Academic Sciences International Journal of Pharmacy and Pharmaceutical Sciences

ISSN- 0975-1491 Vol 5, Suppl 2, 2013

Research Article

A NOVEL BIPHASIC ELECTROLYSIS METHOD FOR THE OXIDATION OF 4-METHYLBENZYL ALCOHOL BY *IN-SITU* GENERATED HYPOCHLOROUS ACID USING NaCl AS ELECTRO CATALYTIC MEDIATOR

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Received: 21 Mar 2013, Revised and Accepted: 30 Apr 2013

ABSTRACT

Objective: The objective of the present work is to investigatethe electrochemical oxidation of 4-methylbenzylalcohol to4-methylbenzaldehyde in the presence of water soluble electrocatalytic mediator sodium chloride with newly generated hypochlorous reactive species by biphasic electrolysis system.

Methods: Optimization studies have been carried out on an undivided beaker-type cell. The various parameters of 4- methylbenzyl alcohol influencing the reactions such as current density, mediator, acid and solvent have been investigated.Comparative study has been carried out for chemical and electrochemical method.

Results: The Chloride containing mediator showed 96% yield of 4-methylbenzaldehyde under biphasic electrolysis. HPLC analysis confirms the existence of High quality of the yield. The plausible mechanism for the chloride oxidation system is shown in scheme 2.

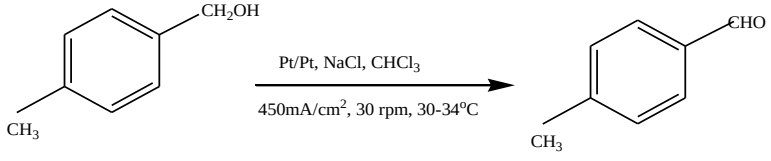
Conclusion: The electrolysis was carried out with the passage 3F of electricity which showed the good yield of 96%4-methylbenzaldehyde may serve as a leads for further optimization.

Keywords: Biphasic electrolysis, 4-methylbenzylalcohol,Chloroform, Sodium Chloride, Undivided cell.

INTRODUCTION

Selective catalytic oxidation of alcohols to corresponding aldehydes or acids is of great importance for both laboratory and synthetic industrial applications [1**].**In recent years, electro organic synthesis has attracted attention as an environmentally friendly process because electrons are inherently environmentally friendly reagents compared with conventional oxidizing and reducing reagents.Traditionally electrochemical oxidation is carried out using transition metal compounds such as chromium (VI) oxide, permanganates, ruthenium (VIII) oxide and dichromates to accomplish these transformations. Most of these reagents are, however, required in stoichiometric quantities which results in the production of large amounts of environmental waste**[**2–4**].** Generally alcohol oxidation requires stoichiometric amounts of toxic heavy metal salts or expensive catalysts containing transition metals[5–12].The development of green chemical processes has become one of the most important tasks for chemical researchersto date [13**].**In particular, aldehydes represent an important class of products and versatile intermediates in the field of fine chemicals such as fragrances or food additives [14**].**Benzylic and allylic alcohols are selectively oxidized to aldehydes under the conditions of anodic oxidation of alcohols at the hydroxide nickel anode in the two-phase system K_2CO_3 (aq) petroleum ether. In the case of primary alcohols, the process can be directed to the predominant formation of aldehydes by their extraction in the course of electrolysis into the non-polar organic phase thus preventing further oxidation to carboxylic acids [15**].** Nowadays green innovatory practices have great impact on organic synthesis as they create awareness on environmental issues. Thus, silica-supported reagents [16] and carbon-supported platinum catalysts [17]reported in the literature as environmental benign reagents for the synthesis of aldehydes.Quaternary ammonium salt [18]was used to oxidize alcohols with electro-generated hypobromite as emulsionelectrolysis. Mainly in direct electrolysis system oxidation of alcohols is in most cases not selective, yielding mixture of benzyl alcohols, benzaldehydes and oligomers and polymers [19-24]. Biphasic electrolysis has a distinct advantage over conventional homogeneous electrolysis recycling [25].In homogeneous systems, lower selectivity is observed due to over-oxidation of the substrate on the surface of the electrode leading to a mixture of products. In biphasic electrolysis systems, the reactive species formed by electrolytic oxidation of a halide ion in the aqueous phase can be taken continuously into the organic phase, and then reacted with the substrate selectively to yield the products. After completion of the electrolysis, separation and evaporation of the organic layer affords the product.Presently, only a few reports are available on the syntheses of fine chemicals by biphasic electrolysis method [26-27].4-methoxybenzylalcohol has beenoxidisedby photochemical reaction using TiO_2 as electrode [28]**.** Recently [29-30]we reported that a two-phase electrolytic system can be used readily to convert the oxidation of benzyl alcohols using sodium nitrate and CAS mediators. Herein we further developed a novel method for the controlled oxidation of 4-methylbenzylalcohol using *in-situ* generated hypochlorous reactive species to the corresponding 4-methylbenzaldehyde.The Present study yields maximum of 96% without usingPhase transfer catalyst than the work reported earlier using PTC [31]

The objective of the present investigation is two-fold Procedure. Firstly to study the indirect electrochemical selective oxidation of 4-methylbenzylalcohol by biphasic electrolysis to get optimum operation conditions,and secondly to obtain reliable data on yields and selectivity of the corresponding parameters. The maximum yield of 96%4-methylbenzaldehyde production at room temperature was achieved.



Scheme 1: Electrochemical oxidation of 4-methylbenzylalcohol by biphasic electrolysis.

Experimental conditions for oxidation for 4-methylbenzyl alcohol

S. No.	Parameters	Value
1	Temperature	30 -34°C
2	Stirring rate	30 (rpm)
3	Current density	30 (mA/cm²)
4	Substrate 4-methyl benzyl alcohol	10 mmol (1.045 g)
5	Pressure	atmospheric pressure
6	Current rate	450 (mA)
7	Anode Platinum	(15 cm²)
8	Cathode Platinum	(15 cm²)
9	Electrolyte	60 mL aqueous solution of 12% NaCl + 2mL HCl
10	Cell Capacity	120 mL
11	Charge passed	3 (F mol⁻¹)

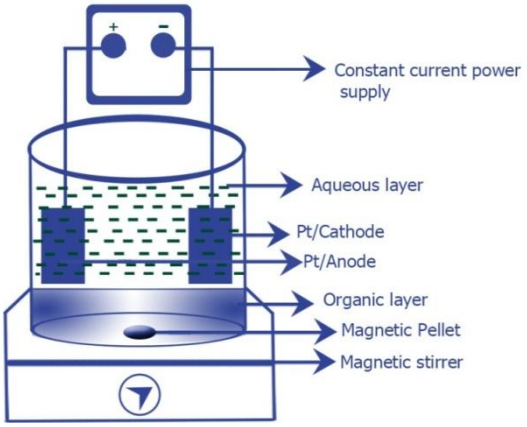


Fig. 1: Experimental Cell set up for the oxidation 4-methylbenzyl alcohol by Biphasic electrolysis.

MATERIAL AND METHODS

Standard 4-methylbenzyl alcohol was supplied by Sigma-Aldrich. All the other reagents were of Analytical grade. Sodium chloride solution was prepared by using deionized water. Aplab power source was used as a direct current source for the electrolysis. A beaker type glass cell (120 ml capacity) equipped with a magnetic stirrer was used for the biphasic electrolysis. In biphasic electrolysis of 4-methylbenzylalcohol two platinum sheets were used as electrodes (both had areas of 15 cm²). Saturated solution of sodium chloride containing catalytic amount of hydrochloric acid (2 g) was used as supporting electrolyte for higher conductivity. The electrolysis was monitored by HPLC (Shimadzu, Japan, Model. no. CLASS. VP-10) using (250 mm x 4.6 mm) as the stationary phase. The eluent consisted of acetonitrile/water (80:20) at a flow rate of 1 mL min⁻¹. Samples were analysed at a wavelength of 254 nm with a UV detector (Shimadzu UV–vis detector) coupled to a printer. Authentic samples of 4-methylbenzaldehyde and 4-methylbenzoic acid were used to calculate the peak area of the corresponding experimental product for yield calculation.

Optimization Condition for Electrochemical method

A solution of 4-methylbenzyl alcohol (1.045 g, 10 mmol) dissolved in 20 mL chloroform was transferred to an undivided electrolytic cell. An aqueous solution (60 mL) of sodium chloride (7.04g, 12%) containing 0.36 M HCl was added to the above solution. Deionized water was used for preparing sodium chloride solution. Two platinum electrodes each of 15 cm² area were placed in the upper layer of the aqueous phase without touching the organic phase but very close to the interphasial region. The aqueous upper phase acted as the supporting electrolyte and chlorine cationic source. The organic phase alone was stirred with a magnetic stirrer at a rate of 30 rpm in such a way that the organic layer did not touch the electrodes. The temperature of the contents electrochemical cell was maintained at 30–34°C throughout the electrolysis. The electrolysis was conducted Galvanostatically at a current density of 30 mA/cm²until the quantity of 3F charge was passed. An aliquot was drawn periodically from the organic phase and was monitored by HPLC. After completion of the electrolysis, the lower organic phase was separated; washed with water (2 x 25 mL), dried over anhydrous Na_2SO_4 and the solvent was removed by distillation. HPLC analysis of the residue indicated the presence of 96% of 4-methylbenzaldehyde (1.172 g) along with 4% unconverted 4-methylbenzyl alcohol.

Optimization condition for Chemical method

A solution of *p*-methylbenzyl alcohol (1.045 g, 10 mmol) dissolved in 20 mL chloroform was transferred to an undivided electrolytic cell. An aqueous solution (60 mL) of sodium chloride (7.04g, 12%) containing 0.36 M HCl was added to the above solution. Deionized water was used for preparing sodium chloride solution. The cell does not contain any electrodes, the aqueous upper phase acted as the supporting electrolyte and chloride as cationic source. Biphasic electrolysis was achieved with a magnetic stirrer at the lowest speed (30 rpm.) to prevent the separation of the two phases.

The temperature of the electrochemical cell contents was maintained at 30–34°C throughout the electrolysis. The reaction was allowed to stir up to 71 mts.After completion of the electrolysis, the lower organic phase was separated; washed with water (2 x 25 mL), dried over anhydrous Na_2SO_4 and the solvent was removed by distillation. HPLC analysis of the residue indicated the presence of 6 % of the yield 4-methylbenzaldehyde and 94% unreacted substrate 4-methylbenzylalcohol.

RESULTS AND DISCUSSION

Effect of Method

The experimental result reveals that Ex-cell method has only 6% of yield 4-methylbenzaldehyde.

But in the case of In-Cell method the maximum yield of 96% was obtained. So, the electrode plays a pivitoal role in order for the anodic oxidation of 4-methylbenzylalcohol in the In-Cell method.

Effect of Current Density

Biphasic Electrolysis conditions. Current density = 30 mA/cm², Anode/Cathode: Pt/Pt (area = 15 cm²), Electrolyte: 60 mL of aqueous solution of 12% NaCl and (0.36 M) HCl, Solvent: chloroform (20 mL), Stirring rate: 30 rpm, Cell volume: 120 mL, Type of cell: undivided glass cell, Temperature: 30-34°C

Table 1: Effect of Current Density

S. No	Current Density mA/cm²	Yield %		Time (min)	Current Efficiency % for the formation of 4-methylbenzaldehyde
		4-methylbenzyl alcohol	4-methylbenzaldehyde		
1	20	23	72	98	72
2	30	22	73	58	73
3	40	34	65	43	19
4	50	34	62	35	62
5	60	57	41	29	41

Biphasic electrolysis oxidation of 4-methylbenzyl alcohol was carried out in an undivided cell at a current density from 20 to 60 mA/cm². Table 1 and Figure 2 shows the effect of current density for 4-methylbenzaldehyde. At an optimum current density 30 mA/cm²(450mA), the current efficiency and yield were found to be 73 and 73% respectively.

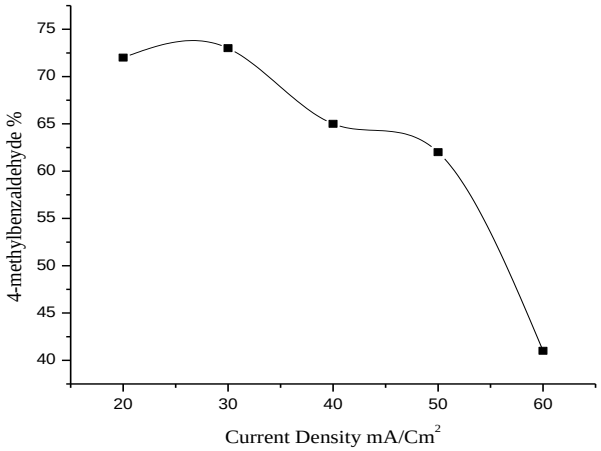


Fig. 2: Effect of Current density

Effect of Charge Passed

Biphasic Electrolysis conditions. Current density = 30 mA/cm², Charge Passed: 3F; Anode/Cathode: Pt/Pt (area = 15 cm²), Electrolyte: 60 mL of aqueous solution of (12%) NaCl and (0.36 M) HCl, Solvent: chloroform (20 mL), Stirring rate: 30 rpm, Cell volume: 120 mL, Type of cell: undivided glass cell, Temperature: 30-34°C.

The study of charge passed was carried out for the indirect electrochemical oxidation of 4-methylbenzyl alcohol.The time taken for each faraday is given in Table2and Figure 3 represents the effect of charge passed . Maximum yield of 4-methylbenzaldehyde 85% was reached at a charge of 4F/mole; the same identical result also obtained for 3F and 5F/mole. However, the minimum time and charge passed is required to conduct the biphasic electrolysis for the following parameters, so the optimum faraday choose for the biphasic electrolysis as 3F and the corresponding time can be fixed as 87mts .

Effect of Acid

Biphasic Electrolysis conditions. Current density = 30 mA/cm², Charge Passed: 3F; Anode/Cathode: Pt/Pt (area = 15 cm²), Electrolyte: 60 mL of aqueous solution of (12%) NaCl and (0.36 M) various acids, Solvent: chloroform (20 mL), Stirring rate: 30 rpm, Cell volume: 120 mL, Type of cell: undivided glass cell, Temperature: 30-34°C.

Table 2: Effect of Charge Passed.

S. No.	Charge Passed (F)	Yield %		Time (min)	Current Efficiency % for the formation of 4-methylbenzaldehyde
		4-methylbenzyl Alcohol	4-methylbenzaldehyde		
1	2	21	76	58	76
2	3	16	84	87	56
3	4	11	85	116	44
4	5	13	86	145	28

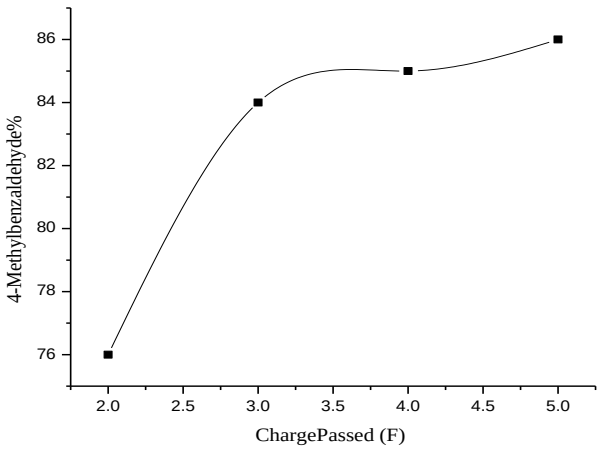


Fig. 3: Effect of Charge passed

Table 3: Effect of Acid.

S. No	Acids	Yield %		Current Efficiency % for the formation of 4-methylbenzaldehyde
		4-methylbenzyl alcohol	4-methylbenzaldehyde	
1	HCl	16	84	56
2	H_2SO_4	18	82	55
3	$HClO_4$	16	84	56
4	HNO_3	34	65	43

Acid can act as a supporting electrolyte for the biphasic electrolysis. This supporting electrolyte plays a key role in defining the environment surrounding an electrode. The Biphasic electrolysis was attempted with various acid media such as H_2SO_4, HNO_3 and $HClO_4$. It was observed that all other acids performed equally well, this means that current utilization will be the same for all the three acids except HNO_3.Hence the suitable acid for the indirect electrochemical oxidation is HCl due to its low cost. The oxidant capacity of Sodium Chloride increases in presence of the acids in the following order $HCl>HClO_4>H_2SO_4>HNO_3$.

Effect of pH

Biphasic electrolysis conditions: Current density = 30 mA/cm^2, Charge Passed: 3F; Anode/Cathode: Pt/Pt (area = 15 cm^2), Electrolyte: 60 mL of aqueous solution of (12%) NaCl and pH range (1.0, 7.0 and 12) ,Solvent: chloroform (20 mL), Stirring rate: 30 rpm, Cell volume: 120 mL, Type of cell: undivided glass cell, Temperature: 30-34°C.

Different pH ranges were conducted at room temperature using alkaline range, Neutral range, and acidic range .The pH range has been continuously monitored during the experiment by using pH meter. Prior to all other ranges the acidic pH range giving the maximum yield of 96%, so acidic pH range can be chosen for the indirect electrooxidation of 4-methylbenzyl alcohol to 4-methylbenzaldehyde. Table 4 represents the effect of pH.

Effect of Solvent

Biphasic electrolysis conditions: Current density = 30 mA/cm^2, Charge Passed: 3F; Anode/Cathode: Pt/Pt (area = 15 cm^2), Electrolyte: 60 mL of aqueous solution of (12%) NaCl Chloride mediator and (0.36M) HCl, Solvent: (20 mL) of various solvents (Table 8), Stirring rate: 30rpm, Cell volume: 120 mL, Type of cell: undivided glass cell, Temperature: 30-34°C. [a]CH_3CN Homogenous system.

Table 5 shows the effect of various solvents. Studies were conducted at room temperature using different solvents. Among the various solvents used for controlled oxidation of 4-methylbenzyl alcohol, Chloroform gave the best result for 4-methylbenzaldehyde (96%) a marginal increase compared to the other solvents. Carbon tetrachloride can also give the identical result for 4-methylbenzaldehyde.Since it is expensive it cannot be chosenfor the biphasic electrolysis .Similarly acetonitrile which is miscible with water forms a homogenous phase with electrolyte leading to abnormal higher cell voltage (4.5 V) and eventually higher energy consumption which also poses problems in the separation of spent mediator for recycling purposes. Therefore the ideal choice was chloroform for the biphasic electrolysis.

Table 4: Effect of pH

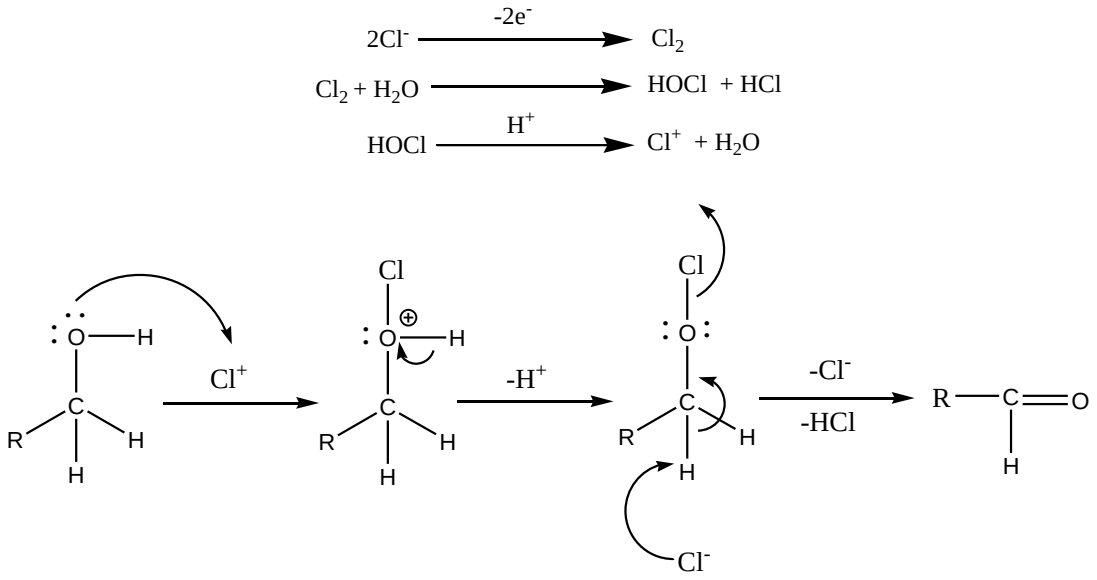
S. No.	Different pH	Yield %		Current Efficiency % for the formation of 4-methylbenzaldehyde
		4-methylbenzyl Alcohol	4-methylbenzaldehyde	
1	[a]Acidic	4	96	64
2	Neutral	31	66	44
3	[b]Basic	36	62	41

[a]Acidic (HCL), [b] Basic (NaOH)

Table 5: Effect of Solvents

S. No.	Solvents	Yield %		Current Efficiency % for the formation of 4-methylbenzaldehyde
		4-methylbenzyl alcohol	4-methylbenzaldehyde	
1	$CHCl_3$	4	96	64
2	CCl_4	6	94	63
3	[a]CH_3CN	7	89	59
4	CH_2Cl_2	19	71	47

A possible mechanism for the oxidation, based on a literature report, is outlined in Scheme 2.[32] As the electrolysis proceeds; the chloride ion is oxidized at the anode to chlorine which, on hydrolysis, results in the formation of hypochlorous acid and HCl. The unstable hypochlorous acid forms Cl^+ due to its ionic nature which subsequently oxidizes the 4-methylbenzylalcohol to the corresponding 4-methylbenzaldehyde (Scheme 2).



Scheme 2: The Possible mechanism for the biphasic electrolysis of 4-methylbenzylalchol.

CONCLUSION

In conclusion, this novel controlled electrochemical method for the oxidation of 4-methyl benzyl alcohol to the corresponding 4-methylbenzaldehyde gave excellent yields using *in- situ* prepared hypochlorous acid via biphasic electrolysis constitutes a novel and an efficient alternative procedure to traditional oxidation. Easy separation of the product, a simple work-up, room temperature reaction conditions, and the reuse of the electrolyte are advantages of this biphasic electrolysis procedure. The reactions are carried out under mild condition with a simple electrochemical setup and present several advantages such as absence of secondary products, low cost of production, high conversion and yield.

ACKNOWLEDGEMENT

The authors thank Dr. K. Kulangiappar, Electro Organic Division, Central Electrochemical Research Institute, Karaikudi-630006, India, and Mr. J. Sebastian Raja, Institute of Physical Chemistry 'Rocasolano', Department of Biophysical Chemistry, Madrid, Spain-28006, for their generous support and encouragement to carry out this work successfully.

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