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Electrochemical Reduction of Selected Cyclohexanones

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ABSTRACT

The environmental friendly reduction of 2-tertbutylcyclohexanone, 4-tertbutyl cyclohexanone and 4-Ethylcyclohexanone was carried out by electrochemical method. The electrochemical behavior of substrates was studied with the help of cyclic voltammetry. Information obtained from cyclic voltammetric studies was used for establishing optimum conditions for electrochemical reduction. Electrochemical reduction was then carried out galvanostatically using economically viable stainless steel (SS-316) electrodes. The reduction products were isolated and purified by chromatographic techniques and characterized on the basis of spectral analysis.

Key words: 2-tertbutylcyclohexanone, 4-tertbutylcyclohexanone, 4-Ethyl cyclohexanone, Cyclic Voltammetry, Stainless Steel Electrode (SS-316)

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INTRODUCTION

Electron transfer is one of the important processes in organic chemistry, and many organic are driven by electron transfer processes [1]. Among several methods for electron driven reactions, the electrochemical methods serve as a straightforward and powerful method. Electrochemical technique is a novel alternative method in organic synthesis, where one can synthesize the desired compound by oxidation or reduction of the substrate [2-4]. In the field of electrochemistry, electro-analytical techniques like Polarography, Cyclic Voltammetry etc. and synthetic techniques like Electrolysis at Constant Current and Constant Potential are now known. Cyclic Voltammetry, is finding extensively use to provide information regarding potential corresponding to reduction, oxidation and formation of intermediates and also about the reversible nature of electrode transfer processes. Shape of cyclic voltammograms provides valuable information related to the kinetics of the electrode processes and on the rates of the processes [5-7]. A number of industrial processes have now replaced routine methods of their synthesis by the electrochemical methods. Since, electro-organic synthesis is much more economical, eco-friendly, avoid massive chemical effluents. Such type of reactions is easy to control automatically as well as the reactions conditions are generally mild and effects of potential, pH, buffer, solvent and structural modifications of substrate can also be studied. It is with this background then it is proposed to make use of these electroanalytical techniques for carrying out synthesis of the selected substances [8-10]. In electro synthesis, reactions can take place in a low-temperature environment, reducing the local consumption of energy, and reducing the risk of corrosion, material failure [11].

Cyclohexanol derivative like 2-tert-butyl -4-methyl cyclohexanol is a versatile scent which can be used in acidic as well as in alkaline media and has an earthy woody vetiver – like fragrance [12]. 2-(2-alkoxy-1-methylethyl)-5-methyl cyclohexanol has the properties like it refrigerates not only the mouth mucosa but also the skin, is practically odorless and is dissolved in various bases [13].

2-tertbutylcyclohexanol has camphoraceous – piney and minty odor and is used in perfumes where woody, Cedar-like, Pine-like or even Patchouli-like effects are emphasized. However, its major use is as a starting raw material for OTBCHA. OTBCHA (ortho tert butyl cyclohexyl acetate) has a fruity citrus odour with a woody camphoraceous undertone.

4-terbutylcyclohexanol has a dull woody camphoraceous odor and is used in perfumes to provide these impressions. However, its major use is as a starting raw material for PTBCHA, a very important perfumery chemical. PTBCHA (para tert butyl cyclohexyl acetate) is widely used in perfumeries along with ionones, cedarwood products, floral and non-floral perfume chemicals. 4-Ethyl cyclohexanol is an important intermediate in the formation of ionic crystals.

The present work therefore describes electrochemical reduction of selected cyclohexanones to Cyclohexanols. Then for electrochemical reduction, first cyclic voltammogram of reactants were recorded at different pH and different scan rate to check the

reversibility of the process. On the basis of results obtained from cyclic voltammetry, conditions were determined for electrolysis at stainless steel electrode (SS-316) galvanostatically.

MATERIALS AND METHODS

Reduction using electroanalytical technique

First of all cyclic voltammogram were recorded at different pH and different scan rate using a computer based Basic Electrochemistry system ECDA-001, supplied by Con-serv enterprises, Mumbai, using 3 electrode cell assembly with 1mm diameter glassy carbon as working electrode, Ag/AgCl as reference electrode and Pt wire as counter electrode. The voltammographic curves were recorded for compounds in aqueous methanol solution using 1M potassium chloride as supporting electrolyte and BR buffer of different pH (5, 7, and 9). For this purpose potassium chloride (1ml, 1.0M), 4ml of BR buffer of desired pH, were taken in the electrochemical cell and methanol was added to this mixture so as to make up the final solution volume to 10 ml. After purging this solution with nitrogen for 10 minutes to remove the dissolved oxygen, 0.01M reactant was added to blank solution then initial potential, final potential, scan rate and current sensitivity were provided and the resulting current was measured as a function of applied potential. These conditions were subsequently applied for carrying electrochemical reduction at stainless steel electrode (SS-316) galvanostatically. The conventional H-type cell with two limbs separated by G-4 disc was used for electrolysis. The supporting electrolyte (1M) sodium acetate was filled in both the limbs. The reactants (0.01M) were dissolved in alcohol and placed in cathodic chamber and the pH of cathodic solution was 9. Methanol was also added in cathodic chamber. The stainless steel (SS-316) was used as cathode as well as anode. The constant current of 1 amp was passed through the electrolyte for suitable period (Table -1) hours with the help of a galvanostate (CDPE make, University of Rajasthan, Jaipur). There after the working up of the reaction mixture involved extracting the solution with diethyl ether (3×25ml). The ether layer was then separated and washed with aqueous saturated NaCl solution. The organic extracted were dried over anhydrous Na₂SO₄ and than characterized.

The resulting final products obtained were characterized by spectral analysis viz. IR, NMR, Mass. The purity of products was checked by single spot obtained by thin layer chromatography (TLC). NMR spectra were recorded in CDCl₃ solution on Joel (Japan) 300 MHz spectrophotometer and IR spectra were recorded by using Nicolet (USA) FTIR Spectrophotometer. Samples were sent to CDRI for mass spectral analysis. These results are shown in Table-1.

RESULTS AND DISCUSSION

Reduction using electroanalytical technique

The reduction of carbonyl compounds in aqueous solution depends on the pH of the system. Cyclic voltammograms were recorded in acidic, neutral and basic conditions. Reduction

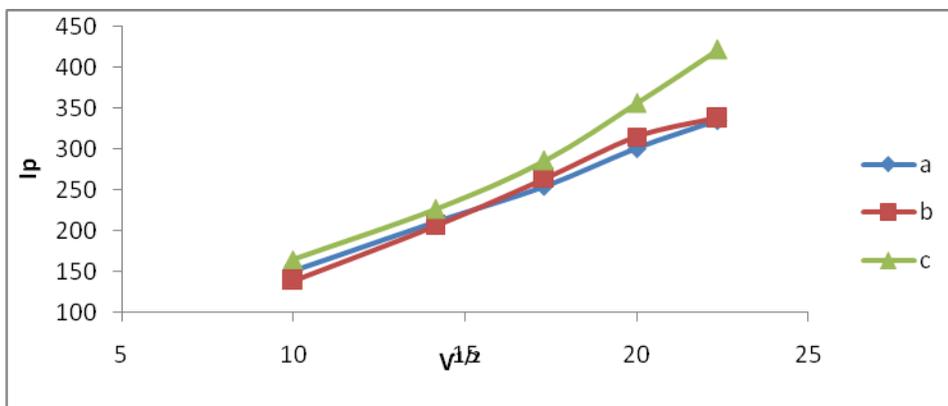
was carried out in basic medium. In alkaline solutions electrons come from water which decomposes to yield hydrogen and hydroxyl ion. Parameters evaluated from cyclic voltammograms are shown in Table 2.

Table-1 Spectroscopic results of products obtained by electrochemical reduction:

Product Name	Reaction time (In hours)	Boiling point (°C)	Yield	IR Data (cm ⁻¹)	NMR Data(δ-Value)	Mass Spectra (m/z)
2-tertbutyl Cyclohexanol	7	208	79	3340(OH Str) 2930(CHStr) 1440&1330(CH ben.) 1365&1395(Tertbutyl) 1110(C-O)	2.2(OH) 3.15(CH) 1.48(CH) 1.38(CH ₂) 1.43(CH ₂) 1.57(CH ₂) 1.05(CH ₃)	156 82 67 57
4-tertbutyl Cyclohexanol	7	212	81	3410(OH) 2945(CHStr) 1435&1320(CHben.) 1365&1390(Tertbutyl) 1130(C-O)	2.1(OH) 1.57(CH ₂) 3.15(CH) 1.40(CH) 1.42(CH ₂) 1.05(CH ₃)	156 82 67 57
4-Ethyl Cyclohexanol	6	184	82	3370(OH) 2975(CHStr) 1475&1385(CHben) 1150(C-O)	2.3(OH) 1.27(CH ₂) 1.41(CH) 1.37(CH ₂) 3.18(CH) 1.58(CH ₂) 0.95(CH ₃)	128 81 57 43

Effect of scan rate

From cyclic voltammograms it is clear that as the sweep rate was gradually increased to 100,200,300, 400 and 500 mV/sec, peak potential (E_p) gradually shifted towards higher values. The cathodic peak current (I_p) increases with increasing scan rate. The current function (I_p / ν) has been found to be fairly constant with respect to scan rates indicating that the electrode process is diffusion controlled. The dependence of the voltammetric peak current (I_p) of the wave on the square root of scan rate ($\nu^{1/2}$) is linear with correlation coefficients close to unity at all the pH(Graph 1).



Graph 1: Variation of the cathodic peak current (I_p) with $v^{1/2}$ for 'a' (2-tertbutylcyclohexanone), 'b' (4-tertbutylcyclohexanone), 'c' (4-Ethylcyclohexanone) at pH 9.0

Table 2: Voltammetric data evaluated from cyclic voltammogram at pH 9.0

Compound	Scan rate (v) (mV/s)	Epc (mV)	Ipc (μ A)	$I_p/v^{1/2}$
2-tertbutyl cyclohexanone	100	-635	151	15.1
	200	-662	211	14.92
	300	-674	255	14.72
	400	-693	301	15.05
	500	-702	335	14.98
4-tertbutyl cyclohexanone	100	-829	139	13.9
	200	-885	206	14.56
	300	-908	264	15.24
	400	-937	315	15.75
	500	-957	338	15.11
4-Ethyl cyclohexanone	100	-680	165	16.5
	200	-707	227	16.05
	300	-727	286	16.51
	400	-729	356	17.8
	500	-735	422	18.87

Effect of pH

Typical voltammogram of 2-tertbutylcyclohexanone, 4-tertbutyl cyclohexanone and 4-Ethylcyclohexanone has been shown in Fig. 4-6. From this it is clear that the reduction of compound can be carried out in acidic, neutral and basic medium. As it is clear from cyclic voltammogram peak height is high in case of basic medium so the reduction is expected to be feasible and will provide good yield. It was concluded that reduction can be best carried out in basic medium.

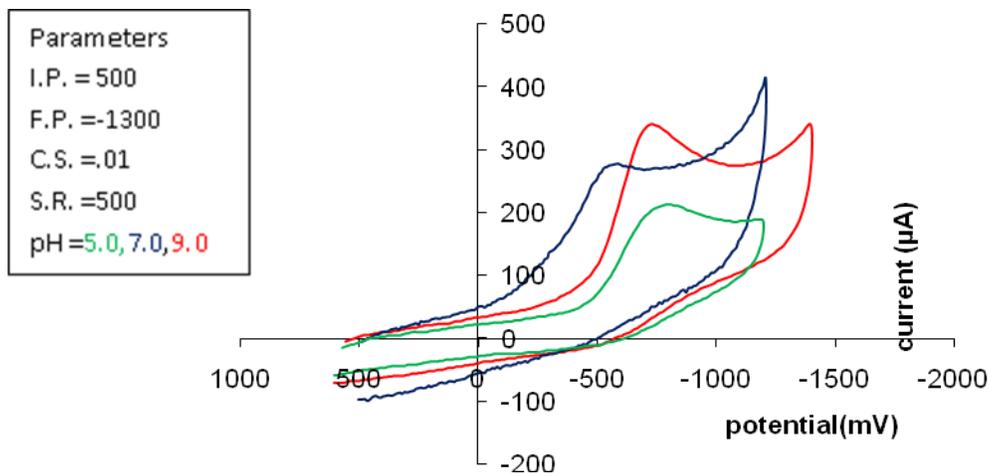


Fig 4: Effect of pH on reduction of 2-tertbutylcyclohexanone

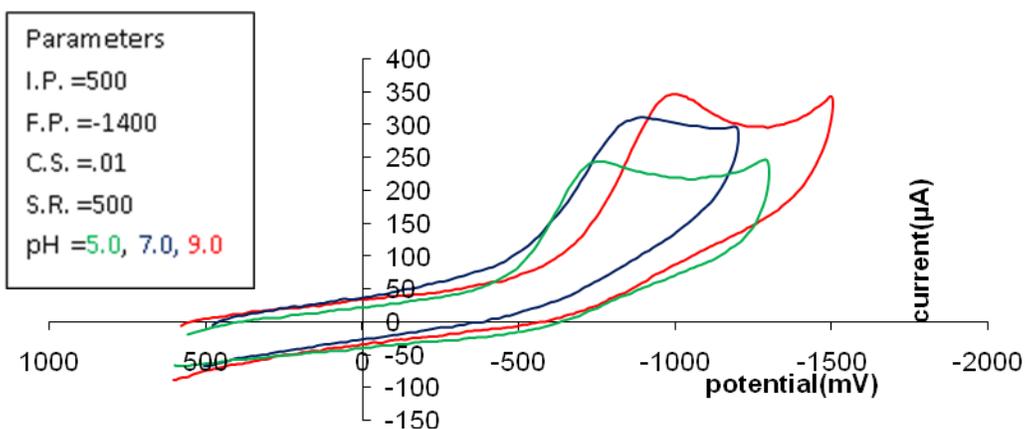


Fig 5: Effect of pH on reduction of 4-tertbutylcyclohexanone

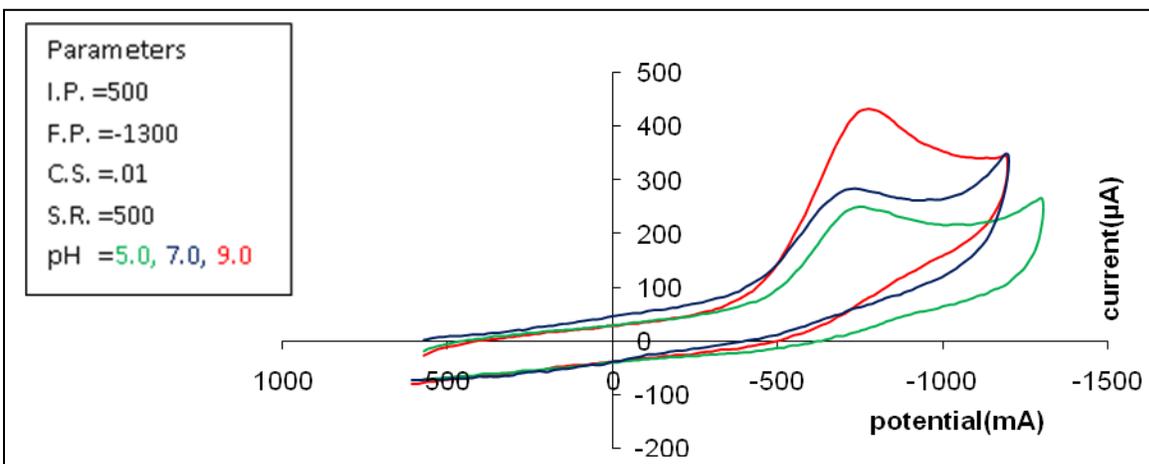


Fig 6: Effect of pH on reduction of 4-Ethylcyclohexanone

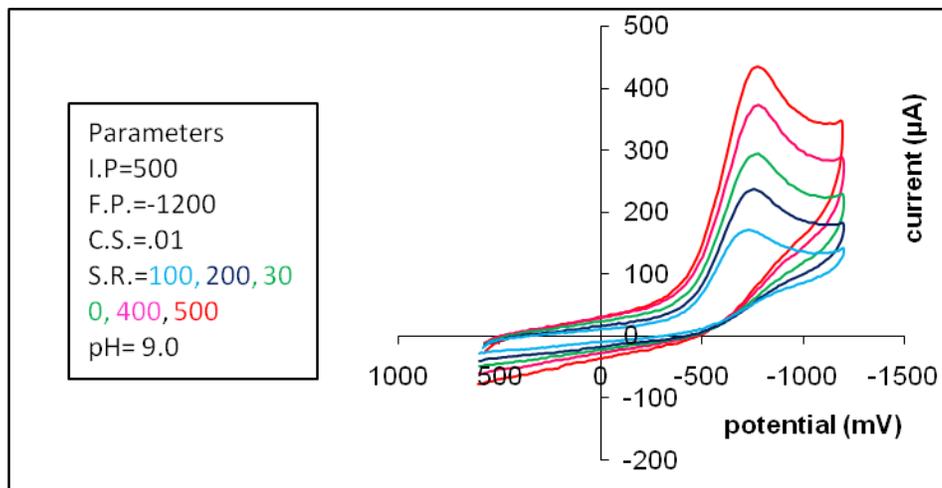


Fig 3: Effect of scan rate on reduction of 4-Ethylcyclohexanone

CONCLUSION

The present work is an attempt to apply alternative synthetic routes using electrochemical reduction of substrates into useful products and has merits like specificity & cost effectiveness. It is expected to reduce the ever-increasing problem of pollution caused by hazardous, corrosive chemicals and harsh reaction conditions.

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