Electroreduction of p-Nitrophenol at Stainless Steel Macro Electrodes

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Polarisation curves of p-nitrophenol at a stainless steel macro electrode in acidic, neutral and basic media are similar to the polarographic behaviour. The products formed during electrolysis at constant cathode potential are reported here.

Extensive studies have been carried out on electroreduction of nitrocompounds at d.m.e. [1]. Stainless steel electrodes have been used for electroreduction in our laboratories successfully [2,3]. The present investigation deals with electroreduction of p-nitrophenol in acidic, neutral and basic media at these macro electrodes with cathode maintained at a constant potential on the diffusion current plateau of the wave. The products formed are identified and reported.

EXPERIMENTAL

p-Nitrophenol was crystallised from methanol and the purity was tested using TLC and melting point (114°C). Sodium acetate, acetic acid and KCl were of A.R.grade. Distilled methanol and water were used to prepare solutions. Solutions were prepared in 1:1 aqueous methanol.

Two rectangular plates of SS - 316, each of size 4 cm X 6 cm, were used as stationary macro electrodes in a 2 compartment (H type) glass cell. A 100 ml of the same solution was filled into the two compartments. An area of 3 cm X 3 cm of each electrode was dipping into the electrolyte. The luggin capillary of a SCE was placed very close to the cathode surface on the side facing counter electrode. A hot plate and a magnetic stirrer were used during the electrolysis. The temperature of the solution were checked periodically as required.

An Elico model CL-95 potentiostat cum galvanostat coupled with a sweep generator and an x-y recorder was used for recording the polarisation curves and for carrying out controlled potential electrolysis.

F.T.IR spectra of p-nitrophenol and the products obtained were recorded and used for identification.

RESULTS AND DISCUSSION

The polarisation curve of p-nitrophenol at SS macro electrodes in 1:1 aqueous methanol

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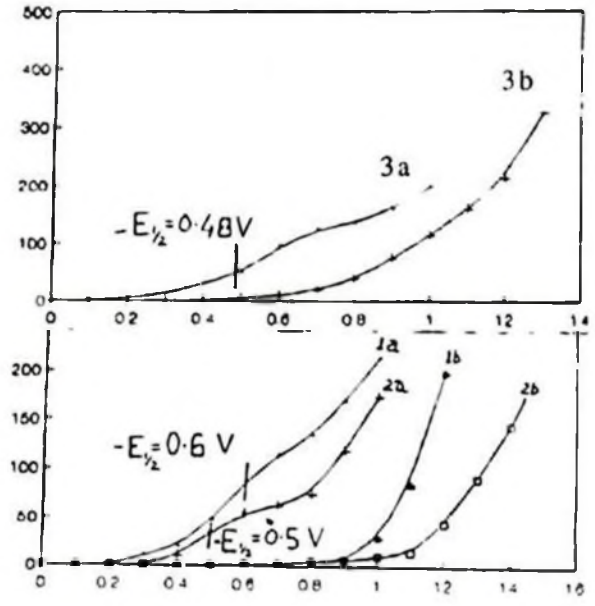


Fig 1 Polarisation Curves of p-Nirophenol at SS Macro Electrodes
a. Conc 2 x 10^{-2} in 1:1 Aqueous methanol
b. Blank
1. Medium of pH 8.5; 2. Medium of pH 6.66; 3. Medium of pH 4.18

under different conditions are presented in Fig 1. The number of steps of reduction and the relative currents correspond to polarographic behaviour. Reduction at pH = 8.5 shows a step ($E_{1/2}$ = -0.6 V) corresponding to a 4 electron change. p-Hydroxy phenylhydroxylamine and a small amount of p,p'-dihydroxy azoxy benzene were identified in the solution after electrolysis at a cathodic potential of -0.8 V. Two bands appeared in FTIR - 1520 cm^{-1} and 1345 cm^{-1} due to N=O symmetric and asymmetric stretch. A peak at 850 cm^{-1} due to C-N stretch of $ArNO_2$ were observed in the starting material; this disappeared in the products. A broad band at 3600 - 3000 cm^{-1} due to -NHOH was seen in p-hydroxy phenylhydroxylamine. In the starting material, -OH peak was observed at 1260 cm^{-1} because of to hydroxyl group in

Table 1

Results of Potentiostatic Electrolysis

Electrolyte: 100 ml of 2 X 10^{-2} M p-Nitrophenol
Medium: 1:1 Aqueous Methanol at different pH
Potential of Electrolysis: -0.8 V vs SCE

Electrolyte /pH	C.D A/dm^2	C.Eff. %	Yield of Products A	B	C	D
1 M Sodium	4.30	78.12	nil	90.4	3.1	nil
acetate	4.57	79.90	nil	90.0	3.2	nil
pH = 8.5	4.92	77.38	nil	90.6	3.0	nil
2 N KCl	3.46	86.56	nil	nil	nil	90.4
pH = 6.66	3.62	91.04	nil	nil	nil	90.8
	4.03	87.32	nil	nil	nil	90.0
0.5 M Sod	1.87	73.76	91.2	nil	nil	nil
acetate +	2.12	80.78	91.4	nil	nil	nil
2 M acetic	1.54	75.21	91.0	nil	nil	nil
acid pH = 4.18						

A = p-amino phenol;
B = p-hydroxy phenylhydroxxyl amine
C = p,p'-dihydroxy azoxybenzene
D = p-hydroxy aniline hydrochloride

para position. In p-hydroxy phenyl-hydroxylamine, free -OH and that in -NHOH merged and appeared at higher wave number at 1410 cm^{-1}. The results are summerised in the Table 1.

The formation of azoxybenzene in sodium acetate medium may be attributed to a change in pH during electrolysis. This change in pH can be observed during intermittant checking of pH with pH paper and corrected with addition of drops of acetic acid.

In 2 M KCl (neutral, pH = 6.66), a single reduction wave ($E_{1/2}$ = -0.5 V) corresponds to a 4 electron step. Reduction at -0.8 V results in isolation of p-hydroxy anilinehydrochloride (IR absorption bands of amine salts were seen in the region of 3600 - 2800 cm^{-1} along with N-H bending peaks of primary amine salts). This actually corresponds to a 6 electron reduction. Such behaviour has been observed earlier. Though polarisation curve shows 4 electron step, bulk electrolysis consumes 6 electrons [4]. This has been attributed to the large time available during constant potential electrolysis for secondary reactions [4].

In sodium acetate + acetic acid (acidic pH of 4.18) a single reduction step ($E_{1/2}$ = -0.48 V) corresponds to a 6 electron change. Preparative electrolysis at constant potential of -0.8 led to the isolation of p-hydroxy aniline in high yield. The product was isolated and identified by melting point (184°). The results are included in the Table.

Thus both acidic and neutral solutions, the product corresponds to a six electron reduction step. Further, the product in acidic medium is the base but in neutral medium it is the salt. At first sight, this is surprising. However, this can be easily be understood, because the neutral solution contains sufficient chloride and the product is a hydrochloride. In acidic medium, no chloride is present. The only acid present is the weak acetic acid which can not form salt with a weak base like aniline

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