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Cathodic Synthesis of Cinnamic Aldehyde

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Cinnamic aldehyde has been synthesized by cathodic reduction of cinnamic acid at zinc and amalgamated copper electrodes using galvanostatic method. Polarization curves obtained in the presence and absence of depolarizer indicated the proper range of current densities to be investigated. Isolated product was characterized by TLC and NMR spectral analysis. Effect of various parameters like current density, temperature and nature of cathode material on yield percentage have been investigated.

INTRODUCTION

Electrochemical reduction of carbonyl group in carboxylic acids is more difficult than their corresponding aldehydes and ketones. Electroreduction of carboxylic acids proceeds to aldehydes which may further reduce to the corresponding alcohol[1, 2]. Reduction of carboxylic group occurs at high hydrogen over-voltage cathodes[3]. The cathodic reduction of a carboxyl group can give either the corresponding aldehyde in a two-electron process or the alcohol in an overall four electron process. Generally aliphatic acids are more difficult to reduce or do not undergo reduction although formic acid may be reduced to the corresponding aldehyde or alcohol at high overvoltage cathodes[4]. The reduction of aromatic carboxylic acids is generally more facile than aliphatic acids. Electrochemical reduction of aromatic acids leads to the corresponding benzyl alcohol, since the intermediate aldehyde is more easily reduced than the parent acid[5]. Wagenknecht[6] has recently described the reduction of substituted aromatic carboxylic acid to the corresponding aldehyde. The success of the reduction depended on the use of a buffer medium containing benzene. The benzene extracts the aldehyde from the vicinity of the electrode and prevents its further reduction. There is practically no reference available in literature on the study of the reduction of cinnamic acid at metal electrodes being investigated. Polarization characteristics of the reduction of cinnamic acid and its ester have been studied at rotating disk-electrodes of gold, gold amalgam and platinum[7]. Cook and Sammells[8] studied the reduction of cinnamic acid at mercury cathode in 2 M H_2SO_4 solution by constant potential electrolysis. Cinnamic aldehyde, which is one of the expected reduction products of cinnamic acid, is a very important spice perfume and it is also used as flavour[9]. Cathodic synthesis of cinnamic aldehyde has never been reported although it is an industrially important compound and hence the reduction of cinnamic acid has been studied at zinc and amalgamated copper electrodes and the results of the same are presented.

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EXPERIMENTAL

Cinnamic acid used was of laboratory grade and other chemicals like sulphuric acid, ammonia solution, boric acid etc. were of Excelar grade. All the solutions were prepared in conductivity water.

Cell assembly

Experimental procedure and cell assembly used were same as reported earlier[10].

Electrolysis

Cathodic solution (catholyte) was prepared by neutralizing cinnamic acid by ammonia solution and the solution diluted to 75 mL by double distilled water. To this 5 g boric acid was added and the solution was diluted to 100 mL. pH of the solution was now adjusted to 6.5 by adding ammonia or dil. HCl. 50 mL benzene was added and kept in ice bath for cooling to 20°C. The whole cell assembly was kept on magnetic stirrer to agitate the catholyte. Current regulated power supply was used to apply current across the working electrode (cathode) and counter lead (PbO_2) electrode (anode). The desired current according to current density was passed for a theoretical time depending upon the cinnamic acid taken.

Isolation and Identification

After electrolysis the catholyte was transferred into a separating funnel to settle the liquid. After some time two layer were separated. Benzene layer was washed with distilled water two or three times and taken into a watch glass. Benzene was evaporated and a cinnamon smelling liquid was obtained. This isolated liquid was identified to be cinnamic aldehyde by TLC, usual qualitative tests and spectral analysis.

1. Isolated product was miscible with benzene, alcohol, chloroform and ether which resembles the characteristics of cinnamic aldehyde.
2. The product boiled at 250°C and the b.p. of cinnamic aldehyde is reported to be 248°C, which is in close agreement.
3. Product was treated with ammonical silver nitrate (Tollen's reagent) solution (usual test for aldehydic group) and put in hot water for some time; it gave a black precipitate and silver mirror on the sides of test tube which confirms the presence of aldehydic group in the product.
4. Slowly gets oxidised in air into cinnamic acid.
5. When strongly heated with acidic $KMnO_4$ yields benzoic acid.
6. Final product was confirmed by NMR spectroscopy.

^1H NMR spectrum in $CDCl_3$ of cinnamaldehyde displayed a doublet at δ 9.71 (J = 5.4 Hz) for aldehydic proton. It showed a sharp doublet at δ 7.55 for —CH═ (β) and a double doublet in the region δ 6.70 for ═CH— (α) proton (J = 5.4 Hz). In addition to this, a very broad resonance signal due to phenyl protons is observed.

RESULTS AND DISCUSSION

Polarization curves have been drawn between cathodic potential *vs.* log current density and are given in Fig. 1. Comparison of these polarization curves in presence and in absence of depolarizer shows that suitable current density ranges for reduction are 0.002–0.030 and 0.003–0.100 amp/cm^2 for zinc and amalgamated copper electrodes respectively.

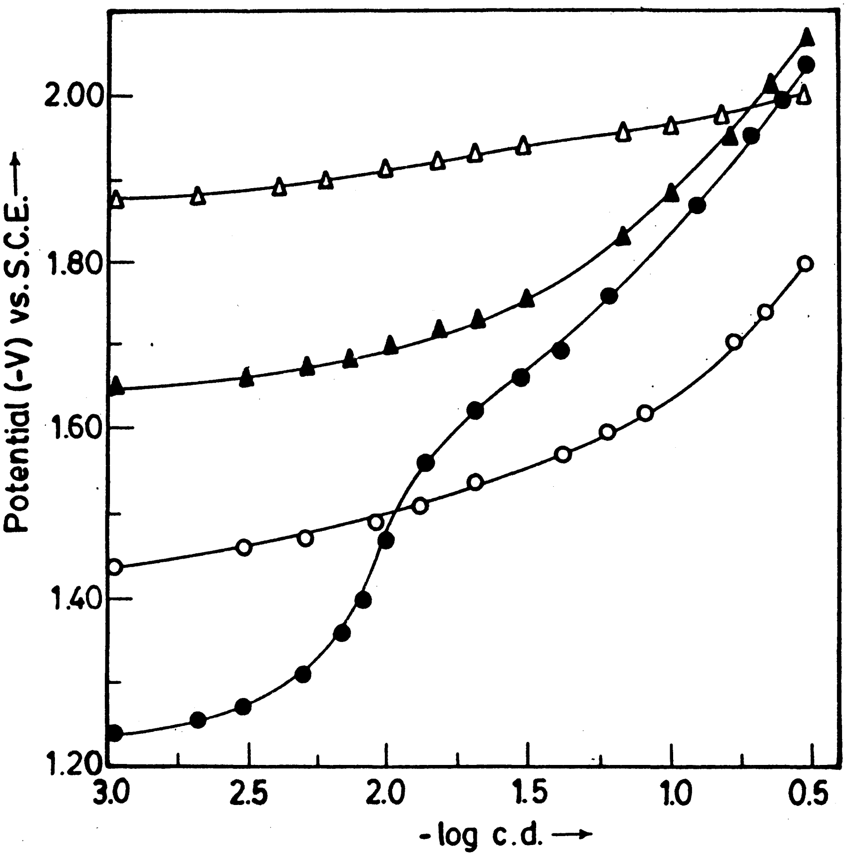


Fig. 1. Cathodic polarization curves of cinnamic acid in buffer solution. Without depolarizer—O—Zinc, Δ—Amalgamated copper. With depolarizer: ●—Zinc, ▲—amalgamated copper. Temperature –20(±1)°C.

Effect of current density

To study the effect of current density on yield percentage different current densities have been chosen from these current density ranges of each electrode to investigate the proper current density at which yield is maximum. The experimental data are given in Table-1.

From Table-1, it is inferred that the best current densities are 0.008 and 0.020, for zinc and amalgamated copper cathodes respecively.

TABLE-1
EFFECT OF CURRENT DENSITY

Catholyte 100 mL buffer solution containing 5 g cinnamic acid; temperature = 20 ± 1°C

S. No.	Cathode	Curent density Amp/cm^2	Yield of the product (%)
1.	Zinc	0.002	75
		0.008	85
		0.030	80
2.	Amalgamated copper	0.003	62
		0.020	72
		0.100	67

Effect of temperature

After deciding the proper current densities, effect of temperature on yield percentage has been studied and the results at different temperatures are given in Table-2.

TABLE-2
EFFECT OF TEMPERATURE

S. No.	Temperature (±1°C)	Yield of the product at different cathodes (%)	
		Zind (c.d. = 0.008) Amp/cm^2	Amalgamated copper (c.d. = 0.020) Amp/cm^2
1.	10	76	62
2.	20	85	72
3.	30	84	70
4.	40	74	60

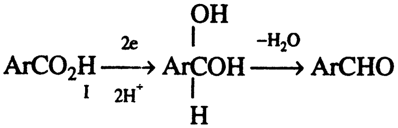
From the above experimental results at different temperatures, it is clear that the best temperature for reduction is 20°C which yields maximum for all the electrodes.

The electrochemical reduction of a carboxyl group can give the corresponding aldehyde in a two-electron process (Eq. (1)).

$$\mathrm{ArCOOH} \xrightarrow[2H^+]{2e^-} \mathrm{ArCH(OH)_2} \xrightarrow{-H_2O} \mathrm{ArCHO} \qquad (1)$$

Protection of the aldehyde

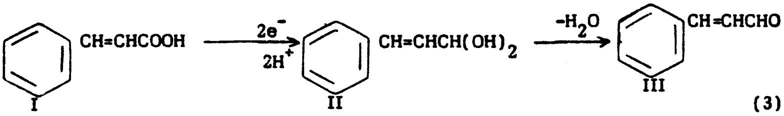
The efficiency of aldehyde removal by benzene extraction is remarkable. In the case of salicylaldehyde, only about 4% of the alcohol, saligenin, was obtained in a reduction carried out for more than 50% conversion of the acid. Further, the yield of salicylaldehyde based on unrecovered starting material was 80%. The initial reduction product of an aromatic acid is probably the hydrated aldehyde I. Since aromatic aldehydes are known to be reducible, it would seem that any aldehyde formed



$$ArCO_2H \xrightarrow[\text{I}\quad 2H^+]{2e} Ar\overset{\overset{\text{OH}}{|}}{\underset{\underset{\text{H}}{|}}{C}}OH \xrightarrow{-H_2O} ArCHO \qquad (2)$$

at the electrode surface would be immediately reduced to the benzyl alcohol derivative. Thus, apparently the rate of dehydration of I is slow enough to allow the species I to leave the electrode surface. Dehydration in the bulk solution to the aldehyde is followed by rapid extraction into the organic solvent. The fact that a buffer is necessary for the reaction is consistent with the above scheme, since aldehyde hydration reactions are base catalyzed .[11]

The reduction of cinnamic acid to cinnamic aldehyde is similar to that of benzoic acid and can be explained in the following manner (Eq. (3)).



(3)

The formation of cinnamic aldehyde (III) involves two electrons. This is confirmed from the working electrode potential *vs.* time curves which show that the reaction is completed in the theoretical time required for two electrons on each of the electrodes investigated.[12]

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