ELECTROCHEMICAL REDUCTION OF DIAZOAMINO BENZENE ON GLASSY CARBON ELECTRODE IN ALKALINE SOLUTION

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The electrochemical reduction of diazoamino benzene is studied on glassy carbon electrode in aqueous methanolic alkaline solution using voltammetry techniques. Tafel slope value derived from steady state voltammograms has indicated that the first electron transfer is irreversible. Cyclic voltammetric data have shown that a single wave is formed in methanolic alkaline medium and the overall reduction process is a diffusion controlled irreversible process. Product analysis of the preparative electrolysis experiments has confirmed that the reduction is a two electron transfer process.

Key words: Voltammetry, diazoaminobenzene, glassy carbon electrode

INTRODUCTION

Electrochemical reduction of diazoaminobenzene (triazene) has been studied by polarographic method [1, 2]. As the compound is unstable in acid solutions, reduction studies are reported in neutral and alkaline medium. It has been found that the nature of the polarograms and the number of wave formation depends on pH. However, the reduction mechanism of diazoaminobenzene is not clearly reported.

In the present investigation, the results of the voltammetric studies of the reduction of diazoaminobenzene in alkaline medium on glassy carbon electrode and preparative electrolysis studies for product identification are reported.

EXPERIMENTAL

Cell

A H type glass cell with three electrode assembly was used for these experiments except for the preparative electrolysis. This cell was divided into two compartments by a fine porous glass frit. The glassy carbon disc of dia 5 mm (working electrode) was connected to the saturated calomel electrode (SCE) (reference electrode) by a capillary containing agar agar-potassium chloride bridge. Platinum sheet electrode was used as the counter electrode. All other details of the cell and instrumentation are same as reported earlier.

Chemicals

Double distilled water and single distilled LR grade methanol were used for the preparation of supporting electrolyte. AR grade NaOH was used for the voltammetric measurements and LR grade NaOH was used for the preparative scale experiments. Diazoaminobenzene was prepared according to Standard Procedure [5], recrystallized and used.

Electrochemical measurements

Electrolytic hydrogen purified by passing through alkaline pyrogallol, concentrated sulphuric acid and double distilled water was passed through the electrolyte for 20 minutes for deaeration as well as for maintaining an inert atmosphere within the cell. The glassy carbon electrode tightly inserted into a glass tube, finished and polished mechanically was used for the voltammetric studies. The above electrode was degreased with trichloroethylene, washed with double distilled water and was positioned into the cell containing solvent supporting electrolyte. Both catholyte and anolyte were the same. All the experiments were done at a constant temperature of 295K.

Potentials were applied from a potential scan generator through a potentiostat and the current output was recorded using a fast response x-y recorder. The electrode surface was electrochemically pretreated by cycling the potential of the electrode between the potential $-0.2V$ and $-1.6V$ vs SCE for a few minutes before actual recording of the current.

Preparative electrolysis experiments were done in a divided cell of 500 ml capacity. 400 ml of catholyte was used and it was separated by a cation exchange membrane and catholyte was stirred by a mechanical stirrer during electrolysis. 20 cm^2 area GCE was used as cathode and stainless steel was used as anode. The temperature of the cell was maintained at 295-297K.

RESULTS AND DISCUSSION

Steady state voltammetry

Figure 1 shows the potential vs log current density plot derived from the steady state voltammogram recorded for the reduction of 1.89×10^{-3}M diazoaminobenzene on GCE in 1:1 methanol water mixture containing 0.25M NaOH. Tafel slope analysis gives Tafel slope value of about 100 mV per decade change of current.

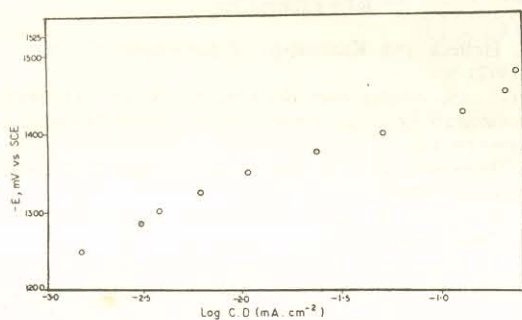This value indicates that the first electron transfer is irreversible.

Fig. 1: E vs log C.D. for the reduction of diazoaminobenzene (1.89 × 10⁻³) on GCE in alkaline medium

Cyclic voltammetry

Figure 2 shows the typical cyclic voltammogram recorded for the reduction of 1.845×10^{-3}M diazoaminobenzene in alkaline aqueous methanol medium at 40 mV.s^{-1}. Well defined single peak shaped voltammogram with no complimentary anodic peak on reverse scan was observed.
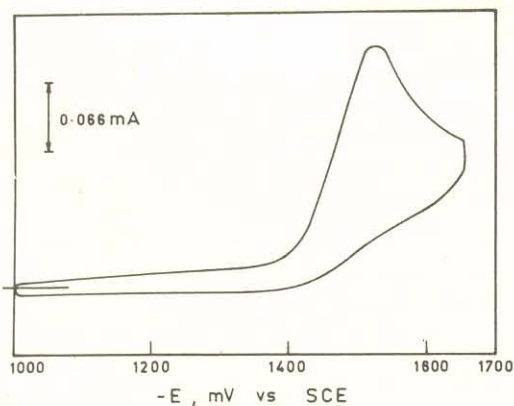

Fig. 2: Typical cyclic voltammogram recorded for the reduction of 1.845 × 10⁻³M diazoaminobenzene on GCE in 1:1 methanol water mixture containing 0.25N NaOH. Temp. 297 K. Sweep rate 40 mV.s⁻¹

Effect of sweep rate

Figure 3 shows the effect of sweep rate on the cyclic voltammograms obtained for the reduction of 1.30×10^{-3} diazoaminobenzene in alkaline methanol medium on GCE. The cathodic peak current was found to increase with increasing sweep rate. The current function values ($i_p/V^{1/2}$) were found to be almost constant as shown in Table I. This observation has indicated that the reduction process is diffusion controlled. Peak potential (E_p) was found to shift in the cathodic direction with sweep rate. E_p varies linearly with log V giving a slope of 50 mV (Fig. 4) which corresponds to the Tafel slope value of 100 mV. The cathodic shift of peak potential with sweep rate, absence of anodic waves on reverse scan and constant $i_p/V^{1/2}$ values confirm that the reduction process is a diffusion controlled irreversible process.
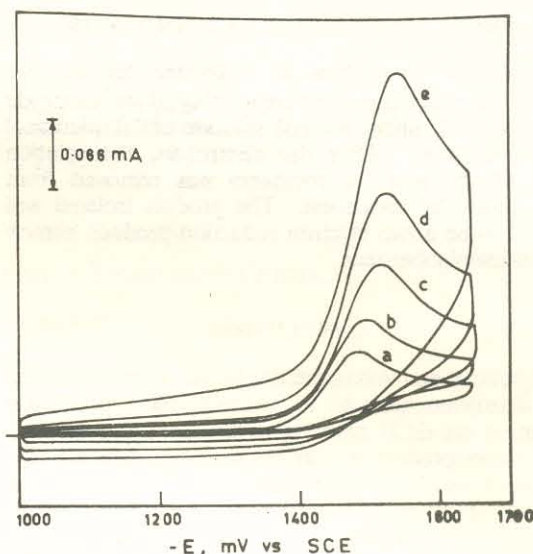

Fig. 3: Effect of sweep rate on the cyclic voltammograms recorded for the reduction of 1.30 × 10⁻³M diazoaminobenzene on GCE in 0.25 N NaOH. Sweep rate (mV.s⁻¹) (a) 10 (b) 20 (c) 40 (d) 80 (e) 160

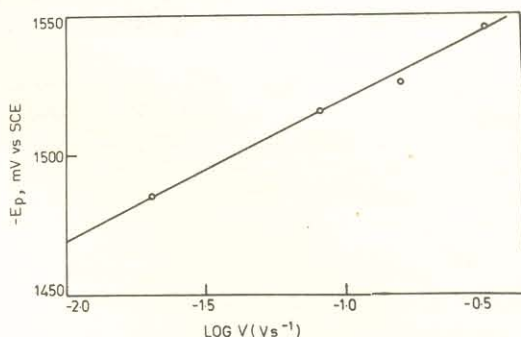*Fig. 4: Dependence of E_p on log V for the reduction of diazoamniobenzene (1.30 × 10⁻³M)*

TABLE I: Cyclic peak parameters obtained for the reduction of 8.40×10^{-4} M diazoaminobenzene in 1:1 methanol water mixture containing 0.25V NaOH on glassy carbon electrode

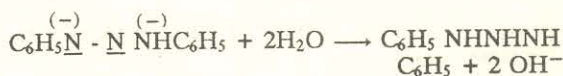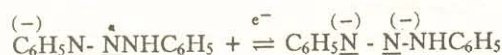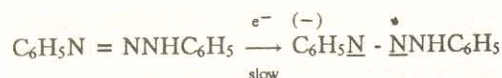| Sweep rate (V.s⁻¹)	i_p (mA)	$i_p/V^{1/2}$ (mA (V.s⁻¹)$^{1/2}$)	$-E_p$ (mV)	$-E_p$ (mV)
0.020	0.0583	0.4221	1485	1450
0.040	0.0929	0.4645	1500	1455
0.080	0.1332	0.4710	1520	1460
0.160	0.1848	0.4620	1540	1480
0.320	0.2614	0.4621	1560	1500

Effect of concentration

Concentration of the reactant was varied and recorded the effect of concentration on the cyclic voltammograms at constant sweep rate. Peak current was found to increase linearly with increase in concentration and peak potential was slightly shifted in the cathodic direction with concentration. These observations show that no kinetic control and adsoprtion complication are involved in the reduction process on GCE under alkaline condition.

PREPARATIVE SCALE ELECTROLYSIS

Experiments were done in a divided cell for the reduction of diazoaminobenzene using 20 cm^2 electrode area of GCE under alkaline solution of 1:1 methanol water mixture. After the electrolysis, the solution was filtered and the methanol was removed from the filtrate by distillation. The product isolated was found to be a two electron reduction product, namely hydrazoaminobenzene.

CONCLUSION

Preparative and voltammetric studies on the reduction of diazoaminobenzene in aqueous alcoholic alkaline solution on GCE have revealed that a two electron reduction product is formed with the first electron transfer as irreversible process. Therefore, the reduction of diazoaminobenzene in alkaline medium may occur as follows:

$$C_6H_5N = NNHC_6H_5 \xrightarrow[\text{slow}]{e^- \;(-)} C_6H_5\underset{..}{\underline{N}} - \underline{N}NHC_6H_5$$

$$\overset{(-)}{C_6H_5\underline{N}} - \overset{..}{\underline{N}}NHC_6H_5 + \rightleftharpoons C_6H_5\overset{(-)}{\underline{N}} - \overset{(-)}{\underline{N}}\text{-}NHC_6H_5$$

$$C_6H_5\overset{(-)}{\underline{N}} - \overset{(-)}{\underline{N}} NHC_6H_5 + 2H_2O \longrightarrow C_6H_5 \, NHNHNH \\ C_6H_5 + 2 \, OH^-$$

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