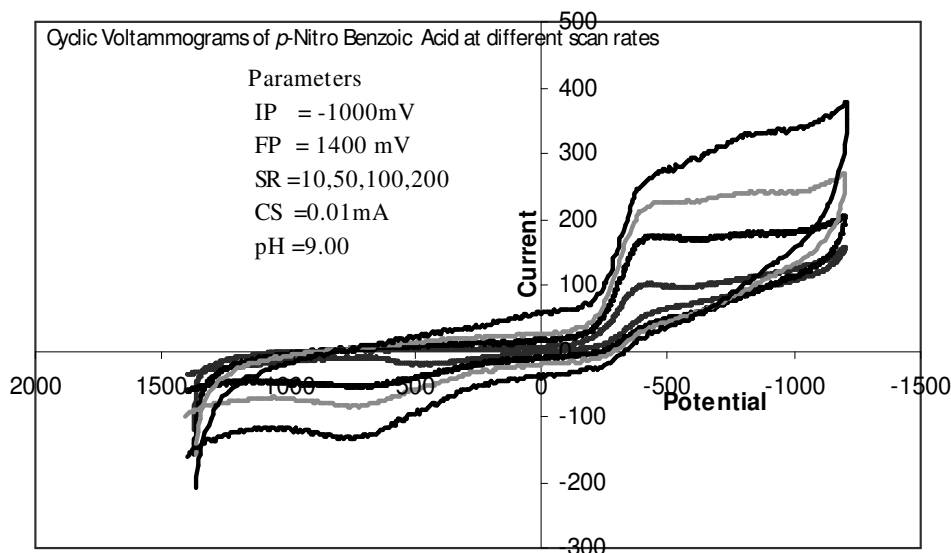


Fig. 1. Cyclic voltammogram of *p*-nitro benzoic acid at 5.0 pH

Fig. 2. Cyclic voltammogram of *p*-nitro benzoic acid at 9.0 pH

p-Nitro benzoic acid at scan rate of 100 mV/s and pH 5, 9 appeared at -141 mV, -487 mV, respectively. As the sweep rate was gradually increased to 200, 300 and 500 mV/s, peak gradually shifted towards higher values as is expected for an irreversible electron transfer processes. Table-1 summarizes current potential measurements by cyclic voltammetry for *p*-nitro benzoic acid in acidic and basic media that confirm irreversible nature of the reduction process of *p*-nitro benzoic acid.

TABLE-1
CURRENT POTENTIAL MEASUREMENT BY CYCLIC
VOLTAMMETRY FOR *p*-NITRO BENZOIC ACID
Initial Potential $E_i = 1400$ mV; Working electrode: Glassy carbon final potential
 $E_s = -1000$ mV; Reference electrode: Ag/AgCl; Auxiliary electrode: Platinum

| S. No. | pH | Scan rate (mV/s) | E_p | $E_{p1/2}$ | Effect of scan rate | Remark |
|--------|----|------------------|-------|------------|--|--------------|
| 1 | 5 | 10 | -135 | -44 | With increasing scan rates potential shift towards negative side of potential | Irreversible |
| 2 | 5 | 100 | -141 | -50 | | |
| 3 | 5 | 200 | -161 | -59 | | |
| 4 | 5 | 500 | -177 | -65 | | |
| 5 | 9 | 10 | -357 | -239 | Peak potential shift towards negative side of potential with increasing scan rates | Irreversible |
| 6 | 9 | 50 | -369 | -244 | | |
| 7 | 9 | 100 | -487 | -327 | | |
| 8 | 9 | 200 | -502 | -337 | | |

Electrolytically reduced products *i.e.*, *p*-amino benzoic acid and 4,4'-dicarboxy azobenzene were obtained in reasonably good yields. Single spot TLC checked the purity of compounds. The identity of products was further confirmed on the basis of IR and NMR data have been given below in Tables 2 and 3.

TABLE-2
CHARACTERIZATION TABLE FOR SYNTHESIS IN BASIC MEDIA

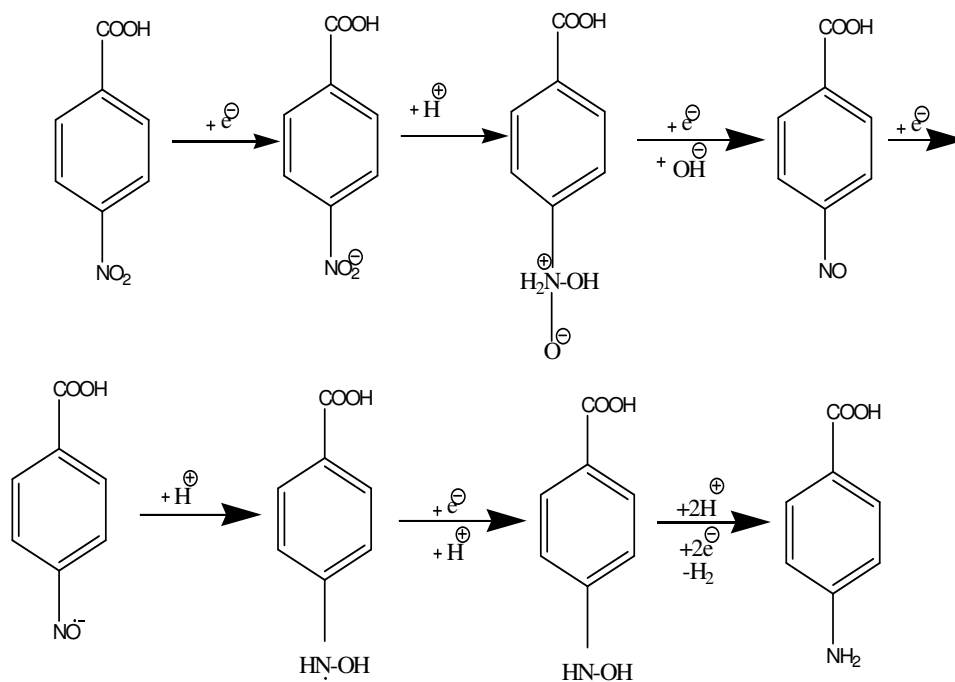
| Starting material | NMR data (δ) | IR data (cm^{-1}) | Product confirmed |
|------------------------------|--|--|---------------------------|
| <i>p</i> -Nitro benzoic acid | 4H, $\delta = 6.0-8.4$ (aromatic proton) 1H, $\delta = 9.0-11.0$ (Carboxyl proton) | 1650-1440 b,s (aromatic ring) 2950-2880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

TABLE-3
CHARACTERIZATION TABLE FOR SYNTHESIS IN ACIDIC MEDIA

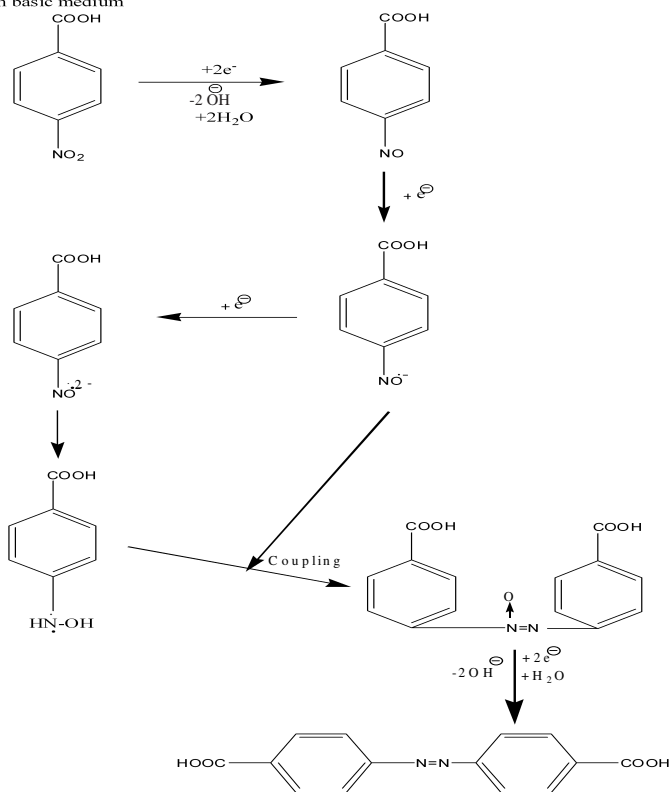
| Starting material | NMR data (δ) | IR data (cm^{-1}) | Product confirmed |
|------------------------------|---|--|------------------------------|
| <i>p</i> -Nitro benzoic acid | 4H, $\delta = 6.6-8.4$ (aromatic ring). 1H, $\delta = 9.0-11.0$ (COOH) 2H, $\delta = 3.8$ (NH_2) | 3030s (Ar-H stretching), 2950 s (C-H stretching), 3420s (N-H symm. stretch), (1640 b (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>p</i> -Amino benzoic acid |

On the basis of all above studies a proposed mechanism for reduction of *p*- nitro benzoic acid has been suggested as follows:

Proposed mechanism in acidic medium



Proposed mechanism in basic medium



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