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Electroreduction of *p*-Chlorobenzaldehyde by Galvanostatic Method

MS MADHU†
Departmenmt of Chemistry
University of Rajasthan, Jaipur 302 004, India

Electroreduction of *p*-chlorobenzaldehyde has been studied at metal electrode like nickel under acidic conditions using galvanostatic method. Polarization curves drawn in presence and absence of depolarizer indicated the proper range of current densities to be investigated. Isolated product was characterized to be *p*-chlorobenzyl alcohol by TLC, usual functional group tests, IR and NMR spectral analysis. Effect of various parameters such as current density, temperature, medium concentration, depolarizer ratio and nature of cathode material on yield percentage have been investigated.

INTRODUCTION

Electroreduction of aromatic aldehydes may be controlled to give alcohols, benzoins or hydrocarbons. The course of reduction of carbonyl group strongly depends on reaction conditions, especially pH of the medium and nature of the cathode material. Under alkaline conditions, generally alcohols are the main products whereas under acidic conditions, the dimeric products are often formed;[1–4] however, several exceptions are reported.[5, 6] The pH of the medium may have an efect on starting material or on reduction product. For example, aliphatic aldehydes and ketones may undergo self-condensation and aromatic aldehydes may form benzoin under basic conditions.[7] On the other hand during reduction under acidic media at temperatures greater than 40°C the pinacol product may rearrange itself to the corresponding pinacolone. Similar rearrangements of electrochemical reduction have also been reported.[8–10]

The reduction of *p*-chlorobenzaldehyde has not been systematically studied as there is no reference available till 1974.[11] Polarographic reduction of *p*-chlorobenzaldehyde and substituted benzaldehydes has been studied in methanol solution.[12] Kinetics of electrochemical reduction of *p*-chlorobenzaldehyde was studied in aqueous acidic solutions at mercury pool electrode using controlled potential electrolysis and potentiostatic steady-state techniques.[13] Reishakhrit and coworkers[14, 15] studied the polarographic reduction of benzaldehyde and its derivatives including *p*-chlorobenzaldehyde in aqueous ethanol solutions. Survey of

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†Present address: Department of Chemistry, Government (P.G.) College Sujangarh (Rajasthan), India.

literature revealed that reduction of *p*-chlorobenzaldehyde has not been studied at metal electrodes except of some polarographic studies. *p*-Chlorobenzyl alcohol, one of the expected reduction products is a costly and industrially important compound. Reduction of *p*-chlorobenzaldehyde has, therefore, been studied at nickel metal electrode. Effects of various parameters such as current density, temperature, concentration of medium, depolarizer ratio and nature of cathode material on the yield percentage of *p*-chlorobenzyl alcohol have been studied in order to obtain optmum conditions for its synthesis.

EXPERIMENTAL

Reagents and cell assembly

p-Chlorobenzaldehyde was laboratory grade and other chemicals like sulphuric acid, potassium chloride, mercuric nitrate, sodium hydroxide were of Excelar grade. All solutions were prepared in conductivity water. Galvanostatic method was used. Experimental procedure and cell assembly used were same as reported earlier.[16]

Electrolysis

The catholyte was prepared by dissolving 2.5 g of *p*-chlorobenzaldehyde in 100 mL aqueous sulphuric acid solution. Direct current was passed from the current regulated power supply. The cathodic potential was measured against SCE by digital multimeter. In all cases a theoretical quantity of electricity was passed depending upon the amount of depolarizer taken.

Isolation and identification

After electrolysis the catholyte was filtered, unreduced compound remained on filter paper and product went into the filtrate The filtrate was neutralized with 5% sodium hydroxide solution to pH 6.5–7.0 and cooled to 5–10°C. The solution was treated 2–3 times with ether. Ether extract was washed with ice-cold water to remove the acid or salt (if any), and was evaporated. The product obtained was confirmed by TLC, usual physico-chemical methods and spectral analysis to be *p*-chlorobenzylalcohol.

(1) The product is soluble in alcohol, ether, benzene and sparingly soluble in hot water.

(2) A single clear spot on silica gel-G plate was obtained in iodine chamber, confirming that the product was a single compound and not a mixture.

(3) The melting point of the compound was found to be 70°C in close agreement with the reported boiling point of 70–72°C for *p*-chlorobenzyl alcohol.[17]

(4) The product was treated with a few drops of ceric ammonium nitrate. It gave a red colour which confirms the presence of alcoholic group in the product.

(5) Usual tests, for aldehydic group in the product gave negative results.

(6) The IR spectrum of *p*-chlorobenzyl alcohol in KBr displayed a broad absorption band at 3350 cm^{-1}. A peak at 1010 cm^{-1} corresponded to C—O stretching vibration. A band at 740 cm^{-1} indicated the *para* substituted nature of benzene ring.

(7) The ^1H NMR spectrum (90 MHz) in $CDCl_3$ of *p*-chlorobenzyl alcohol showed a broad singlet at δ 7.50 for four aromatic protons. Benzylic protons appeared at δ 4.83 as singlet integrating for two protons. Signal for OH proton appeared at δ 2.23 ppm as broad peak.

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 range for reduction is 0.0040 to 0.0600 amp/cm^2 for nickel cathode.

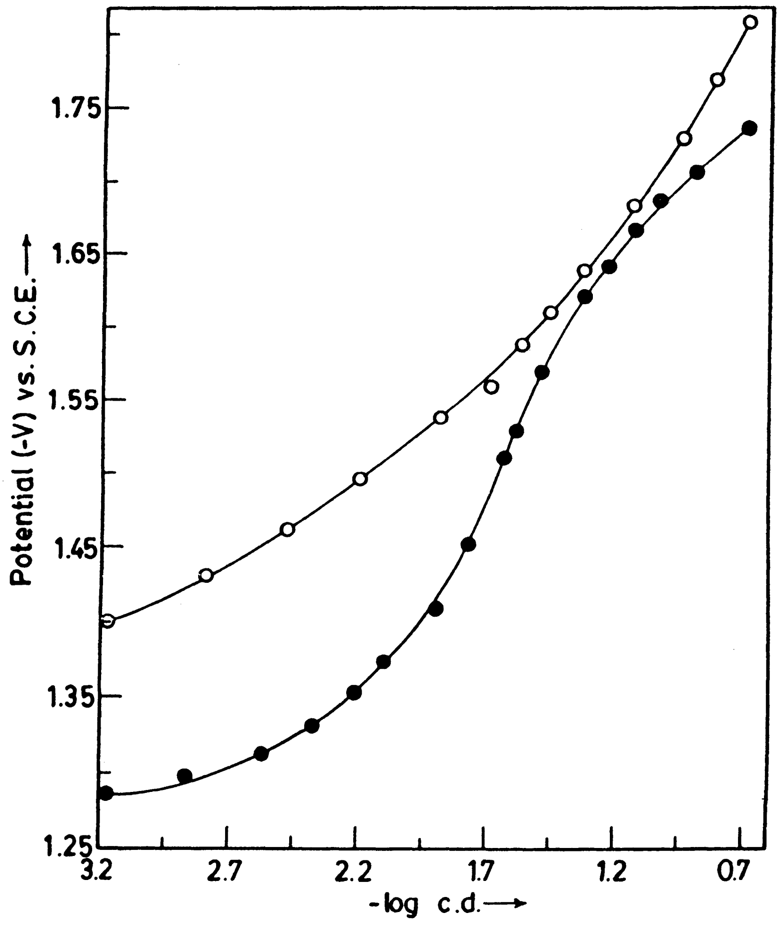

Fig. 1. Cathodic polarization curves of *p*-chlorobenzaldehyde in 10% H_2SO_4. Without depolarizer—○-Nickel, with depolarizer—●-Nickel, Temperature—40(±1)°C.

From these current density ranges, various current densities were chosen and the experiments were conducted at each current density for all the electrodes. The quantitative results of the product yield are given in Table-1. From Table-1, it can be easily seen that favourable current density is 0.0166 amp/cm^2 for nickel cathode. Effect of parameters such as temperature, depolarizer ratio, medium concentration on percentage yield was now investigated and the results are given in Table-2.

TABLE-1
EFFECT OF CURRENT DENSITY

Catholyte 100 mL 10% aqueous H_2SO_4 containing 2.5 g of *p*-chlorobenzaldehyde. Temperature = 40 ± 1°C

S.No.	Cathode	Current density amp/cm^2	Yield of the product (%)
1.	Nickel	0.0040	70
		0.0166	75
		0.0600	65

TABLE 2
EFFECT OF EXPERIMENTAL PARAMETERS

Temperature D.R. = 1 : 40 H_2SO_4 = 10%		Depolarizer Ratio Temperature = (40 ± 1) °C H_2SO_4 = 10%		Effect of medium Temperature = (40 ± 1) °C D.R. = 1 : 40	
Temp. (±1)°C	Yield (%)	D.R.	Yield (%)	H_2SO_4	Yield (%)
		Nickel cathode, C.D. = 0.0166 amp/cm^2			
20	55	1 : 20	70	5	65
30	60	1 :30	75	10	75
40	75	1 : 40	75	15	75
50	70	1 : 50	72	20	70

The formation of *p*-chlorobenzylalcohol involves two electrons. This is confirmed from the working electrode potential *vs.* time curve which shows that the reaction is completed in the theoretical time required for two electrons on each of electrode investigated.[18]

The results tabulated above clearly indicate that about 75% yield of *p*-chlorobenzyl alcohol may be obtained under optimum conditions using nickel electrode. About 20% *p*-chlorobenzaldehyde was recovered and hence a single product *p*-chlorobenzyl alcohol is formed. *p*-Chlorobenzyl alcohol is an industrially important compound and it is about four times costlier than the starting material and hence this method may be used for its production on a large scale.

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