Electrochemical Deoxygenation of N-Benzylidene Phenylamine N-Oxide

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Electrochemical deoxygenation of N-benzylidene phenylamine N-oxide in acidic, neutral and alkaline aqueous alcohol over the pH range 4.0 to 13.3 has been studied by cyclic voltammetry, chronocoulometry and controlled potential coulometry on glassy carbon electrode. One well-defined, irreversible, diffusion-controlled, cathodic peak is observed in neutral and acidic media. Two peaks are observed under basic conditions. The diffusion coefficient is calculated by chronocoulometry. The overall reduction of nitrone group to azomethine group involves the uptake of two electrons and expulsion of oxygen. The product obtained on exhaustive electrolysis is isolated and characterized by IR and NMR spectra.

Nitrones undergo a variety of reactions because of the double bonded structure [1-3]. Electrochemical reduction of nitrones received lesser attention than the carbonyl rival, in spite of their use in the fields of organic synthesis, pharmaceutical, corrosion and biological fields [4-6]. Polarographic studies of nitrones are reported in aqueous and non-aqueous media [7-9]. Nitrones containing N-alkyl substitutent undergo $4e^-/4H^+$ (first wave) and $1e^-/1H^+$ (second wave) reductions [7-8]. The former leads to dimerisation and the latter results in substituted amine. Chemical deoxygenation leads to the formation of imine and can be effected by Zn and acetic acid, sulphurdioxide or triphenyl phosphine [10]. The present investigation reports electrochemical reduction of N-benzylidene phenylamine N-oxide on glassy carbon electrode.

EXPERIMENTAL

Cyclic voltammetric, chronocoulometric and controlled potential coulometric studies were carried out with an electrochemical analyser - BAS 100A - using glassy carbon electrode of area 0.0774 cm^2 (supplied by Bio Analytical System, USA) as working, silver-silver chloride and platinum as reference and counter electrode respectively.

The compound (N-benzylidene phenylamine N-oxide) was prepared by condensing benzaldehyde and N-phenylhydroxylamine [11]. It was purified by repeated recrystallisation from distilled ethanol. IR and ^1H NMR spectra agree with literature values [12]. The stock solutions of the compound was prepared in double distilled water and distilled alcohol. Solutions of 0.1M H_2SO_4, 0.1M KCl, 0.1M KOH and B.R. buffers (over the pH range 1.0 to 13.3) were prepared in 50% aqueous alcohol and used. All the experiments were conducted after nitrogen purging and blanketing.

Substrate concentrations in the cyclic voltammetric experiments were 1 to 5 mM

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and scan rate was in the range of 20 to 800 mV/sec. Chronocoulometry experiments were carried out with 1 x 10^{-5} mole.cm^{-3} substrate in 50% aqueous ethanolic solution using BAS 100A in a cell similar to that used for cyclic voltammetric studies. Instead of measuring current directly, it was integrated and charge was measured. The charge vs $t^{1/2}$ plot was obtained. Controlled potential coulometry were made in the same medium using the same working electrode and cell to determine the number of electrons (n) transferred. The coulometer in the BAS 100A was employed. Exhaustive electrolysis was made separately using glassy carbon coated graphite electrode of area 15 cm^2 in a cell of 500 ml capacity and the product was isolated from the mixture with chloroform and dried under low pressure conditions.

RESULTS AND DISCUSSION

Cyclic Voltammetric Behaviour

The cyclic voltammograms of title compound was recorded over the pH range 4.0 to 13.3 with different sweep rates and concentrations. It shows only one reduction peak around -1.2V in acidic and neutral media. But two peaks (around -1.1V and -1.5V) are observed in basic medium (Fig. 1). No anodic peak is found in the reverse scan which indicates the irreversibility of the electron transfer. At acidic and neutral conditions, the second peak (at -1.5V) might not be seen because of the early reduction of the medium.

The effect of pH on i_p and E_p have lesser significance. The i_p value is independent of pH indicating no effect of protonation or deprotonation on the electron transfer rate.

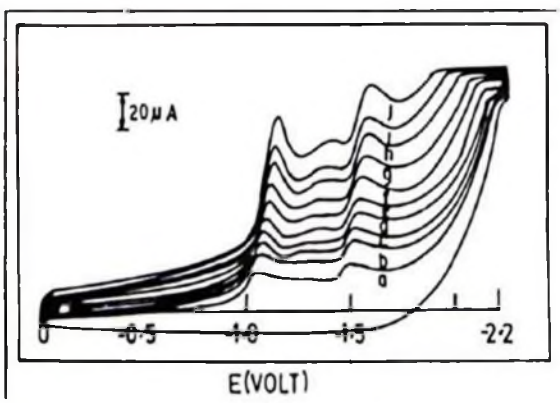


Fig. 1: Cyclic Voltammetric behaviour of N-Benzylidene Phenylamine N-oxide in 0.1M KOH / 50% Aqueous Alcohol at different sweep rates a)20, b)40, c)60, d)80, e)100, f)150, g)200, h)250, i)300 and j)400 mV/sec.

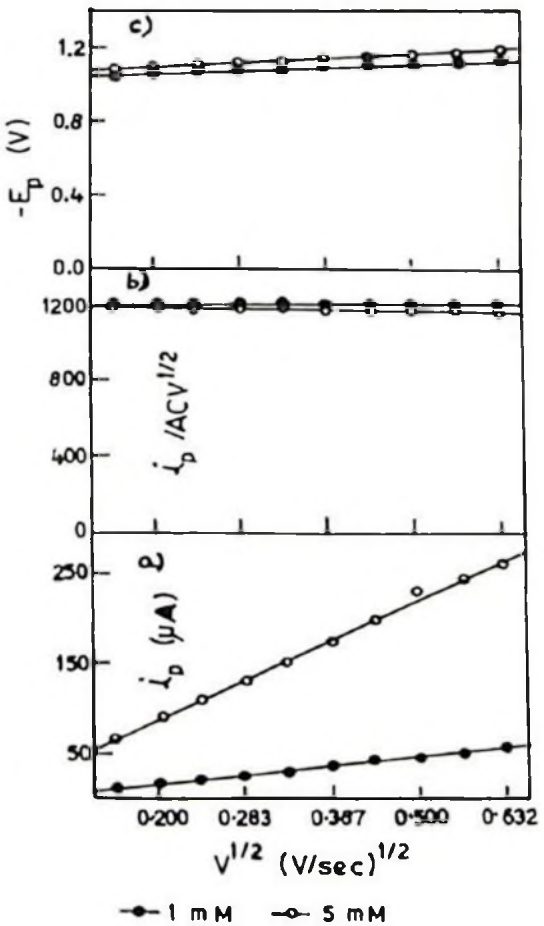


Fig. 2: Plots of N-benzylidene Phenylamine N-oxide in 0.1M KOH / 50% Aqueous Alcohol Medium. a) i_p vs $v^{1/2}$ b) current function vs $v^{1/2}$ c) $-E_p$ vs $v^{1/2}$

A decrease in $-E_p$ with an increase in pH may be due to increased stabilization of the intermediate at neutral conditions. A representative case at pH 13.3 (0.1M KOH) is taken up for further studies.

The variation of sweep rate from 20 to 800 mV/sec at this pH (13.3) shows an increase in peak current and a cathodic shift in potential with sweep rate. The plot of peak current *vs* square root of sweep rate, current function and peak potentials (Fig.2) give straight lines with good correlation. The peak current function shows constancy with sweep rate and concentration changes. These facts show that the electron transfer is diffusion controlled over the pH studied. The transfer coefficient values (α) are calculated from the slope obtained from E_p *vs* log v plots and are found to be fractional. The fractional value of α and the absence of anodic peak, confirmed the reaction to be irreversible.

Chronocoulometric Behaviour

Diffusion coefficient of the compound is determined by using chronocoulometry. The initial potential where no electrolysis occurs and the final potential where complete electrolysis occurs are obtained from cyclic voltammetry. The concentration of the substrate is $1x10^{-5}$ mole.cm^{-3} and the pulse width is 250 msec. A plot of total charge, Q *vs* time (Fig.3) led to a line in which the slope of the straight line portion is $2nFAD^{1/2}$. From the slope of the forward step (Fig.3a) the diffusion coefficient (D) is calculated by substituting the values of other parameters. The value of D is found to be $7.9931x10^{-6}$ cm^2/sec. By employing αn_a and diffusion coefficent values in the Randles - Sevick equation for irreversible system, the number of electron transferred was found to be 2.

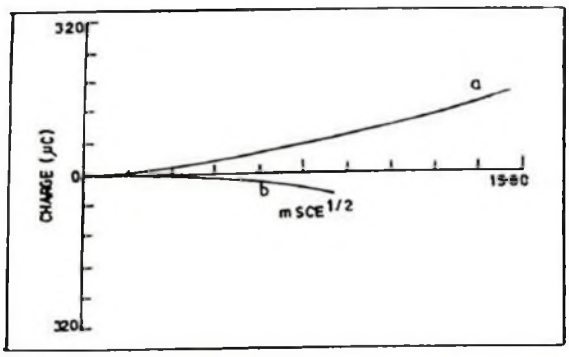


Fig. 3: Chronocoulometry of N-Benzylidene Phenylamine N-oxide in 0.1M KOH / 50% Aqueous Alcohol Medium.
concentration = 1 x 10^{-5} mole/cm^3
a) Forward step b) Reverse step.

Controlled Potential Coulometry

Controlled potential coulometry at pH 13.3 was employed to measure the charge required (n) for electrolysis. Representative charge *vs* time plot is given in Fig.4 for the electrolysis of the substrate at pH range studied. The charge, Q,

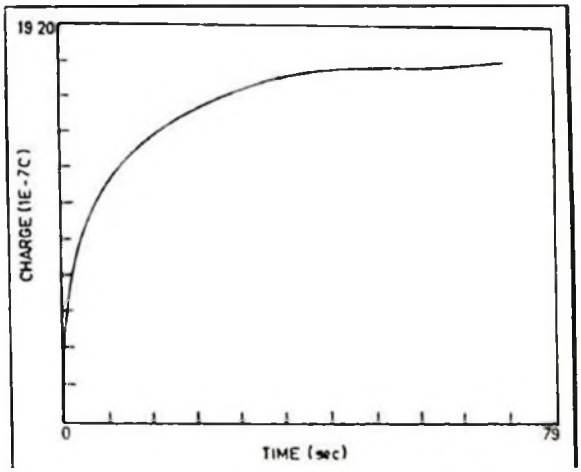


Fig. 4: Controlled potential coulometry for N-Benzylidene Phenylamine N-oxide in 0.1M KOH/50% Aqueous Alcohol Medium.
variation of charge with time

accumulated in the cell is used to calculate the n value, using the relation Q=nFN. The coulometric results are presented in Table 1. The n is equal to two, indicating that only two electron transfer is involved in the electrochemical process.

Table 1

Controled potential coulometric study
N-Benzylidene phenylamine N-oxide in 50% Aqueous Alcohol Medium.

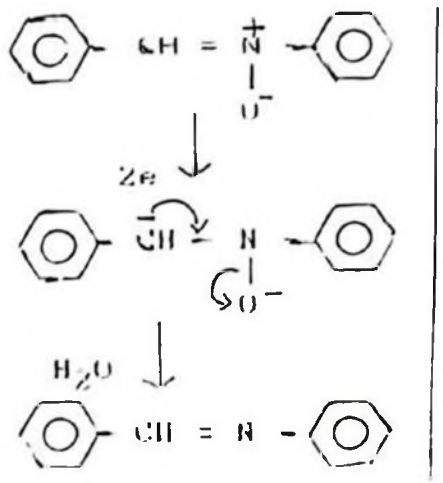
pH of medium	Amount x10^{9} Mol	Potenl used	Q Coulomb x 10^{7}	n Tran.
4.0	3.0	-1.000	5732	1.98
7.0	2.0	-1.100	3783	1.96
9.2	2.0	-1.050	3821	1.98
13.3	1.0	-1.050	1920	1.99

Bulk Electrolysis

Bulk electrolysis was carried out using 0.5 g of the compound in the medium of pH 13.3 for 5 hours on glassy carbon coated graphite electrode of 15 cm^2 at constant potential of -1.0V. After completion of electrolysis, the products were extracted with chloroform and chromatographed on silica gel column. The reduction product was established as benzylidene aniline by comparison of IR & NMR spectra with those of authentic sample (82.5% yield, melting point 50°C).

Mechanism of Reduction

On the basis of the above results the following deoxygenation mechanism is proposed for the reduction peak I



Benzylidene imine

This deoxygenation leading to the formation of imine is the first step in the reduction (peak I). Peak II may correspond to the subsequent reduction of the intermediate imine to amine.

CONCLUSION

Voltammetric studies of N-benzylidene phenylamine N-oxide in aqueous medium at various pH conditions on glassy carbon electrode were carried out. Only one peak at acid and neutral conditions and two peaks in alkaline condition were observed. No anodic peak is observed in the reverse scan. The transfer coefficient αn_a was calculated from E_p *vs* log v plots. The value of D was found out using chronocoulometry. The electroreduction process is irreversible and diffusion controlled with two electron transfer. The 'n' value was confirmed by controlled potential coulometry. The product was isolated after exhaustive electrolysis and identified by spectral studies as benzylidene aniline.

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