

Electrochemical Reduction of O-Aminoacetophenone at Stainless Steel Cathode in Basic Aqueous Ethanol Medium

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Abstract - Electrochemical reduction of the O-aminoacetophenone was carried out at the controlled potential in 1 M acetate buffer at pH 9 for the purpose of investigating this type of reduction as a possible synthetic procedure for the preparation of 1, 2-glycols. The products formed during electrolysis at constant cathode potential are reported here.

Keywords - O-aminoacetophenone reduction, polarography, cyclic voltammetry and constant potential synthesis.

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INTRODUCTION

The electrolysis of carbonyl compounds has been carried out for almost one and half century, but for a long time there was a rather limited understanding, of the process (formation of intermediates and products) involved. Often suggested reaction schemes were deduced only from knowledge of the initial and final composition of the electrolyzed solution. Polarography, cyclic voltammetry [1] and constant potential synthesis [2] have contributed more to the understanding of process involved in the electrolysis of organic substances. Constant potential synthesis [3-4] is being studied in our laboratory.

In the present work the reduction of some simpler carbonyl compounds, specially aryl alkyl ketones and aldehydes viz., (o-aminoacetophenone) is discussed. The reduction potential of the carbonyl compounds was recorded by polarography technique and cyclic voltammetry was used to decide the reversibility of the process. On the basis of experimental knowledge thus obtained, these compounds were then reduced electrochemically at constant potentials using a potentiostat.

EXPERIMENTAL

The chemicals used. O-aminoacetophenone Hg, KCl and CH₃COONa are of AR grade. The C₂H₅OH and H₂O used were double distilled.

The polarography measurements were made with a Princeton applied Research Model 170 electrochemistry system. Cyclic voltammetry studies were carried out using a three electrode cell assembly having glassy carbon as the working electrode Ag/AgCl as the

reference electrode and platinum wire electrode as the counter electrode.

An Elico Model CL-95 Potentiostat cum galvanostat coupled with a sweep generator and X-Y recorder were used for recording the polarization curves and for carrying out controlled potential electrolysis.

RESULTS AND DISCUSSION

Electrochemical reduction process depends on pH. Most of the experimental work reported, is connected with the reduction of carbonyl compounds [5-6]. Electrochemical reduction of Aryl Alkyl Ketones [7-8] and aldehydes is a free radical process. It is proposed that it proceeds through the following steps.

- (a) formation of free radical as the fundamental process.
- (b) the above process changes with pH and results in the formation of the corresponding free radical carbinolate in acidic media and the corresponding free radical carbinolate ion in alkaline medium.
- (c) These free radical carbinolate and carbinolate ion then undergo either dimerisation or reduction as the case may be.

Reduction in acidic media

The mechanism of the reduction can be best explained as follows

- (a) As the carbonyl compounds diffuses into the field of the electrode, it initiates polarization of the carbonyl compound
- (b) Simultaneously, the carbonyl oxygen is attracted by neighboring protons, thus favouring increased polarization (the possibility that some of the ketone 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 within the field of electrode) and
- (c) The carbonyl compound, under the influence of both the protons and the field completes the diffusion (now supplemented by electromigration) into 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 and a proton is simultaneously bonded to the carbonyl oxygen. The role of hydrogen ion in the “potential-determining” steps are consequently in the transition state or species is made apparent by the strong pH dependence of the reduction process (see Fig. 1).

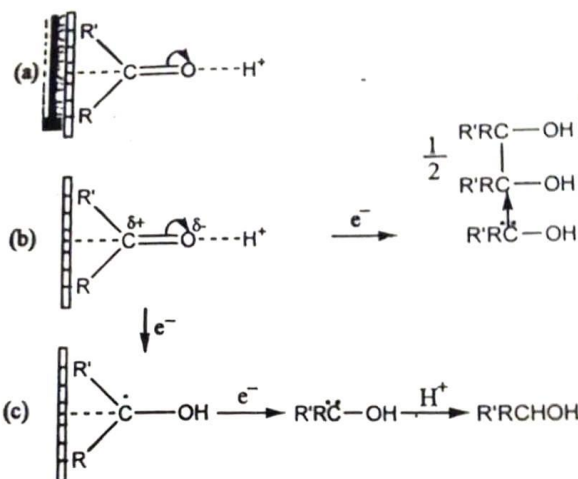


Figure 1: Stepwise diagrammatic representation of reduction of a ketone in acidic media where

Step (a) represents the initial diffusion polarization process

Step (b) represents the formation of carbinol free radical and

Step (c) represents the reduction of the carbinol free radical and subsequent acquisition of a proton

The free radical produced, dimerises to the pinacol until a potential is reached at which it is reducible, it can either dimerise to pinacol or be reduced to carbinol, the latter process, which occurs almost exclusively, depends on the structure of carbonyl compound.

Reduction in alkaline media

Several factors differentiate reduction behavior in alkaline media from that in acidic solution. The mechanism outlined in the previous section satisfactorily accounts for these facts with only slight modification of the fundamental process of the generation of free radicals.

The observed pH 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. Consequently, increasing amounts of carbinolate free radical are formed. The latter is not reduced at its formation potential and so dimerises until its reduction potential is reached.

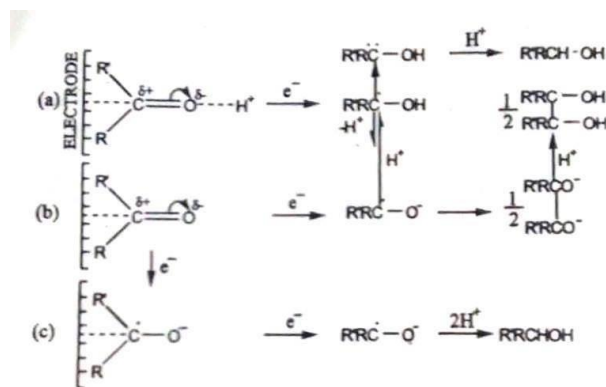


Figure 2: Diagrammatic representation of the reduction of a ketone in alkaline media

The need of addition energy for electroreduction [9] of the anionic free radical arises from the coulombic repulsion between the electrode and the anion, further the electron effecting the reduction now has to enter an area of increased electron density (see Fig. 2).

The polarographic measurements were made using DME (as working electrode) and SCE (reference electrode) in 10 ml H-type polarographic cell. The solution of each carbonyl compound (10 ml containing 1 ml carbonyl compound solution (M/40) + 4 ml KCl (2.5 M) + 5 ml BR-Buffer (pH = 9), taken in a H- cell, is purged with N₂ for 10-15 minutes before each run. In each case a blank polarogram of the solvent and BR buffer were recorded to ensure

that they were actually due to the carbonyl compound.

The voltammographic curves of o-aminoacetophenone in 1:1 (v/v) ethanol water at 0.5 mM concentration, 2.5 M KCl as supporting electrolyte and BR buffer (pH 9) at glassy carbon electrode using Ag/AgCl as reference electrode are taken. All curves are reported in Fig. 3.

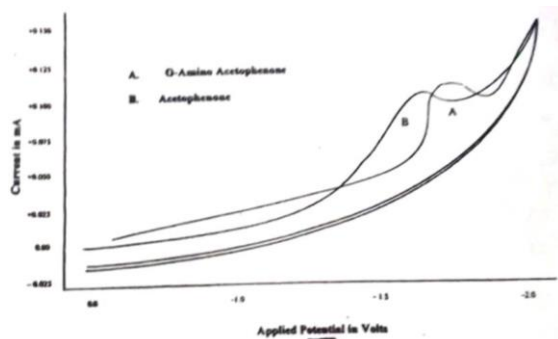


Figure 3: Voltammographic curves of o-aminoacetophenone 1:1 (v/v) ethanol water at 0.5 mM concentration

The electrolysis cell used was a conventional three electrode system consisting of a working electrode (cathode – stainless steel), a counter electrode (platinum) and a reference electrode (calomel). All reductions were carried out under N₂ atmosphere. In each experiment CH₃COONa (1 M) was used as a supporting electrolyte. Prior to each electrolysis, the system was purged with N₂ for approximately 20 minutes. The pH of the solution as maintained constant at 9. All the electrochemical reductions were carried out at their corresponding reduction potentials as given in Table 1 v/s SCE and were complete in 2 hours. In all cases, the workup involved extracting the aqueous solutions three times with ethyl ether (50 ml each). The ether extracts from each reaction were combined and washed with an aqueous solution of saturated NaCl. The organic extracts from each reduction were then dried over

Table I: Experimental conditions of electrolysis

Compound name	Amount of compound (in gms)	Applied potential (mV)	Solvent system (V:V)	Yield (%)	IR Data (cm ⁻¹)	NMR Data (δ value)	Mass spectra (m/z)
O-aminoacetophenone	10.00	1770	50:50 water & ethyl alcohol	78.17	3330, 1650, 1550	3.126	126, 80, 160

anhydrous Na₂SO₄ and thereafter the separation and identification of the product was carried out.

Bands appeared in FTIR at (1) 1400-1310 cm⁻¹ (s) (ii) 1150 cm⁻¹ (s) due to C-O stretching (tertiary alcohols). A peak at 1710 cm⁻¹ due to C=O stretching of carbonyl compounds was observed in the starting material,

which disappeared in the products. A broad band at 3570-3200 cm⁻¹ due to O-H (stretching) was seen in products, which suggests that the product is a pinacolone.

CONCLUSION

Electrochemical reduction of carbonyl compounds at constant potential, provides an attractive synthetic route for synthesis of the corresponding pinacolones.

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