Electrochemical Oxidation of Cinnamic Acid Using Stainless Steel Electrodes

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Abstract. The electro-organic technique is observed to be the modern tool in achieving the oxidation of organic acids to some other useful organic molecules. In the present study, the favourable experimental conditions for carrying out the electrochemical oxidation of cinnamic acid, the experimental set up required and probe for the various products formed have been tried. The anodic process has been carried out at low cost and readily available stainless steel electrode under aqueous conditions. On identification of the products using chromatographic and spectroscopic techniques, the most probable mechanism has been proposed. To confirm the positive occurrence of the oxidative process under electrolytic conditions, the current – potential study was carried out. The product was analysed by TLC technique, UV and IR spectral studies and identified as 1,4-diphenylbut – 1,3-diene. This work paves a humble way of opening up a new area wherein other electro analytical parameters like polarography, cyclic voltammetry, electrode variation, temperature variation, solvent effects etc. can be studied, along with innumerable substituent effect studies.

1. Introduction

Organic electrochemistry is not a new field of endeavour. Electrochemical reduction and oxidation of organic compounds are elegant methods of preparative organic chemistry and quite a number of interesting reactions could be achieved by their adoption. The importance of the electrode potential is controlling the course of an electrolytic reaction [1].

Electrolysis is an important synthetic tool for both laboratory and industrial reactions. The electrochemical techniques and instrumentation are initially developed for analytical uses, but capable of providing much deeper information concerning the electrode process. Development of organic fuel cells and high-energy density batteries using organic electrolytes has also contributed to the awakening of interest in electro-organic synthesis. Polarography is one of the most useful techniques in electrochemical processes [2]. This technique involves a recording of the current-potential relationship at a dropping mercury electrode and normally employed for investigation of reduction process [3,4].

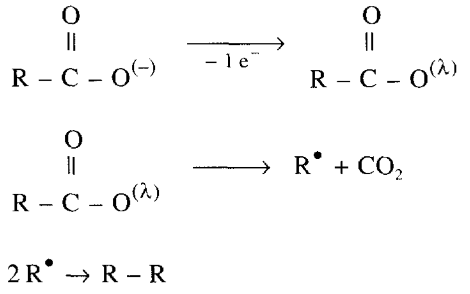
Electrochemical oxidation of aromatic amino compounds has received considerable attention from a number of workers. The first voltammetric studies on oxidation was carried out by Lord and Roges [5]. Similarly a study on electrochemical oxidation of 2-amino thiazole and oxidation of acetals has been found to be superior to conventioal chemical methods [6]. The electrochemical oxidation of aromatic acids is based on Kolbe's reaction.

The Kolbe's electrolysis is probably one of the earliest reactions applied in organic synthesis, namely in the formation of dimeric products from the oxidation of carboxylic acid salts.

$$RCO_2. \xrightarrow{-CO_2} R^\bullet + CO_2 , \qquad 2R^\bullet \rightarrow R - R$$

The early work of this reaction centered on the preparation of dimeric products from the radical intermediates obtained from the oxidation of carboxylic acid salts. Several explanations which are mostly related to the surface of the electrode have been advanced. Depending on the nature of electrodes such as graphite and platinum various products were formed [7]. In the structure of acid, it was shown by Fichter and co-workers that the Kolbe synthesis does not take place in aqueous solution when a double bond is too close to the carbonyl group [8].

The formation of radical intermediates in the Kolbe reaction was first advanced by Brown and Walker and was latter developed by Walker and co-workers [9,10].



$$R-\overset{\overset{O}{\|}}{C}-O^{(-)} \xrightarrow[-1e^{-}]{} R-\overset{\overset{O}{\|}}{C}-O^{(\lambda)}$$

$$R-\overset{\overset{O}{\|}}{C}-O^{(\lambda)} \longrightarrow R^{\bullet} + CO_2$$

$$2R^{\bullet} \rightarrow R-R$$

Thus the evolution of the mechanism of the Kolbe electrolysis was observed in the formation of acyl peroxides. Formation of hydrogen peroxide and formation of carbonium ions.

Using the above methods and mechanism, a probable mechanistic pathway has been suggested for the oxidation of cinnamic acid using low cost and readily available stainless steel electrodes.

2. Experimental Description

The experimental part of the project comprises the following stages :

1. Purification of materials
2. Fabrication of the electrolytic cell
3. Construction of the electric circuit
4. Polarization studies
5. Product analysis

2.1. Purification of Materials. Cinnamic acid was recrystallised from a mixture of 3 volumes of water and one volume of alcohol.

Rectified spirit was distilled, dried over anhydrous calcium oxide and used. Deionised water was used as such. Analar sodium hydroxide was employed as the supporting electrolyte.

2.2. Fabrication of the Electrolytic Cell. H-cell with a sinter disc in between the compartments was employed as a divided cell. Two low cost and readily available stainless steel plates were used as electrodes. The electrodes were pretreated before introducing them in the cell. Both the electrodes were polished with emery sheets in the regular increasing order of fineness. They were then washed in running stream of water and then cleaned with detergents to remove greasy and oily impurities.

The other organic impurities were removed by dipping the electrodes in acetone. Finally, the electrodes were washed with water and rinsed with deionized water. They were kept inside the deionized water to prevent aerial oxidation of electrode surfaces. Before the experiment, they were dried using an air drier.

The electrolyte used was ethanol, water mixture in the ratio 3:1, which was sufficient to dissolve the cinnamic acid (10^{-2} M). The concentration of sodium hydroxide in the medium was kept as 2 M.

2.3. Construction of the Electric Circuit. A locally fabricated transisterised DC power supply regulated by means of a potentiometer was employed. Resistance of 100 Ω was used to control the flow of current, thereby maintaining the desired current chosen for the system. The current flowing through the cell was in the range of 0 to 125 mA. Enough care was taken in maintaining the potential below the decomposition potential of the solvent system. The electrolytic process was carried out under constant current conditions. Milliammeter and vaccum tube voltmeter (VTVM) (RS Model 322-I, ruttonsha simposon private Ltd.) were used.

2.4. Polarization Studies. The cell consisting of the solvent mixture and the supporting electrolyte (2 M) was introduced in the electrical circuit. All the potentials were measured as cell potential between the working electrode viz, anode and the counter electrode. By working at the DC power supply, the current applied is regularly and constantly varied. The corresponding potentials in volts were noted from the VTVM and were tabulated (Table 1). A current - voltage graph (Fig. 1) was drawn. The current – potential values were noted after adding adequate amount of cinnamic acid into the anode compartment, to realise 10^{-2} M concentration.

The results were tabulated and a graph showing the relationship between current and potential was drawn along with that for the pure solvent system.

From the graph, the working potential for the oxidation was fixed as 4 (four) Volts.

2.5. Product Analysis. After passing 65 mA current for about 5 hours, the anolyte was observed to have changed its colour from colourless to dark brown. It was shaken with ether and the ether extract was neutralised with 1:1 HCl. Then the ether extract was thoroughly washed with saturated sodium bicarbonate solution and then with excess of deionised water. The ether layer was concentrated by evaporation, dried over anhydrous calcium chloride and analysed for the products.

Table 1. Potentials in Volts from the VTVM.

Electrode : Stainless steel		Depolariser : Cinnamic acid (10^{-2} M)	
Temperature : 30 °C		Supporting electrolyte: Aqueous ethanolic NaOH	
Without Depolariser		With Depolariser	
Cathode Potential in Volts	Current in mA	Cathode Potential in Volts	Current in mA
0.07	0	0.20	0
1.00	2	0.40	1
1.50	4	0.80	5
2.00	15	1.75	21
2.50	23	2.00	26
3.00	25	2.80	38
3.50	30	3.00	57
4.00	45	4.00	66
4.25	45	4.50	75
4.50	50	4.70	87
5.10	67	4.80	92
5.50	81	5.50	112
6.00	100	5.90	130
6.30	110	6.10	139
6.50	125		

A Co-TLC was run for the product solution along with cinnamic acid as the reference, using (i) benzene as the eluent (ii) petroleum ether (60-80 °C) as the eluent.

A preparative TLC was run and the product obtained as a band was extracted with ether. Thus, the spectrally pure sample of the product was obtained. The UV spectrum of the reaction product and cinnamic acid were taken. The IR spectrum of the above two compounds were also taken.

The product was subjected to regular analysis with a number of confirmatory tests for specific functional groups.

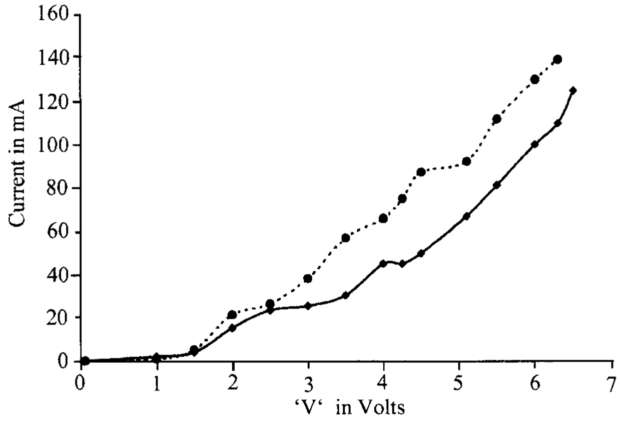


Fig. 1. Current - Potential Study.

3. Results and Discussion

3.1. Polarization Study. The polarization study was carried out with and without depolarizer.

From the graph, it is understood that at any given potential, the solution with the depolarizer absorbs more current than the solvent. This indicates that the excess current absorbed is being utilized for the oxidation of the substance.

3.2. Thin Layer Chromatographic Analysis of the Oxidation Product. The ether extract of the product (brown coloured) on thin layer chromatographic investigations has developed the chromatogram.

In the chromatogram run with non-polar eluents namely benzene and petroleum ether, the oxidation product has moved cloe to the solvent front indicates that the product is highly non-polar.

3.3. Other Chemical Tests Carried out with the Product.

(1) It decolourises bromine water, alkaline KMnO$_4$ solution and iodine solution, which shows the presence of C = C group in the product. None of the previous electrochemical works in the conversion of C = C into – C ≡ C – have resulted. Hence, the possibility of – C ≡ C – in the product is ruled out.

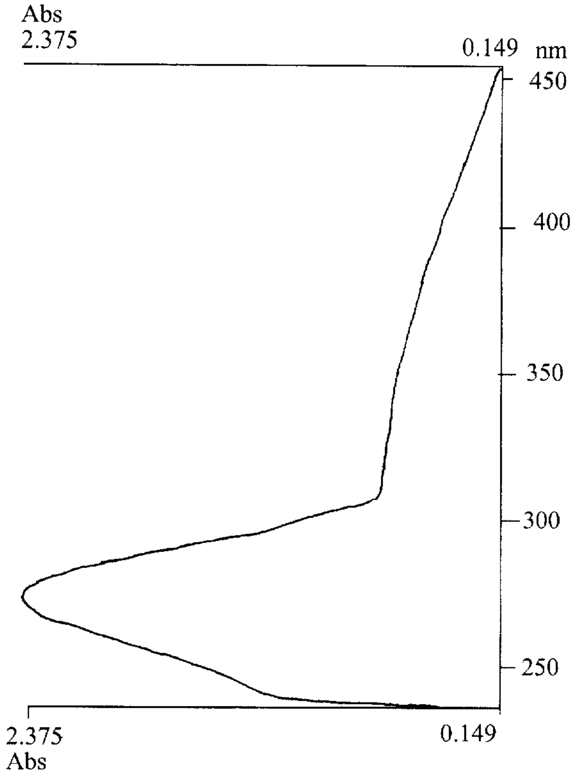


Fig. 2. UV spectrum of the product.

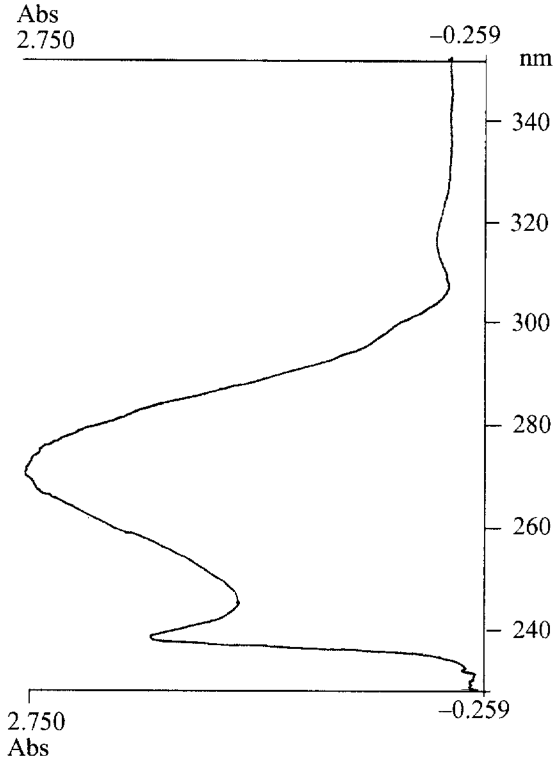


Fig. 3. UV spectrum of Cinnamic acid.

(2) It gives no effervescence with saturated sodium bicarbonate solution. This indicates the absence of –COOH group in the product.

3.4. Spectroscopic Investigation. The ultra-violet spectrum (Fig. 2) of the product obtained can be used to identify the nature of the substituent on the benzene ring.

In order to carry out any correlative work it is necessary to know the type of transitions involved in a particular absorption peak. This problem was investigated in detail by Doub and Vandenbelt [7] who determined the spectra of a large number of substituted benzenes. From the data obtained, they were able to identify three distinct absorptions around 180 nm; 210 nm (< 250 nm) and 260 m (> 250 nm). These regions are known as E band, K band and B band, respectively.

They also found that γ_K/γ_B showed characteristic values depending on the nature of substituent on the benzene nucleus.

The UV absorption peaks (Fig. 3) for the product at 239.5 nm and 272.0 nm correspond to the K band and B band respectively. Usually E band absorption is not observed. The wave number ratio of the K band to B band absorptions is found to be 1.135. This value [8] is in good agreement with the reported value of 1.14 for styrene molecule. In addition, comparison of these absorptions with that of the cinnamic acid (starting material) indicated that the product showed a slight bathochromic shift which can be taken as an evidence for the nature of product obtained, which contains styrene moity.

3.4.1. Mechanism. Based on the above facts, the reaction product formed is predicted as 1,4-diphenylbut-1,3-diene. The most probable mechanism for the formation of the above product from cinnamic acid in the presence of NaOH is given below (Fig. 4):

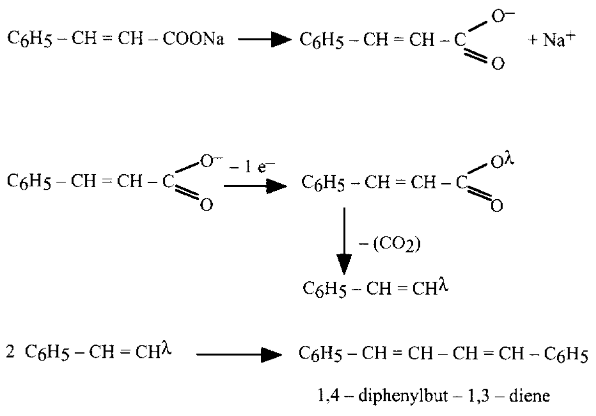


Fig. 4. Mechanism.

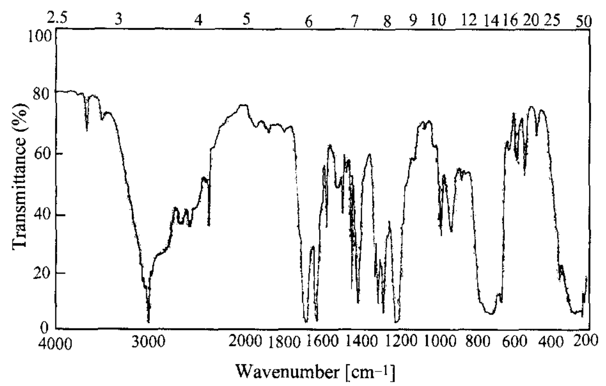


Fig. 5. IR Spectrum of Cinnamic acid.

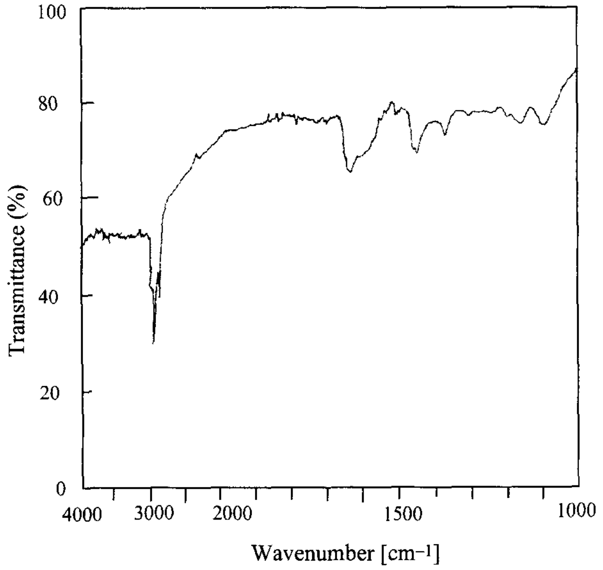


Fig. 6. IR spectrum of the product.

3.4.2. IR Spectrum. The IR spectra of the reaction product and cinnamic acid are given in Figs. 5 and 6, respectively. The IR spectrum of the product shows absorption peaks with reduced intensity and this is characteristic of the IR spectra taken using film technique. The IR spectrum of the product has absorption frequencies corresponding to aromatic stretching (2910 cm^{-1}), aroamtic substituted alkene (1640 and 1630 cm^{-1}) and C=C aromatic ring stretching (1450 cm^{-1}). In addition, the spectrum shows the absence of the absorption peak at 1710 cm^{-1}, which is characteristic of C=O frequency of the α,β-unsaturated acid.

4. Conclusion

The present work is an attempt to oxidise cinnamic acid using low cost and readily available stainless steel electrodes in aqueous ethanolic medium. To confirm the positive occurrence of the oxidative process under electrolytic conditions, the current-potential study was carried out. The product was analysed by TLC technique, UV and IR spectral studies and identified as 1,4-diphenyl but – 1,3-diene. The most probable mechanism for the anodic oxidation process is proposed.

5. Acknowledgement

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6. References

[1] M.M. Baizer, and Marsel Dekkar, Organic Electrochemistry, New York (1983).

[2] R.N. Adams, and M. Dekkar, Electrochemistry at Solid Electrode, New York (1969).

[3] Hevrovsky, J. Chem. Listy **16**, 256 (1922).

[4] D. Ilkovic, Collection Czech. Chem. Commun. **6**, 300 (1952).

[5] S.S. Lord and L.B. Rogers, Text book of Analytical Chemistry **26**, 284 (1954).

[6] T.K. Krishnamoorthy and S.J. Arulraj, J. Electrochem. Soc. **36**, 194 (1987).

[7] N.J. Kochl, Am. Chem. Sco. **91**, 1227 (1969).

[8] F. Fichter and T. Holbro, Chem. Acta. **20**, 333 (1937).

[9] S. Shukla and J. Walker, J. Trans Faraday Soc. **27**, 35 (1931).

[10] S. Shukla and J. Walker, J. Trans. Faraday Soc. **28**, 547 (1932).

[11] L. Doub and J.M. Vandenbelt, J. Am. Chem. Soc. **69**, 2714 (1949).

[12] F. Schienmann, An introduction to the Spectroscopic Methods for the Identification of Organic Compound, Vol. 2, 108, 109.

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