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Biphasic Inspired Electrocatalytic Oxidation of Substituted Alcohols to Aldehydes or Ketones with Platinum Electrode Using Potassium Iodate as a Mediator

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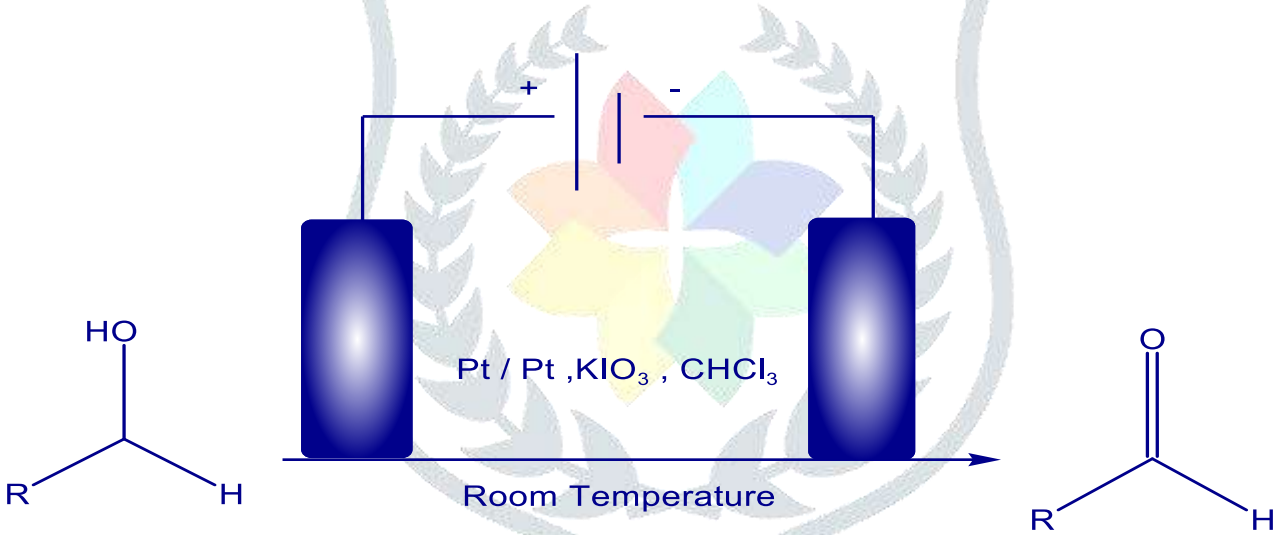
Abstract: Electrochemical oxidation of substituted benzyl alcohols including primary and secondary alcohols was performed in an undivided cell equipped with platinum electrodes in a biphasic medium using a potassium iodate as a mediator with con. sulphuric acid. The various substituted alcohols were efficiently oxidized to aldehydes and ketones in good yields with maximum selectivity (> 99%). The iodate-containing mediator showed a 98% yield of benzaldehyde under biphasic electrolysis. HPLC data analysis confirms the existence of a high-quality yield. The plausible carbon-centered free radical mechanism for the iodate oxidation system is explained.

Keywords: electrochemical oxidation; biphasic medium; undivided cell; free radical; substituted alcohols.

I. INTRODUCTION

The selective oxidation of primary alcohols to aldehydes is one the long-standing in organic chemistry. Although a large number of oxidation processes are known, it is difficult to find one that is selective, inexpensive, efficient, and easy to develop. Carbonyl compounds, which are oxidation products of alcohols have many applications as chemical intermediates, pharmaceuticals, agrochemicals, flavors, and /or perfumes [1]. Two-phase electrolysis has a distinct advantage over conventional homogeneous electrolysis in terms of ease of handling and recycling of intermediates [2]. Oxidation of benzyl alcohol with benzaldehyde by two-phase electrolysis has been studied with a platinum anode and a platinum pole. A high yield of benzaldehyde (98%) with high current efficiency (98%) has been achieved [3]. The use of Br^-/ OBr^- and NO^{-3}/NO as a redox mediator for the conversion of some primary and secondary alcohols has been reported [4]. Presently, IO^{-3}/IO using as a mediator for the electrochemical oxidation of alcohol to aldehydes or ketones. After the completion of electrolysis, the separation and evaporation of organic layers provide products. *Pletcher* ***et al*** report on the benefits of electrolysis twice is a convenient process in practical organic synthesis [5].

The chemistry and environmental benefits of electrochemical processes are catalyzed by medical oxidation systems using biological and inorganic mediated materials that have been proven for oxidation of different organic compounds [6]. Two-phase electrolytic systems can be easily used to convert alkyl aromatic compounds to monobromated derivatives with a quantitative yield [7]. Currently, there are only a few reports of chemical synthesis as good as the two-phase electrolysis method [8,9]. Using toxic metal salts and transition metals for the conversion of alcohol oxidation to aldehydes [10-16]. Several reports on synthesis are currently available fine chemicals by two-phase electrolysis process [17,18]. Electrochemical oxidation was performed using a variety of electrodes, as described in the literature [19-21]. The product aldehydes or ketones were determined by HPLC. Authentic samples were used to calculate the peak area of the corresponding experimental products for yield calculation. The alcohols and other reagents were purchased from Sigma-Aldrich, Alfa-Aesar & Merch. They were used without further purification. The novelty of this present method has numerous advantages like it has very simple reaction conditions, undivided cell, constant current electrolysis, low cost, easy scale-up, economically very cheap reagents compared with the conventional reactions, green solvent water used as a maximum, no by-product and almost no waste problems.



Scheme 1. Electrochemical oxidation of alcohols in biphasic medium

II. EXPERIMENTAL SECTION

General procedure for electrochemical selective oxidation of substituted benzyl alcohols:

A (1.08g 10mmol) solution of substituted benzyl alcohol dissolved in 20 ml of chloroform was placed in an undivided beaker-type cell. To this solution was added 1% potassium iodate solution containing 2 ml of H_2SO_4. Platinum electrodes (15 cm^2) were placed on the upper aqueous phase. It was stirred at a speed of 50 rpm with a magnetic stirrer so that only the organic phase did not touch the electrode. Electrolysis was performed in a constant current manner at a current density of 40 mA/cm^2 until the amount of charge indicated in Table 1 was passed. The electrolysis was monitored by HPLC (Shimadzu) using a shim pack ODS-18 column (250 mm,4.6 mm) as the stationary phase. The eluent consisted of chloroform/water (80:20) at a flow rate of 1 ml/min. Samples, including the original, were analyzed using a UV detector at a wavelength of 254 nm. After the electrolysis was completed, the organic phase was separated, washed with water (2x25 ml), dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure to obtain crude benzaldehyde. HPLC analysis of the residue showed 98% purity.

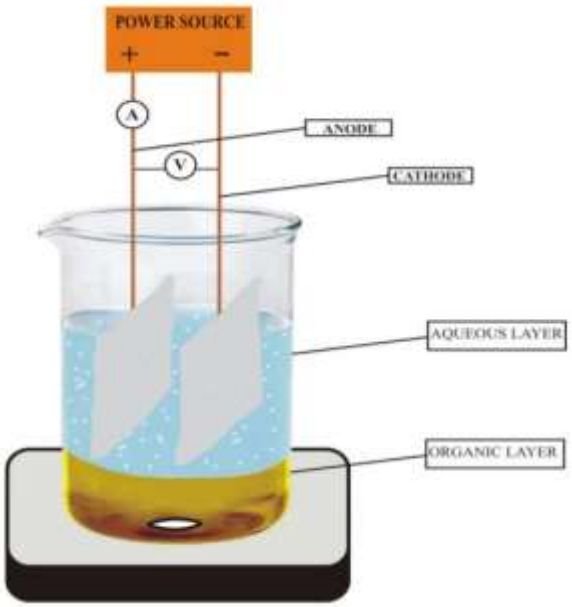


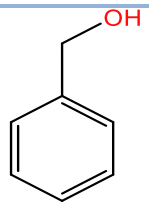
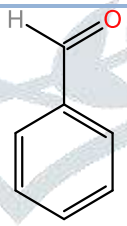
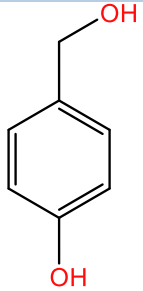
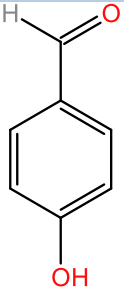
Fig1. The oxidation of benzyl alcohol to aldehyde by biphasic electrolysis

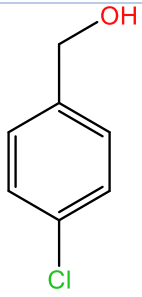
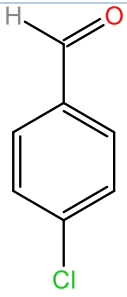
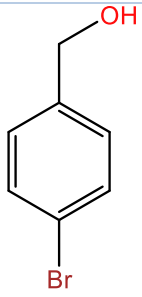
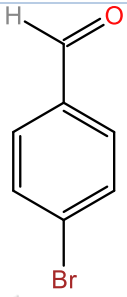
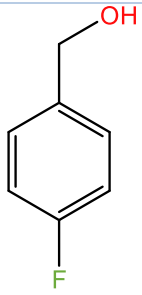
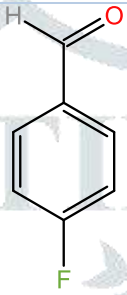
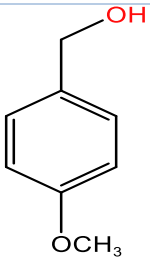
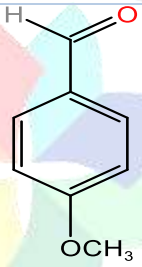
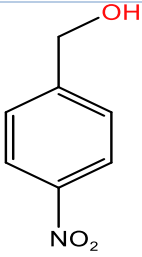
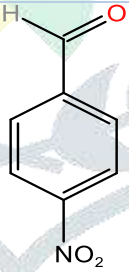
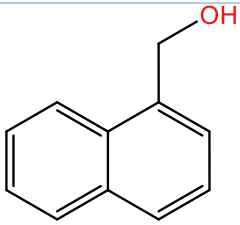
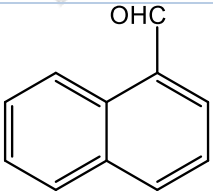
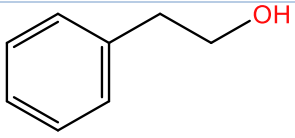
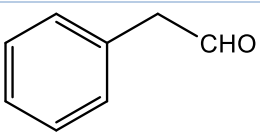
III. RESULT AND DISCUSSION

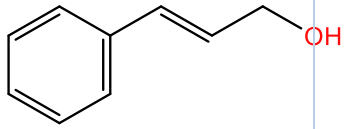
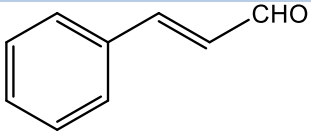
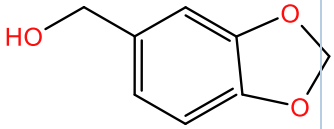
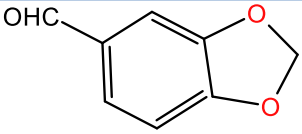
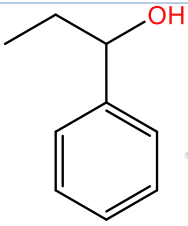
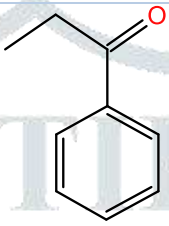
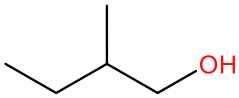
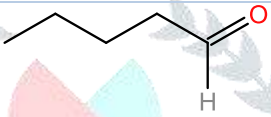
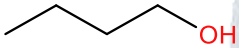
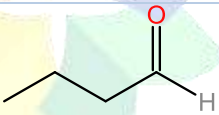
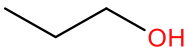
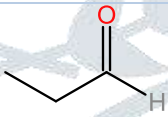
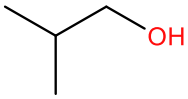
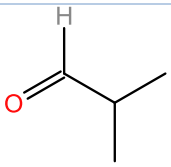
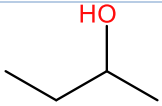
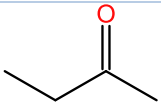
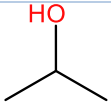
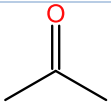
The result of the Electrochemical oxidation of benzyl alcohol was effectively carried out in a biphasic medium with 6 F/mol of charge which resulted in an excellent yield (98%). Using this biphasic system substituted alcohols were oxidized to the corresponding aldehydes and ketones at room temperature in a single compartment cell with high yields. The yields of the products are listed in Table 1.

Table 1

Electrochemical oxidation of primary and secondary alcohols in biphasic medium:

Entry	Substitute	Charge Passed (F/Mol)	Product	Yield (%)	Faraday	Current Efficiency (%)
1		6		98	2	98
2		6		94	2	94

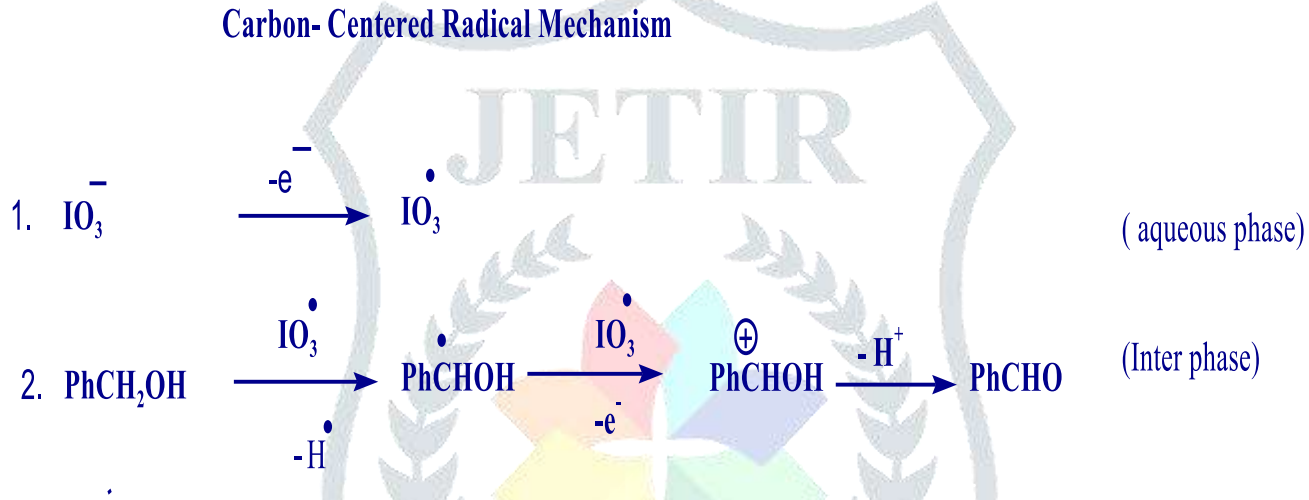
3		6		91	2	91
4		6		86	2	86
5		6		92	2	92
6		6		93	2	93
7		6		4	2	4
8		6		87	2	87
9		6		65	2	65

10		6		88	2	88
11		6		21	2	21
12		6		41	2	41
13		4		52	2	52
14		4		48	2	48
15		4		78	2	78
16		4		50	2	50
17		4		19	2	19
18		4		28	2	28

BIPHASE ELECTROLYSIS CONDITIONS:

Current density	: 40mA/cm^2;
Electrodes	: Platinum/platinum;
Temperature	: Room temperature (30^{0}C);
Stirring rate	: 50rpm;
Aqueous layer	: 1.08 mmol KIO_3 + H_2SO_4(2 ml);
Organic layer	: Substituted alcohols (10mmol) dissolved in chloroform (20 ml)

As a result, the plausible free radical mechanism for iodate the mediation selective oxidation of benzyl alcohol to benzaldehyde by a two-phase electrolysis process is shown in scheme 2.



Scheme 2. Carbon-centered free radical mechanism

Potassium Iodate was chosen as a cheaper mediator to carry out the selective oxidation of alcohols effectively in biphasic electrolysis. In the aqueous phase, one-electron oxidation of iodate ion allows in situ generations of iodate radical which is known to be an efficient hydrogen abstractor. Electrochemically generated iodate free radical reacts with substituted alcohols at the interphase region of the organic and aqueous phase selectively to offer aldehydes or ketones [22-26].

Finally, the Iodate radical can be effectively regenerated at the platinum electrode after reaction with substituted alcohols. After completion of the electrolysis separating the organic phase and evaporation of the organic solvent afford the products. This reinforces the role of reactive free radicals in the primary mechanism of action of free radical scavengers.

Benzyl alcohol was oxidized to benzaldehyde it can be seen from table 1 that oxidation of primary alcohols, in general, resulted in high yields of the corresponding benzaldehydes (86 – 98%) whenever the activating groups were present on the benzene ring (entry 1 – 6)

The current efficiency values varied from low to high depending on the alcohols. It is because of the adsorption of the alcohols on the electrode surface which blocked further reaction and the electrode had to be wiped frequently that the reaction required extra time and the current efficiency values went down in some cases. We observe smooth oxidation of aromatic alcohols substituted with electron-donating substituent like methoxy (entry 6) on phenyl ring have resulted in good yield (93%)to the substituted benzaldehyde while alcohols substituted with an electron-withdrawing substituent like -hydroxy, chloro, -Bromo, -fluoro (entry 2,3,4,5) required 6F/mol of electricity with a yield of 94. 91,86 and 92 % respectively.

The strong electron-withdrawing group like – nitro substituted benzyl alcohol (entry 7) gave only 4% aldehyde due to its poor solubility in chloroform solvent, the reaction did not proceed at all as expected because of the high destabilization of carbocation intermediate that would be formed during the reaction.

The oxidation of 1-naphthyl alcohol yielded 1-naphthaldehyde was 87 % similar to that observed in the case of substituted benzyl alcohols (entry 8).

In the case of 2 -phenyl ethanol (entry 9) yielded phenylacetaldehyde was 65% required 6F/mol of electricity. Biphasic electro-oxidation of cinnamyl alcohol was converted into cinnamaldehyde in high product quantitatively (88%) (entry 10) without disturbing the side chain of the C=C double bond, This is due to the high stabilization of the allylic carbocation intermediate that formed, due to the competitive addition of hypo halogens acids to the double bond[27].

The oxidation of 3,4 (methylenedioxy) benzyl alcohol (entry 11) gave a low aldehyde yield (21%). The low yield is caused by the adsorption of the substrate on the electrode due to the presence of ethereal oxygen atoms present in the molecule, which may hinder the normal oxidation process. Low productivity is due to the adsorption of the substrate on the electrode due to the presence of oxygen atoms in the molecule can interfere with the normal oxidation process.

Secondary alcohol like 1-phenylpropanol (entries 12) required a slightly longer reaction time compared to primary alcohols to afford the corresponding ketone in 41 % yield. This is expected because the presence of an additional methyl group may have steric hindered the bulky iodate radical to come closer to the benzylic hydrogen hence the yield was poor.

In the case of oxidation of linear aliphatic primary alcohols such as amyl alcohol, n-butyl alcohol, n-propyl alcohol, and 2- methyl propanol (entry 13,14,15,16) were converted to the corresponding aldehydes yield 52,48,78 and 50% respectively

In the case of oxidation of linear aliphatic secondary alcohols such as 2 butanol and isopropyl alcohol, gave low yields of the product ketone yield were 19% and 20% (entry 17,18). From the above results, it can be concluded that this method applies to all kinds of oxidation of alcohol. The products were characterized by their IR and NMR spectra and HPLC data analysis.

IV. CONCLUSION

Potassium iodate mediator, platinum electrodes selective electrochemical oxidation of benzyl and substituted benzyl alcohols including primary and secondary alcohols in biphasic media to the corresponding aldehydes in good to excellent yields at temperature. This method brings more advantages than homogeneous systems concerning easy handling. The biphasic electrolysis setup is so simple, inexpensive, and economically accessible that the reactions can be carried out at room temperature and contributes to a more environmentally friendly and pollution-free synthesis. The advantages of two-phase electrolysis over homogeneous electrolysis are emphasized. The current process involving primary and secondary alcohols using iodate mediators to the corresponding aldehydes or ketones is easy and inexpensive to obtain. It's important to remember that primary alcohol is oxidized to the corresponding aldehydes and over-oxidation to the corresponding carboxylic acid does not result. Also, it avoids the use of toxic chemicals and expensive reagents.

V.ACKNOWLEDGEMENT

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