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ECO-Friendly Synthesis of Alcohols by Microbial and Electrochemical Techniques

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Abstract : The reduction of Benzophenone and o-hydroxyacetophenone was carried out via microorganism i.e. Baker's Yeast in free as well as in immobilized forms and electrochemical method. These reduction processes were investigated to explore the alternative eco-friendly routes for the synthesis of alcohols. The products obtained after completion of reaction were isolated, purified and characterized by combined application of chromatography including HPLC and spectroscopic techniques.
Key words : Electrochemical reduction, Baker's Yeast (BY),Immobilized Baker's Yeast (ImBY), Cyclic Voltammetry.

Introduction:

Chemistry plays a pivotal role in the improvement of quality of life around the world. However, these advances frequently came with an increase in contamination of the environment by toxic substances. Nowadays steps are being taken, mainly due to increasing economic, social, legal, and environmental pressures, to avoid further degradation. Therefore, the use of the so-called Green Chemical Processes where the "best available technology" not entailing excessive cost and aspiring to "performance without pollution" can be used in industrial processes is stimulated [1]. We are now seeing momentum building around the green theme, where products, processes, and technologies which are green deemed good for mankind. Catalysis has been and will continue to impact the discovery and development of environmentally attractive technologies and products [2].

In this context, the electro Chemical synthesis is a novel alternative method in organic synthesis,where one can synthesize the desired compound by oxidation or reduction of substrate.Here electron plays an important role and acts as a reagent and is obtained during the electrochemical reaction.This avoids undesirable byproducts and simplifies the otherwise cumbersome work up procedure.A fundamental reason for the importance of the electrochemical technology to minimize environmental problems is that it uses electricity as energy source.

Electrochemical technology can also be used directly in several applications involving the removal and degradation of potential solid and liquid pollutants from industrial wastes in water, soil and atmosphere [3].

The Carbonyl group is an electrophoric group offering interesting synthetic possibilities.The reduction of large number of organic compounds including carbonyl compounds has been carried out using stainless steel electrode in aqueous medium at controlled potential [4-5]and controlled current [6-8] in our laboratory.

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The another green Chemical technique is Biotransformation i.e. synthesis mediated by microbial catalyst such as Baker's Yeast. The Baker's Yeast is a common micro-organism that can be used for this purpose since it is economical and more easily available than the purified reductase which has the additional disadvantage that it needs expensive co-factors like Nicotinamide adenine dinucleotide (NADH), Nicotinamide adenine dinucleotide phosphate (NADPH) etc.

The process based on whole cell catalysts has a host of advantages viz. more efficient, less expensive and last but not the least sustainable with respect to conserving the resources. It is efficient and compared to other routes less expensive. It is sustainable and conservere sources. As a result, the need for effective, selective reactions to create chiral building blocks to make single isomer drugs is only going to increase. In addition to this, the need for these reactions to be cost effective, high yielding and devoid of use of dangerous or corrosive reagents.

Chiral alcohol are important intermediate in the synthesis of pharmaceutically activities such as Dawpharma has been developed a catalytic route to chiral 1-aryl-2-imidazol-1-yl ethanols using asymmetric transfer hydrogenation [9] racemic alcohols with an imidazole group in the alpha position relative to the hydroxyl group are an important.

The aim of present investigation is to explore novel ecofriendly methods of synthesis of optically pure alcohol using free Baker's Yeast (BY) as well as immobilized Baker's Yeast (ImBY) and electrochemical method.

Experimental

1. Electrochemical:

The electrochemical reduction of benzophenone and o-hydroxyacetophenone, utilizing the optimum conditions derived from cyclic voltammetry, were carried out at room temperature. Cyclic voltammograms were recorded at the scan rate of 100 mV/sec using a computer based ECDA-001 instrument, 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 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).

2. Biotransformation:

In a one-liter round-bottom flask, equipped with magnetic stirrer (Remi Make) 200ml water, 50gm fresh baker's yeast and 4gm glucose were placed and the suspension was stirred for 30 minutes. The substrates (2 m mol) were separately dissolved in to ethanol (50 ml) and ethanolic solution was poured into Baker's Yeast Suspension. The resulting mixture was filled in with water until one liter and magnetically stirred for a suitable period. The suspension changed its colour from orange to yellow which indicate the completion of the reaction, thereafter the product was separated from the mixture by filtering the solution. The filtrate was extracted with methylene chloride .The extract was dried over sodium sulphate and on evaporating it, the product was obtained. The product of the reaction was isolated, purified and characterized by combined application of chromatographic technique and spectroscopy.

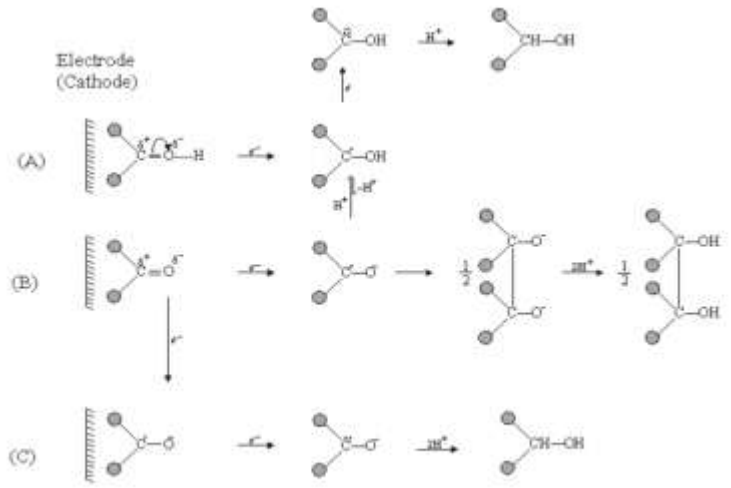
Immobilization of Baker's Yeast:

Micro-organism entrapment in a gel or a membrane or within microcapsules: Applicable for laboratory as well as industrial use (urethane, cellulose, agar, alginate, Collagen, chitosan, k-carragenan and montmorillonite – K10 [10-11] have been used as polymers porous networks for entrapment. Polymerization of unsaturated monomers in the presence of an enzyme often results in its occlusion with in the interstitial spaces of the gel.The polyacrylamide gel was prepared by the method used previously in our laboratory [12-13].

Results and Discussion

1. Electrochemical:

The reduction of carbonyl compounds in aqueous solutions depends on the pH of the system. Thus at low pH values these compounds exhibit two irreversible-single electron waves [14], 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 alcohol [15]. This suggests the mechanism as predicted in Sch. 1



Scheme 1. The 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 wave [16-17]. 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. (Benzophenone, O-Hydroxyacetophenone)was dissolved in the alcohol and placed in the cathodicchamber. The stainless steel (SS 316) electrode having an area 2x3 cm^2 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 Na_2SO_4 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 Table -1.

Biotransformation:

The actual reducing agent in present system is Nicotinamide Adenine Dinucleotide Hydride(NADH).NADH donates H^- (hydride ion) to aldehydes or ketones (and thereby reduces them). The electron lone pair on a nitrogen atom of NADH pushes out H^- which adds to a carbonyl group in another molecule to cause a reduction.

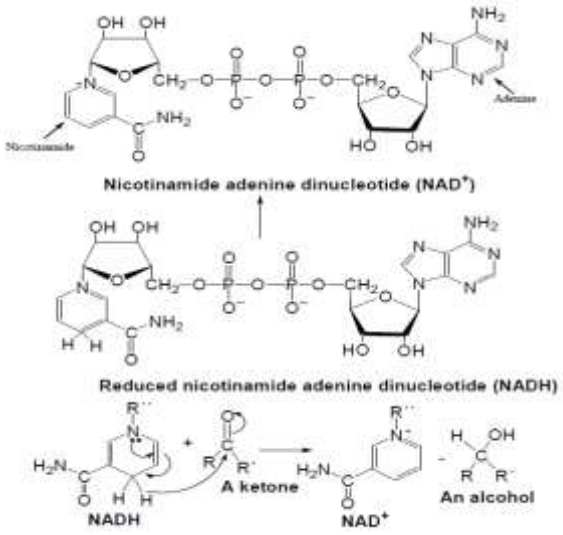


Figure 2.Depicting biological pathway for reduction of carbonyl group bycofactor

The amount of NADH in the yeast cell is limited to a quite low level. In order to allow the reduction continuously, it is therefore necessary to active another biological pathway to reduce (Nicotinamide Adenine Dinucleotide ion) NAD+ in to NADH. Yeast contains some saccharides in the cell, which reduce NAD+ to NADH via pentose-phosphate pathway. The addition of glucose to the reaction mixture ensure simultaneous feeding of the yeast cells which ultimately results in enhanced concentration of NADH, which is regenerated from NAD+ via pentose phosphate pathway. This will ultimately ensure increase in the enantiomeric excess (ee) of the product. Immobilization enhances the operational stability of FBY and isolation of the products becomes easier. In addition, reuse of the catalyst is often possible under these conditions the product formation rates are usually high [18], not only because of the inhibitory influences but also high cell population. It also permits easy continuous operation since immobilized cells can be easily removed from the reaction medium and can be repeatedly reused although with decreasing activity of the immobilized cells.As Compared with classical methods which generally involve use of either corrosive reagent or yield product which are burden to the ecosystem. The use of baker's yeast offer alternative to carry out reduction a quite simple installation, at room temperature with an easy work-up of products and good yields which is essentially green.

The spectroscopic results of product are summarized in Table-1, which suggest that the product is alcohol.

Table 1. Showing the results

S.No.	Substrate Name	Reaction Time (In Hours)with (BY)	FBY Yield (%)	ImBY Yield (%)	Ele.Chem. Yield (%)	Mass Spectra (m/z)	IR Data (cm^{-1}	NMR Data (δ- Value)
1	Benzophenone	48	86.24	71.31	91.74	184,183,77, 107	3407,1623-1593,1055	7.25-7.50 (m, 10H) 4.98(s,1H), 5.56(s,1H)
2	O-Hydroxyacetophenone	48	78.39	68.42	76.13	138,137,93,45	3431,3405, 1619,1602, 1071	6.80-7.22(m,4H), 4.81-4.75(bs,2H) 4.03(q,1H) 1.49(d,3H)

Conclusions

This is an attempt to apply an alternative synthetic routes involving electrochemical as well as microbial catalyst assisted biotransformation of organic compounds and has merits like specificity & cost effectiveness. It is also expected to reduce the ever-increasing problem of pollution caused by hazardous, corrosive chemicals and harsh reaction conditions. Both the above methods can bring about the reduction in

high yield. Immobilization of the microbial catalyst has further additional advantages like reuse and easy work up besides cost effectiveness.

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