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Electrochemical Reduction of *p*-Nitrobenzamide at Stainless (SS-316) Electrode in Basic Media

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Abstract

Cyclic voltammograms of p-nitrobenzamide were recorded at different pH (5.0, 7.0 and 9.0) to establish the optimum conditions of its reduction. The reduction of p-nitrobenzamide was thereafter carried out galvanostatically at pH = 9.0 using Stainless (SS-316) as a working electrode. 4, 4'- icarbamoylazobenzene was obtained in which was good yield (91.2%) isolated then purified by chromatographic techniques and characterized on the basis of spectral analysis.

Keywords: *p*-nitrobenzamide, galvanostatic reduction, stainless steel (SS-316) electrode, cyclic voltammetry.

Introduction

Electrochemistry has been widely used in industry in effluent treatment, corrosion prevention and electroplating as well as in electro chemical synthesis. Electro-organic synthesis is now a well established technique[1-2] for synthesize the desired compound by oxidation or reduction of substrate. Here electron obtained during electrochemical reaction play on important role by acting as a reagent.

In the present work the electrochemical reduction of *p*-nitrobenzamide is described. The reduction potential of the reactant was recorded by polarographic techniques. Cyclic voltammetry was used to decide the reversibility of the process. Different natures of cyclic voltammograms were obtained in different medium (acidic, basic and neutral). This indicates that in different media different electrolysis products were obtained.

Constant current electrolysis[3-9] at stainless steel (SS-316) electrode *p*-nitrobenzamide gave different products in different media,but the present investigation is specific to only basic medium because the SS 316 electrode, which is economically viable and ecofriendly, can successfully be used under such conditions.

Material and Methods

All the used reagents NaOH, CH_3COONa, KCl, *p*-nitrobenzamide etc, were of AR grade. The solutions were prepared in double distilled water.

Cyclic voltammograms were obtained on fully computerized controlled Basic Electrochemistry system ECDA 001, 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, 1.0mM concentration of reactant,1.0 M KCl used as supporting electrolyte to maintain the ionic strength of the solution and BR buffer used to maintain the desired pH viz 5, 7 and 9 were taken in 10 ml cell.Galvanostat designed and made by CDPE (Centre for Development of Physics Education, Univ. of Rajasthan, Jaipur) was used for carrying out controlled current electrolysis.

For constant current electrolysis the conventional H-Cell has been used, stainless steel electrodes were used both as anode and cathode. All electrolysis process was carried out in buffer (1.0M CH_3COONa + NaOH) and the pH of the solution was maintained constant at 9.00.

After electrolysis the water was removed from the solution by distillation. The residue was then extracted with alcohol. The alcohol layer was allowed to evaporate. After evaporation product was isolated, purified and characterized by combined application of chromatographic techniques and spectroscopic methods.

Results and Discussion

Most cyclic voltammograms were recorded with an initial potential Ei of 1200 mV and switching potential Es of -1000 mV at different scan rates vlz. 50,100,200,300,400 and 500 mV/sec figure 1, 2, 3.

p-nitrobenzamide at scan rate of 50 mV/sec and pH 5, 7 and 9 appeared at -324 mV, -195mV and -328mV, 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.

Table-1 summarizes the voltammetric data for *p*-nitrobenzamide in basic medium. Constant values of $Ipc/v^{1/2}$ and linear nature of Ipc vs. $v^{1/2}$ plots indicates that the reduction of *p*-nitrobenzamide is a diffusion-controlled process.

Electrolytically reduced product 4,4'-dicarbamoylazobenzene was obtained in reasonably good yields(91.2%). Single spot TLC checked the purity of compounds. The identity of product was further confirmed on the basis of IR and NMR data have been given below in table 2.

On the basis of kinetic parameter, number of total electrons change during reduction and product of bulk electrolysis the most probable mechanism for the reduction of *p*-nitrobenzamide is given as scheme 1.

Table-1
Current Potential measurement by cyclic voltammetry for *p*- Nitro Benzamide

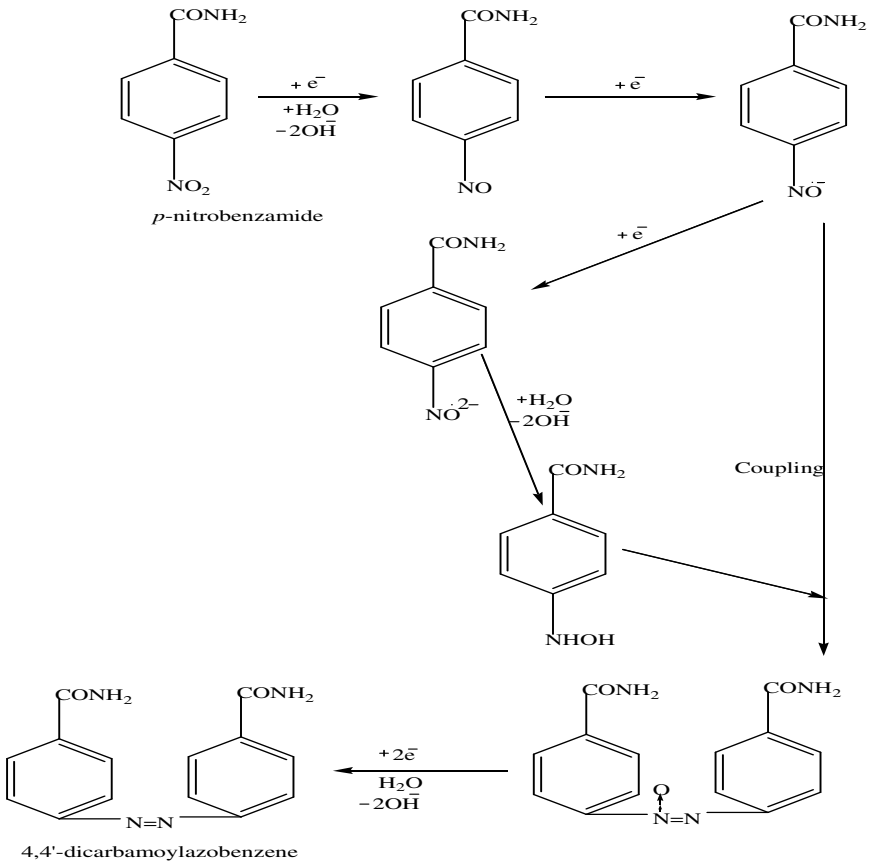
Initial Potential Ei =1200 Mv, Working electrode: Glassy Carbon, Final Potential Es =-1000 mV, Reference electrode: Ag/AgCl, Auxillary electrode: Platinum

S.N.	pH	ScanRate (mV\sec)	Ep	$Ep_{/2}$	Ipc	$I_{pc/v}^{1/2}$	Effect of scan rate	Remark
1	5	50	-324	-269	210	29.7	Peak potential show cathodic shift of potential with increasing scan rates	Irreversible
2	5	100	-341	-277	324	32.4		
3	5	200	-372	-295	567	40.1		
4	5	300	-378	-306	602	34.8		
5	5	400	-394	-315	791	39.5		
6	5	500	-399	-316	805	36.0		
7	5	1000	-434	-349	1777	56.2		
8	7	50	-195	-152	144	20.4	Peak potential shift towards negative side of potential with increasing scan rates	Irreversible
9	7	100	-206	-164	238	23.8		
10	7	200	-217	-173	416	29.4		
11	7	300	-240	-191	567	32.7		
12	7	400	-250	-197	653	32.6		
13	7	500	-258	-213	727	32.5		
14	7	1000	-292	-231	1447	45.7		
15	9	50	-328	-293	176	24.8	With increasing scan rates potential shift towards negative side of potential	Irreversible
16	9	100	-346	-304	259	25.9		
17	9	300	-378	-325	514	29.6		
18	9	400	-390	-336	677	33.8		
19	9	500	-399	-554	904	40.4		

Table-2
Characterization table for synthesis of 4,4'-dicarbamoyl azobenzene in basic medium

Name of substrate	IR Data (cm^{-1})	NMR Data (δ value)	*Compound Confirmed*	Yield (%)
p-Nitro Benzamide	3099-3069 (Ar-H stretching) 3070s (C-H stretching) 3626,3293d (N-Hsym.stretch) 1682-1597 b (N-H bending) 1278-1228 s (C-N stretching) 1733 s (-C=O stretching) 882-829(m) (*p*-substitution) 1550-1450w (-N=N- group)	4.2 (4H) 6.5-8.5 (8H)	4,4'-Dicarbamoyl Azobenzene	91.2

Proposed mechanism in basic medium



Scheme-1

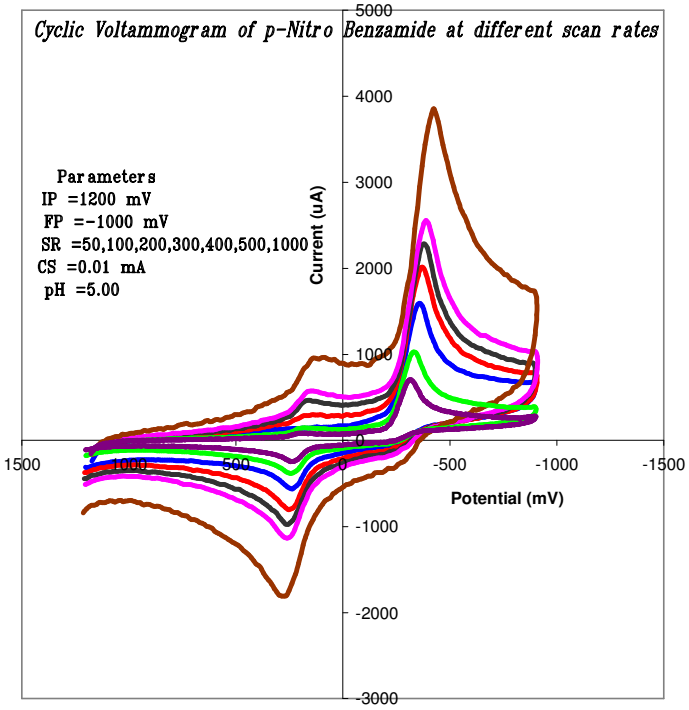


Figure-1
Cyclic Voltammogram of *p*-nitrobenzamide at different scan rates at pH 5

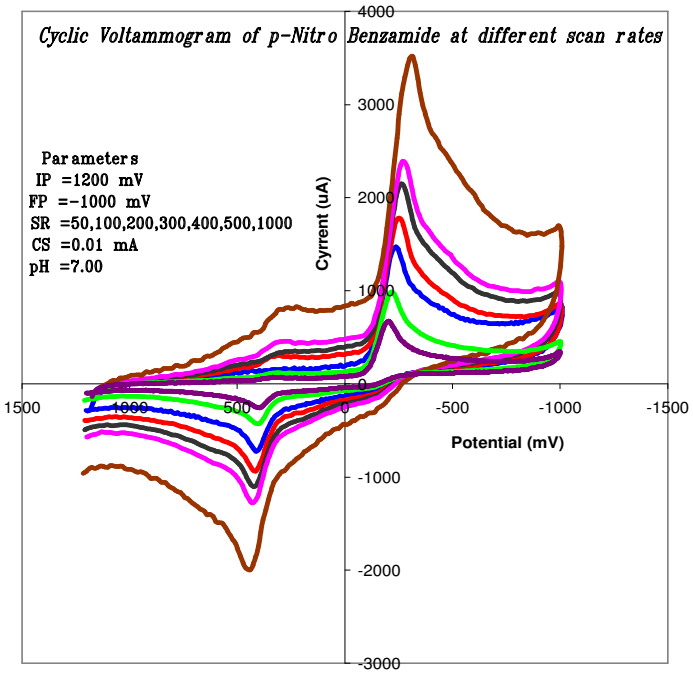


Figure-2
Cyclic Voltammogram of *p*-nitrobenzamide at different scan rates at pH 7

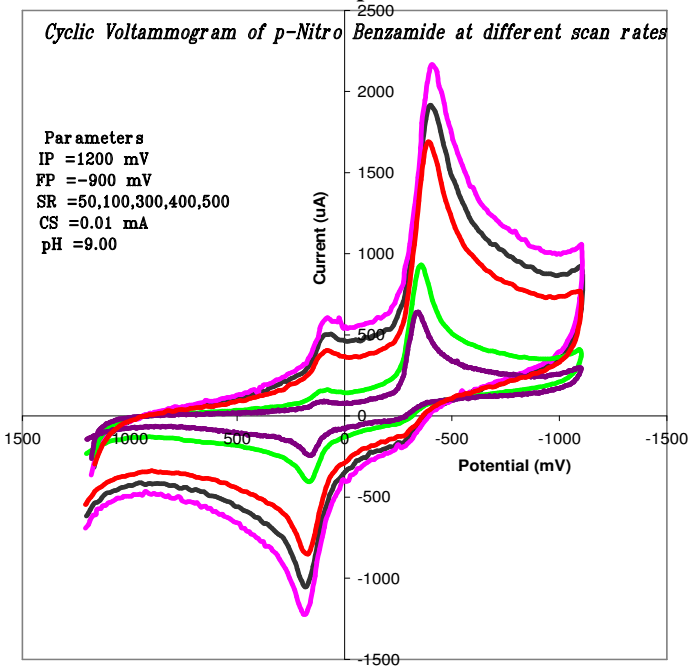


Figure-3
Cyclic Voltammogram of *p*-nitrobenzamide at different scan rates at pH 9

Conclusion

The reduction of p-nitrobenzamide was carried out galvanostatically at pH = 9.0 using Stainless (SS-316) as a working electrode and 4, 4'-dicarbamoylazobenzene was obtained in good yield (91.2%).

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