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ELECTROCHEMICAL REDUCTION OF CARBONYL COMPOUNDS

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Cyclic voltammograms were taken for aromatic carbonyl compounds like benzaldehyde and acetophenone in 0.2M sulphuric acid medium and Mcilvaine buffer at lead electrodes. Galvanostatic reduction of both aliphatic and aromatic carbonyl compounds was carried out at tin and zinc electrodes in alkaline and acid medium, to obtain corresponding pinacols and alcohols.

Key words: Electrochemical reduction, carbonyl compounds, cyclic voltammetry

INTRODUCTION

When ketones are reduced in neutral or alkaline medium pinacols are the main products [1]. Acetone reduced with magnesium amalgam forms pinacol. Saturated aldehydes and ketones are reduced electrochemically to various products depending on the experimental condition. Highest yield of pinacols are obtained in alkaline medium.

The mechanism of reduction of aldehydes and ketones in aqueous medium has been studied [2-7]. The electrochemical and polarographic reduction of acetone, acetophenone and benzaldehyde have also been reported [8-14].

In this paper, the results of galvanostatic experiments of acetone, acetophenone and benzaldehyde at tin and zinc electrodes in aqueous alcoholic acidic and alkaline medium are reported. Voltammetric studies have also been carried out. The different products are isolated at different conditions and are reported.

EXPERIMENTAL

Cyclic voltammetry

Cyclic voltammograms were taken for acetophenone and benzaldehyde in 0.2M sulphuric acid medium and Mcilvaine buffer at a lead cathode.

Galvanostatic experiments

Galvanostatic experiments were carried out in aqueous alocholic acidic and basic media [15-16] for electrolytic reduction of acetone, acetophenone and benzaldehyde.

Alkaline medium

The cell consisted of a 500 ml beaker covered with a PVC cover having opening for the porous pot, plate type cathode, thermometer, stirrer and a provision for adding the compound. A perforated stainless steel sheet inside the porous pot acted as anode. The electrolysis was carried out with zinc or tin as cathode. In the case of acetone, the temperature was maintained between 288 and 293K while for acetophenone and benzaldehyde between 323 and 333K. In the case of acetophenone and benzaldehyde, the electrolysis was carried out with 200 ml of 50 percent aqueous alcoholic solution containing 10% sodium hydroxide while for acetone, alcohol was not used.

Acid medium

Here a plate type zinc or tin was used as cathode, while the anode was lead strip. In the case of acetophenone and benzaldehyde, the electrolysis was carried out with 200 ml of 50% aqueous alcoholic solution containing 10% sulphuric acid while for acetone no alcohol was used.

Isolation of product

Reduction of acetone

After the reduction, the catholyte was distilled into an excess of sodium bisulphite solution [17] until the temperature of the vapour reached 373K. The bisulphite addition compound was shaken with cooling and cold water was added just to dissolve the precipitated salt. Isopropyl alcohol from this aqueous layer was extracted with ether. The ether was removed under a long column and isopropyl alcohol finally distilled at 351-355K.

The residual catholyte liquor after distilling off the unreacted acetone and isopropyl alcohol was then thoroughly extracted with ether to remove pinacol. The etherial solution was dried over anyhydrous calcium chloride and later ether was evaporated. After removing the volatile impurities, the product was found to be a pinacol (mp-308-310K). The unreacted acetone from the bisulphite compound was then estimated by usual method [19].

Reduction of acetophenone

After the reduction, the catholyte and the washings were neutralized with hydrochloric acid and steam distilled to remove unreacted acetophenone and methyl phenyl carbinol formed. The product pinacol was extracted with hot benzene. It was subjected to vacuum distillation till most of the benzene was removed. Mixed to this, exane was added and the solution was cooled well to complete the precipitation of pinacol. Acetophenone and carbinol were separated from the steam distillate by ether extraction and fractional distillation utilising the difference in boiling points.

Reduction of benzaldehyde

After the reduction, the catholyte was neutralized with hydrochloric acid and steam distilled to remove unreacted benzaldehyde. The residual catholyte liquor was cooled and filtered to get white crystalline solid benzopinacol, which was recrystallized from hot water. The filtrate was extracted with ether to get benzyl alcohol.

The same procedures were followed for the catholyte obtained in acid medium after neutralisation with sodium carbonate.

RESULTS AND DISCUSSION

Cyclic voltammetric studies on acetophenone using glassy carbon electrode [18] in acidic, basic and neutral media reveal that the easy reducibility of the compound is probably due to catalytic effect of the electrode. Both benzaldehyde(Fig. 1) and acetophenone show well defined waves at lead electrodes. The e_p for benzaldehyde in acidic medium is almost the same as that of at D. M. E. (-0.98) i. e. 0.975. Benzaldehyde is reduced at more positive values than that of acetophenone.

Acetophenone- e_p in H_2SO_4 = -1.05
e_p in Mcilvaine buffer = -1.35

Benzaldehyde - e_p in H_2SO_4 = 0.975
e_p in Mcilvaine buffer = -1.225

This is in agreement with the view that aldehydes are more prone to reduction than ketones. Further, acetophone is more easily reducible at lead cathode than at mercury or glassy carbon.

Electrolytic reduction of acetone in alkaline and acid media reveals that zinc is preferable to tin as cathode, as the yield of both pinacol and alcohol is more with the former (Table I). Electrolytic reduction of acetophenone or benzaldehyde in aqueous alcoholic sodium hydroxide reveals that the yield of pinacol is more with zinc electrode while the yield of alcohol is more with tin electrode. Although similar trend is observed with benzaldehyde surprisingly the situation is reversed for the acetophenone.

From the Table I, it is seen that when acetophenone and benzaldehyde are compared for the formation of alcohol, the formation of alcohol is easier for benzaldehyde than acetophenone, thereby indicating that aromatic aldehydes are more easily reducible than aromatic ketones. When acetone and acetophenone are compared for the formation of pinacol, acetophenone yields more of pinacol indicating that aromatic ketones are more prone to the formation of pinacols. As there is some surface change on the electrodes during the course reduction, one is tempted to suspect the influence of catalytic activity of the cathode in the reaction, which needs some more basic studies before giving any final explanation.

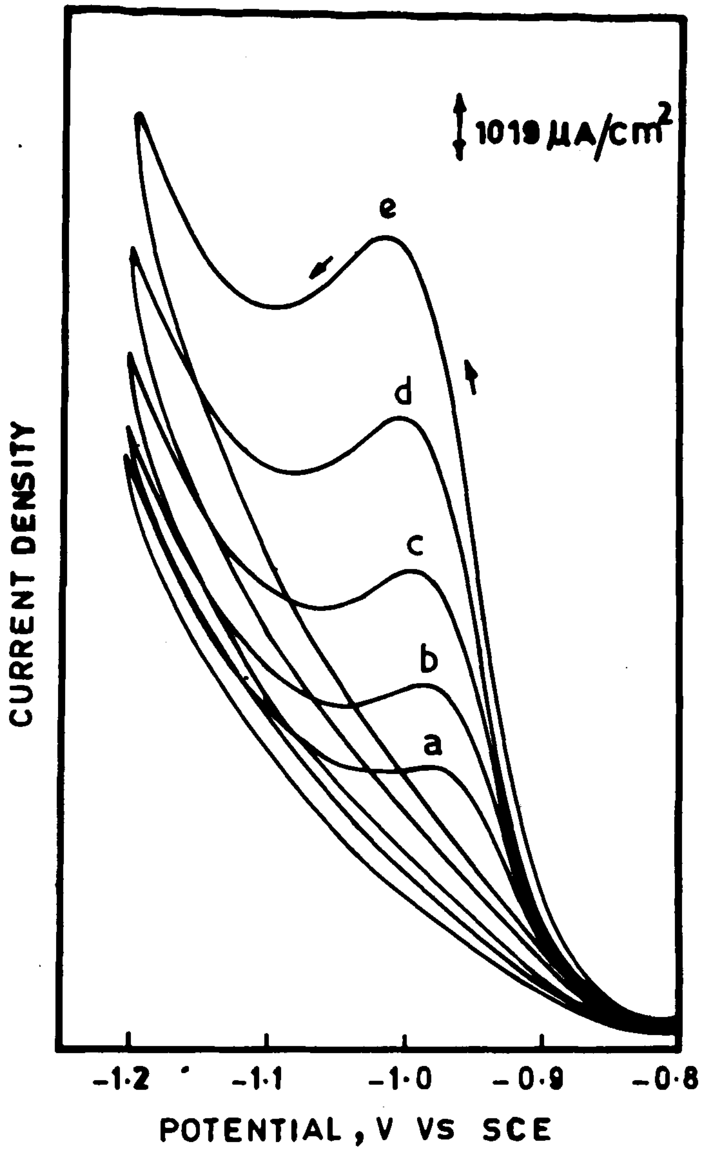

Fig.1 : Potential, V VS SCE

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TABLE-I: Electrolytic reduction of carbonyl compounds at Sn and Zn cathodes

Cathode material	Carbonyl compounds											
	Acetone				Acetophenone				Benzaldehyde			
	NaOH		H_2SO_4		NaOH		H_2SO_4		NaOH		H_2SO_4	
	Pin (%)	Alc (%)	Pin (%)	Alc (%)	Pin (%)	Alc (%)	Pin (%)	Alc (%)	Pin (%)	Alc (%)	Pin (%)	Alc (%)
Tin	8.85	15.25	6.40	30.40	66.40	20.00	59.50	20.00	54.48	30.70	50.00	38.39
Zinc	9.34	17.00	7.84	36.00	79.00	10.00	25.00	25.00	74.29	25.00	56.00	36.00

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