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Electrochemical Reducion of Benzophenone at Stainless Steel Cathode in basic Aqueous Ethanol Medium

Mohanlal Meena [1]

1. Associate Professor, Govt. R R College Alwar, Department of Chemistry, University of Rajasthan, Jaipur, Rajasthan, India

Abstract: The electrochemical reduction of the Benzophenone was carried out at the controlled potential inl M acetate buffer at pH 9 for the purpose of investigating this type of reduction as a possible syntheticprocedure for the preparation of 1, 2-glycols. The products formed during electrolysis at constant cathodepotential are reported here.

Keywords: acetophenone reduction, polarography, cyclic voltammetry , constant potential synthesis

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INTRODUCTION

The carboxyl group is an electrophori group offering interesting synthetic possibilities [1-5]. The course of reduction of aldehydes and ketones is strongly dependent on the reaction conditions, especially the pH of the medium and the nature of the electrode or cathode material. Under acidic conditions, dimeric products (pinacols) are often obtained, while under basic conditions, the corresponding alcohol is generally formed.

EQUIPMENTS

Cyclic voltammagrams were recorded by using the model ECDA-001 Basic Electrochemistry System supplied by Con Serv Enterprises, Mumbai (fig. 4.1). The system is completely computer controlled and its software is menu-driven. This menu driven ECDA program is used for selection of desired electroanalytical technique from the list of techniques displayed in the selective menu and also for entering the value of parameters in the parameter munu, within which the experiment has to be performed.

Figure 1: ECDA-001 Basic Electrochemistry System Along with The computer and The Electrochemical Cell Assembly

CELL AND ELECTRODES

In a cell used for electroanalytical [6] measurement there are always three electrode functions (see below). the first of the three electrodes is the indicating electrode also known as the test or working electrode (WE). This is the electrode at which the electrochemical phenomena being investigated takes place.

The second functional electrode is the reference electrode (RE). This is the electrode whose potential is constant enough that it can be taken as the reference standard against which the potentials of the other electrodes present in the cell can be measured.

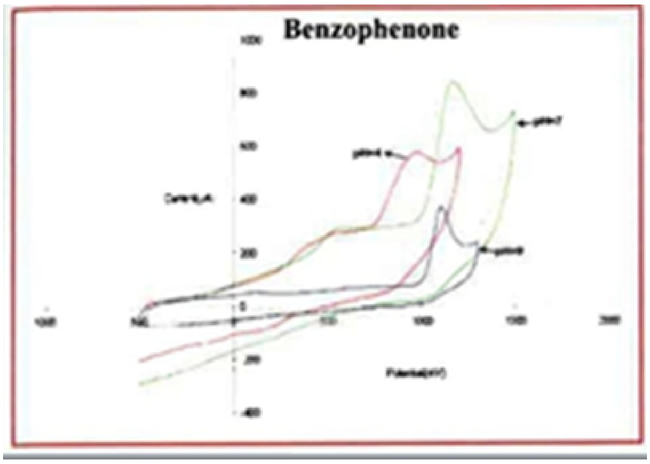
The final functional electrode is the counter or auxiliary electrode (CE) which serves as a source or sink for electrons so that current can be passed from the external circuit through the cell. In general, neither its true potential nor current is ever measured or known.

EXPERIMENTAL PROTOCAL

1.0 M aqueous solution of KCL or KNO_3 which is being used as supporting electrolyte, 0.1 M solution of carbonyl compound, buffer solution of desired pH (4.0, 7.0 and 9.0) were prepared.

One ml of supporting electrolyte (1.0 M aqueous solution) and 5.0 ml of BR buffer (of desired pH) were taken in the electrochemical cell and this mixture was make up to 10 ml with doubly distilled water and purged with nitrogen gas bubbling for 10 minutes to remove the dissolved oxygen. Then the cell was covered with Teflon cell cover. Working, reference and counter electrodes were dipped in the cell (solution) through the holes provided in the cover for this purpose. Then command was given to ECDA program i.e. from the menu of ECDA software, a CV technique was selected and the parameters (initial and final potential, scan rate and current sensitivity etc.) of CV experiment were entered in the menu. After putting the cell on, the software was given the command to execute the experiment within the predetermined parameters. The data so obtained were stored, exported in ASCII format and analyzed with the help of microcal origin and MS Excel programs. Thus blank cyclic voltammograms were recorded.

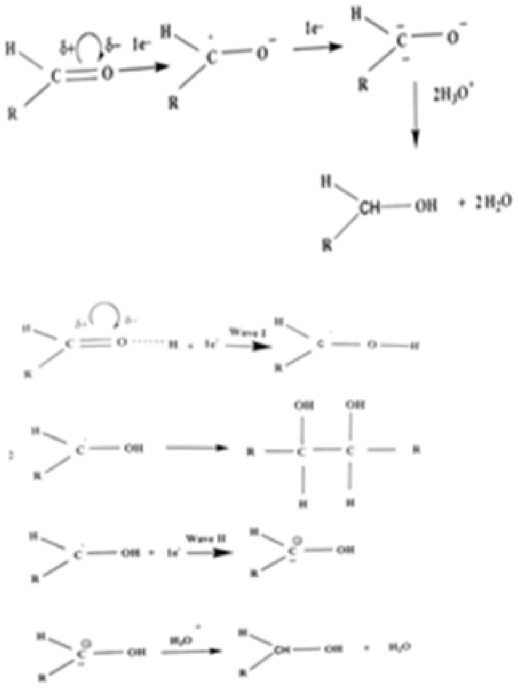
Cyclic Voltammetric studies were carried out to investigate electrochemical behaviour of these compounds and reversibility criteria of the process. Studies were carried out at various scan rates and pit



EFFECT OF PH

The reduction of carbonyl group compounds in aqueous solutions depends on the pH of the system. Thus at low pit these compounds exhibit two irreversible single electron polarographic waves [7]. Electrolysis on the plateau of the first wave usually affords the pinacol while reduction on the second plateau produces the alcohol [8]. This suggests that the following mechanism is operative-

The two polarographic waves merge to form one two electron reduction wave [9-10]. With increase in pH of the medium, under these conditions the primary product is the corresponding alcool.



RESULTS AND DISCUSSION

The reduction process of carbonyl compounds strongly depends on the reaction conditions ie. pH of the medium, nature of electrodes and solvent.

The electrochemical reduction of aldehydes and aryl alkyl ketones [11-12] is reported [13-14] to be a free redical process and proceeds through the following successive steps: (i) Formation of free radical as the fundamental process, (ii) The above process changes with pH and results in formation of corresponding free redical carbionate in acidic media and corresponding free radical carbinolate ion in the alkaline medium, (iii) These free radical carbinolate and carbinolate ion then undergo either dimerisation or reduction as the case may be

(1) Reduction of carbonyl compounds in acidic medium:

The reaction mechanism of the reduction of carbonyl compounds in acidic medium can be best explained with the help of following steps: (a) When the carbonyl compound diffuse into the field of the electrode, it initiates polarization of carbonyl compound; (b) Simultaneously, the carbonyl oxygen is attracted by neighbouring protons thus favouring increased polarization. The possibility that some of the ketones may be protonated before diffusing into the field of the electrode can be overlooked in the general mechanism since the effect of the ionic strength is negligible, indicating that little, if any, of the diffusing material possesses a charge before it comes in the vicinity of electrode), and (c) The carbonyl compound, under the influence of both the protons and the field completes the diffusion now supplemented by electro migration in to the interphase and acquires an electron. The steps outlined are continuous and involve a transition state or species in which an electron is transferred to the carbonyl carbon, a proton is simultaneously bonded to the carbonyl oxygen. The role of hydrogen ion in the "potential-determining" step and consequently in the transition state or intermediate species is made apparent by the strong pH dependence of reduction process.

(2) Reduction of carbonyl compounds in alkaline medium

The behaviour of carbonyl compound Le, aldehydes and ketones in alkaline medium differ from that in acidic medium. The mechanism discussed above satisfactorily accounts for these facts with only slight modifications in the fundamental process of the generation of fres radicals.

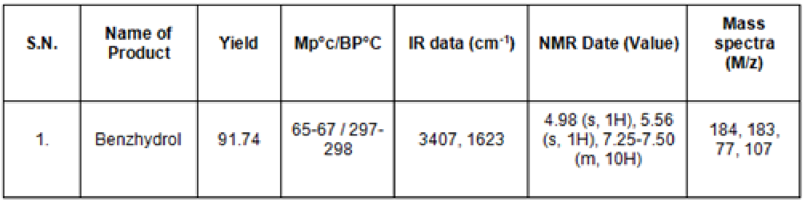
The observed reaction medium dependency, even though lessened, indicates continued participation of protons in the "potential determining" step of the reduction process. However, the decreased ion concentration greatly diminishes the probability of forming an O-H bond simultaneously with electron transfer.

The need of additional energy for electro reduction of the anionic free radical arises from the coulombic repulsion between the electrode and the anion; further the electron affecting the reduction now has to enter an area of increased electron density.

The votammographic curves of chosen carbonyl compounds (0.5mM) in aqueous medium having potassium chloride (IM) as supporting electrolyte and BR buffer (pH 9.0) at glassy carbon electrode using Ag/AgCl as reference and Pt-wire electrode as counter electrode were drawn.

After the electrolysis was over, the workup involved extracting the aqueous solutions three times with methylene chloride (50 ml each). The methylene chloride extract from the reaction was combined and washed with an aqueous solution of saturated NaCl. The organic extracts were then dried over anhydrous Na,SO, after the separation. The purification of the product was then carried out by chromatographic techniques including semi preparative HPLC, Schimadzu make). The compound was then identified by the combined application of spectroscopic techniques i.e. IR, NMR and Mass spectroscopy techniques are summarized in the Table.1

Table – 1: Reduction of substrates by Electrochemical Method



S.N.	Name of Product	Yield	Mp°c/BP°C	IR data (cm^{-1})	NMR Date (Value)	Mass spectra (M/z)
1.	Benzhydrol	91.74	65-67 / 297-298	3407, 1623	4.98 (s, 1H), 5.56 (s, 1H), 7.25-7.50 (m, 10H)	184, 183, 77, 107

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