

CYCLIC VOLTAMMETRIC OXIDATION OF p-NITRO BENZALDEHYDE

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The oxidation of 4-nitro benzaldehyde is studied in the medium of 60% acetic acid using platinum electrode by the cyclic voltammetry technique. The process of oxidation is found to be irreversible, involving two electron transfer. The rate constant for the charge transfer is obtained. The product of oxidation is identified by UV spectra.

Key words: 4-nitro benzaldehyde, oxidation, cyclic voltammetry

INTRODUCTION

Aldehydes are known to get oxidised easily by chemical reagents like Ce(IV), chromic acid and acid permanganate [1-3]. The product of oxidation is the corresponding carboxylic acid. Substituted benzaldehydes with electron withdrawing groups get oxidised more slowly than benzaldehyde [4].

Regarding the electrochemical oxidation of nitro benzaldehydes, very few attempts have been made so far [5,6]. In the present work, electrochemical oxidation of 4-nitro benzaldehyde has been studied using platinum electrode by the cyclic voltammetry technique and the rate constant is calculated.

EXPERIMENTAL

Cyclic voltammograms were recorded using potentiostat and a scan generator coupled to a x-y recorder. The working electrode was a platinum electrode with a geometrical area of 0.0615 cm². Saturated calomel electrode and a platinum foil were used as the reference and counter electrodes respectively. The electrode was cleaned with dichromate-sulphuric acid solution and rinsed with distilled water. Then the electrode was introduced into the cell and electrochemical pretreatment was given to remove the surface oxides. The potential was then changed slightly anodic to reoxidize any adsorbed hydrogen [7]. Before carrying out the experiment, the cell was deaerated by passing N₂ gas through the experimental solution.

RESULTS AND DISCUSSION

Cyclic voltammograms of 4-nitro benzaldehyde were recorded in 60% acetic acid using scan rates between 10 and 320 mV.s⁻¹ for different concentrations (2mM to 10mM) of 4-nitro benzaldehyde. A typical cyclic voltammogram for 4-nitro benzaldehyde (10mM) is shown in Fig. 1. The peak current is measured by subtracting the corresponding background current. The ratio between the peak current and square root of sweep rate ($i_p/\gamma^{1/2}$) is found to remain constant (Table I). The peak potential E_p is also found to shift anodically with increasing sweep rate. In addition, no new cathodic wave corresponding to the anodic wave of p-nitro benzaldehyde oxidation is noticed in the reverse sweep. The current increases with the concentration of p-nitro benzaldehyde. It is known from the literature [5] that this reaction involves two electron transfer.

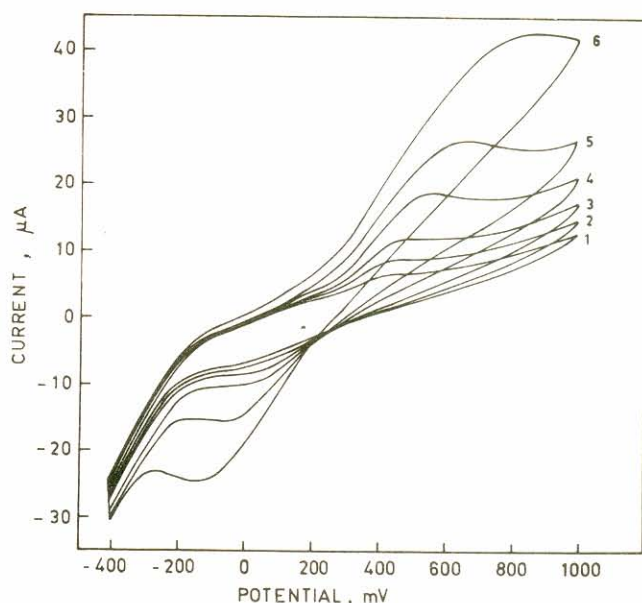


Fig. 1: Cyclic voltammogram for the electro-oxidation of 10mM 4-nitrobenzaldehyde. Scan rate in mV.s⁻¹ (1) 10 (2) 20 (3) 40 (4) 80 (5) 160

Calculation of standard rate constant k_s

K_s is evaluated using the method of Reimuth [8]. It is shown that at the foot of the response, the current is independent of scan rate and can be related to the peak potential and the initial potential. The initial potential is chosen at the foot of the response where no current flows.

$$i_p = nFAC^* \cdot K_s \exp \left[\frac{-\alpha nF}{RT} (E_p - E_i) \right]$$

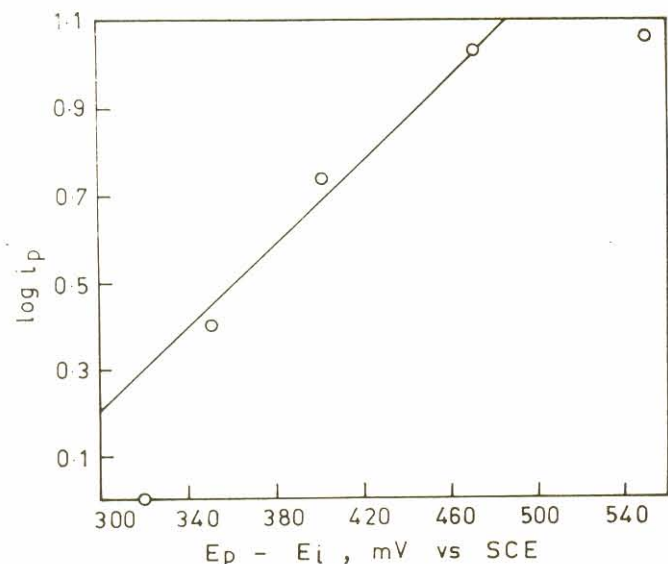
From the plot of $\log i_p$ vs $(E_p - E_i)$ (Fig. 2) for different scan rates for 10mM solution (pH = 1.16), α from the slope and K_s from the intercept are calculated and the values are 0.12 and 1.335×10^{-5} cms⁻¹ respectively.

Identification of product

Controlled potential electrolysis of 4-nitro benzaldehyde (5mM) is carried out using a 9 cm² platinum foil as the working electrode at a potential of + 800 mV. After completion of electrolysis, an aliquot of the electrolysed solution is taken and the UV spectrum is recorded. Absorption maxima is obtained at 266nm which

TABLE-I: Diagnostic criteria for irreversible reaction

p-nitro benzaldehyde (mM)	Sweep rate ($\times 10^{-3} \text{Vs}^{-1}$) mVs^{-1}	Peak current i_p (μA)	γ^2 ($\text{V}^{1/2}\text{S}^{-1/2}$)	$i_p/\gamma^{1/2}$ ($\mu\text{AV}^{-1/2}\text{S}^{1/2}$)	$i_p/C\gamma^{1/2}$ ($\mu\text{AS}^{1/2}\text{V}^{-1/2}$ mM)	Peak potential E_p (V)
2	10	0.4	0.1	4.0	2.0	0.38
	20	0.6	0.1414	4.2433	2.12	0.38
	40	1.0	0.2	5.0	2.50	0.42
	80	1.6	0.2828	5.657	2.83	0.44
	160	2.0	0.4	5.0	2.5	0.5
4	20	0.8	0.1414	5.658	1.414	0.38
6	20	1.0	0.1414	7.072	1.18	0.4
8	20	3.6	0.1414	25.459	3.18	0.46
10	10	1.5	0.10	15.0	1.5	0.4
10	20	2.0	0.1414	14.14	1.414	0.4

Fig. 2: $\log i_p$ vs $(E_p - E_i)$ plot for the electro-oxidation of 10mM 4-nitro benzaldehyde

coincides with the literature value for p-nitro benzoic acid [9] from which it is concluded that the product of oxidation is p-nitrobenzoic acid.

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