

Greener Alternative for the Reduction of P-Aminoacetophenone At Stainless Steel Electrode In Basic Aqueous Ethanol Medium

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Abstract:

This paper studies the electrochemical reduction of p-aminoacetophenone in basic aqueous medium. This may provide a basis for attractive environmental friendly and sustainable synthetic procedure. The reduction process was investigated cyclic voltammetrically to explore it as an alternative synthetic route for the preparation of alcohols. On electrolysis in basic medium (pH-9) controlled current in 1.0 M Sodium acetate, 1-(4-aminophenyl)ethanol was obtained as the major product, which was isolated, purified and characterized by combined application of chromatographic and spectroscopic techniques. Stainless steel (SS-316) electrodes were used as anode & cathode.

Keywords: p-aminoacetophenone, Stainless Steel (SS-316) Electrode, Cyclic Voltammetry, Controlled Current electrolysis.

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I. Introduction:

Electrochemistry offers a very mild and atom efficient method to achieve selective oxidative or reductive transformations using electrons as reactants. It therefore avoids the use of other harsh and often toxic chemical reducing and oxidising agents.¹⁻³ In addition, electrochemistry can offer new reaction pathways that are complimentary to traditional synthetic chemistry procedures and can be particularly interesting for late-stage functionalisation due to its mild and selective nature.⁴ Nonetheless, it is only in the last few years that the synthetic chemistry community has rediscovered this powerful tool for small scale synthetic applications.^{5,6} Its resurgence is in part due to the chemical community being driven towards more sustainable and greener reaction pathways.¹⁻³

Electrochemical reduction offers molecular synthesis by means of cathodic reductive electrolysis to generate radical anions.⁷⁻⁹ This strategy was successfully applied for the reduction of various functional groups such as aldehydes,¹⁰ ketones¹¹ etc.

Electrochemical reduction has since been known as simple and cheap and eco-friendly process for the preparation of organic compounds. The study of the electrochemical reduction of carbonyl compounds was very limited. Therefore aim of the work was to investigate and develop a new synthetic method for the preparation of alcohol on easily available conditions such as reagents, apparatus, temperature and pH.

The p-aminoacetophenone used as one of the important starting material to prepare acetone p-aminoacetophenonebenzoylhydrazone (Hapbh) ligand which is known for their antibacterial and antifungal activities in their free form and as metal complex.¹²

The present work deals with the electrochemical reduction of p- aminoacetophenone was carried out by using the basic aqueous medium. The Electrochemical reduction has been carried out at Constant current at Stainless steel electrode. Stainless Steel electrode has also been used in Constant Potential Electrolysis technique in our laboratory for the electrochemical reduction of carbonyl compounds¹³⁻¹⁶.

II. Material And Methods

All experiments were carried out at room temperature, the chemicals used were of analytical grade and the solutions were prepared in triply distilled water. Prior to the electro-organic synthesis, the optimum conditions of the reaction were worked out by utilizing the concepts of organic reaction mechanism along with the appropriate interpretation of signals obtained from cyclic voltammetry in combination with spectroscopy.

Cyclic voltammograms obtained in acidic, neutral and basic conditions were of dissimilar nature, which clearly indicates formation of different electrolysis products under different condition of pH. At low pH

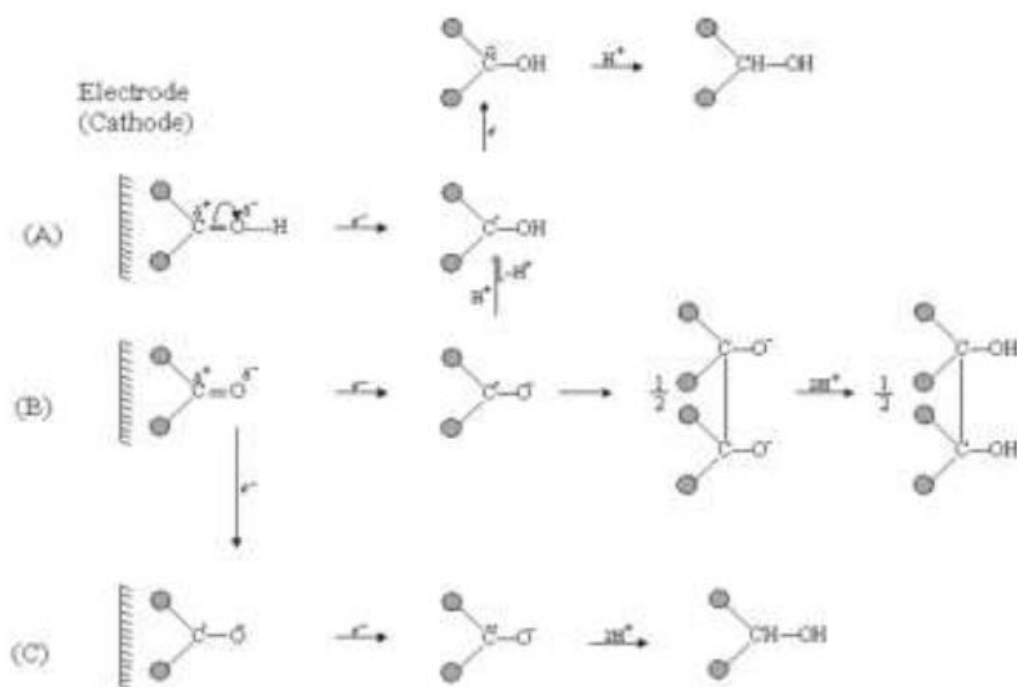
values, reduction of P- amino acetophenone exhibits two irreversible single electron waves and with the increase in the pH of the medium these two waves merge to form one two-electron reduction wave.

In acidic medium pinacol is obtained but under these conditions, stainless steel electrode cannot be used hence no attempt was made to synthesize this product. The present method therefore offered single product in alkaline conditions. The attractive features of the technique are single product [1- (4-aminophenyl) ethanol], economical electrode stainless steel (SS-316), and last but not the least ecofriendly conditions. Cyclic voltammograms were recorded at the scan rate of 100 mV/s using a computer interfaced instrument ECDA-001 supplied by Con-serv Enterprises, Mumbai. The cyclic voltammogramic studies were carried out using glassy carbon as working electrode, Ag/AgCl as reference and platinum electrode as counter electrode.

The results thus obtained were utilized to decide the optimum reaction conditions for the reduction. The electro-organic synthesis was then carried out using a CDPE (Centre for Development of Physics Education, U.O.R. Jaipur) make Galvanostat at Stainless steel electrode (SS-316). The reaction product was isolated, purified and characterized by combined application of chromatographic technique and spectroscopy.

III. Results and Discussion

The electrochemical reduction of carbonyl compounds in aqueous solutions mainly depends on the pH of the system. Thus at low pH values these compounds exhibit two irreversible-single electron waves¹⁷, thus clearly indicating formation of two products. This is further clarified by obtaining cyclic voltammogram, where two peaks were observed only at low pH (i.e. at 4). Electrolysis on the plateau of the first wave usually affords the pinacol while reduction on the second plateau produces the alcohol¹⁸. This suggests the mechanism as predicted in following scheme.



Scheme: Proposed mechanism of electro chemical reduction of carbonyl compound

With increase in the pH of the medium the two waves merge to form one two-electron reduction wave¹⁹. Under these conditions the primary product is the corresponding alcohol.

The voltammographic curves of 0.5 mM selected carbonyl compounds in aqueous medium, 2.5 M Potassium Chloride as supporting electrolyte and BR buffer (pH = 9.0) at glassy carbon electrode using Ag/AgCl as reference electrode are taken. The conventional H-type cell with two limbs separated by G-4 disc was used for electrolysis. The supporting electrolyte sodium acetate (250 ml, 1M) was filled equally in both the limbs. The substrate i.e. (p-amino acetophenone) was dissolved in the alcohol and placed in the cathodic chamber. The stainless steel (SS 316) electrode having an area 2x3 cm² was used as cathode as well as anode.

The constant current (1 Amp.) is passed through the electrolyte for 2 hours with the help of CDPE make Galvanostat.

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 Na₂SO₄ after the separation and then the product formed was identified. The separation of the electrolysis product was carried out with the help of semi preparative HPLC (Shimadzu, Japan) and the identification was made with FTIR (Shimadzu, Japan), GC-MS spectrophotometer (Thermofinnigan Trace-GC) and NMR (JEOL, Japan, 300 MHz) techniques.

The results are tabulated in following table.

Name of substrate	Yield %	IR Data (cm ⁻¹)	Mass spectra m/z	NMR Data δ-value
p-amino-acetophenone	83.43	3404,3425(s) 3445(b)1605 1635,1061	137,136,92,45	7.15-7.20 (d,2H) 7.27-7.32 (d,2H) 7.00 (s,2H) 4.76 (s,1H) 4.00 (q,1H) 1.51 (d,3H)

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IV. Conclusions

Electro-organic synthesis is a sustainable way to achieve functional complexity in a mild, green and atom efficient way as electrons act as the reagents. In contrast with conventional chemical method involve clean and green methodology and have merits like specificity, cost effectiveness. Stainless Steel electrode is used as a cathode in the present work. The peculiarity of this Stainless Steel electrode is that it is economical viable, readily available and long lasting, particularly in solution having pH above 6. The reaction takes place at room temperature and reaction does not requires hazardous chemicals.

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