Highly efficient controllable oxidation of alcohols to aldehydes using metalsalt as catalytic mediator in In-cell method: A comparative study

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[Received:1st October 2014; Revised:31st October 2014; Accepted:31st October 2014]

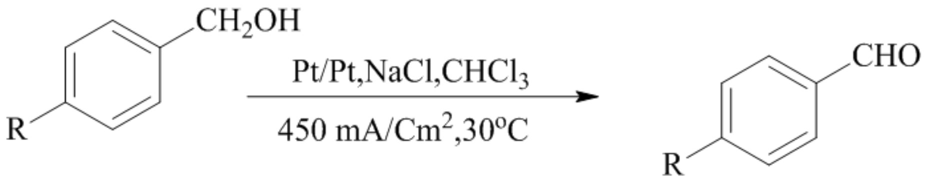
Abstract. Highly efficient controllable oxidation of p-ethyl benzaladehyde and p-ethoxy benzaldehyde form their corresponding alcohols p-ethyl and p-ethoxybenzyl alcohol. This was carried out using NaCl in Hydrochloric acid as a mediator. Reaction conditions and comparative studies were optimized to obtain maximum oxidation efficiency for the aldehyde. The mediator NaCl showed excellent activity for the controllable oxidation of various alcohols under mild conditions. Moreover, different factors which influence alcohol oxidation, for example, current density, charge passed, solvent, and reusability of spent mediator have been investigated. HPLC analysis confirms the existence of High quality of the yield. A plausible mechanism for the controllable oxidation of alcohol has been proposed.

Key words- In-cell synthesis, Indirect oxidation, NaCl regeneration, optimization.

I. INTRODUCTION

In recent times, development of efficient and new catalytic systems for various organic transformations is an active ongoing research area and there is a scope for further improvement towards milder reaction conditions1. The development of heterogeneous catalysts for fine chemicals synthesis has become a major area of research2. Also important aspect of clean technology is the use of environmentally friendly catalysts3. Mediated electro oxidation process offers several advantages: first, the oxidation reaction takes place at ambient temperatures and pressures; second, the products of destruction are contained in the reaction vessel itself with the exception of gases; third production of secondary waste is minimized and this avoids additional treatment methods. The oxidation of alcohols is an important transformation in laboratory and industrial synthetic chemistry, as the corresponding carbonyl compounds can be used as important and versatile intermediates for the synthesis of fine chemicals4–6. The selective oxidation of primary alcohols to aldehydes is crucial for the synthesis of fine chemicals such as fragrances or food additives 7. Numerous oxidizing reagents such as chromium (VI) oxide, permanganates, ruthenium (VIII) oxide and dichromates have been employed 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 8–10. The oxidation of alcohols with molecular oxygen using salts of transition metals V,Co,Cu,Mo, Ru,Rh,Pd and polyoxometalates11-18as catalysts. Most of these systems catalyze the oxidation of primary as well as secondary alcohols to give the corresponding aldehydes and ketones. In-Cell electrolysis has a distinct advantage over conventional homogeneous electrolysis with respect to easy handling and mediator recycling **.** In the In–Cell 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 give the products. After completion of the electrolysis, separation and evaporation of the organic layer results in the product. Presently, only a few reports on two-phase electrolysis are available for electro organic syntheses of fine chemicals. Herein, the authors report a simple method for the preparation of p-substituted benzaldehydes from p-substituted benzyl alcohols by In-Cell electrolysis at 30–34^{0}C as shown in Scheme 1.

The main principle of the electro oxidation is to increase importance for the application of redox agents with regard to environmental protection, since large amounts of a product can be generated in a closed electrical circuit using only relatively small amounts of the redox reagent. The purpose of the present work, is to perform the comparative study for the investigation on the possibility of indirect oxidation of both p-ethyl and p-ethoxy benzyl alcohol by In-cell electrolysis method to acquire consistent facts on yields and selectivity of the consistent parameters. The product yields a maximum of 94-96 % of alcohols. The Plausible mechanism is shown in scheme 2.



Scheme1 : Electrochemical oxidation of alcohols
R=ethyl and ethoxy

II. EXPERIMENTAL

Standard p-ethyl and p-ethoxy benzyl alcohol was supplied by Sigma-Aldrich. All other reagents were of Analytical grade. An undivided beaker-type glass cell (120 mL capacity) equipped with a magnetic stirrer was used for the electrolysis. Substituted Benzylalcohol (1.045 g, 10 mmol) dissolved in 20 mL chloroform was transferred to an undivided electrolytic cell. Deionized water was used for preparing the water soluble mediator NaCl. The aqueous upper phase acted as the supporting electrolyte containing HCl and chlorine as cationic source. Both Platinum electrodes acts as anode and cathode of 15 cm^2 area were placed in the aqueous phase without touching the organic phase but very close to the interphasial region. The organic phase alone was stirred with a magnetic stirrer at a rate of 20 rpm in such a way that the organic layer did not touch the electrodes. The temperature of the electrochemical cell contents was maintained at 30–34^0C throughout the electrolysis. The undivided cell was connected with a dc power supply (Fig. 1).

The electrolysis was conducted by constant current electrolysis at a current density of 30 mA cm^{-2} until a quantity of 3 F of electricity was passed. An aliquot was drawn periodically from the organic phase and was monitored by HPLC using a Shimadzu LC-8A column (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. HPLC analysis of the residue indicated the presence of 96% of p-ethylbenzaldehyde and p-ethoxybenzaldehyde along with 4% unconverted p- ethyl benzyl alcohol and 18% unconverted p-ethoxy benzyl alcohol.

III. RESULTS AND DISCUSSION:

Effect of Current Density

In-cell electrolysis oxidation of p-ethyl benzyl alcohol and p-ethoxybenzyl alcohol was carried out in an undivided cell at a current density from 20 to 60 mA/cm^2. Table 1 and Table 2 and Figure 1 show the effect of current density on oxidation p-ethylbenzaldehyde and p-ethoxybenzaldehyde. The Current efficiency forp-ethylbenzaldehyde and p-ethoxybenzaldehyde generation is decreased with increase in the current density and decreased at higher current density of 60 mA/cm^2.At an optimum current density 20 mA/cm^2 (450mA), was selected for both products . Their corresponding current efficiencies were found to be 75 and 73% respectively.

Table1. Effect of current density on the anodic oxidation of p-ethyl benzyl alcohol.

Electrolysis conditions : In-Cell Method. Current density = 30 mA/cm^2, Anode/Cathode: Pt/Pt (area = 15 cm^2), Substrate: p-ethyl p-ethoxy benzyl alcohol, Electrolyte: 60 mL of aqueous solution of 12% NaCl and (0.36 M) HCl, Solvent: Dichloromethane (20 mL), Stirring rate: 30 rpm, Cell volume: 120 mL, Type of cell: undivided glass cell, Temperature: 30-34°C.

Sl. No.	Current Density mA/cm^2	Yield %		Time (min)	Current Efficiency % for the formation of p-ethylbenzaldehyde
		unconverted p-ethyl benzyl alcohol	p-ethylbenzaldehyde		
1	20	25	75	98	75
2	30	28	72	58	72
3	40	34	65	43	65
4	50	34	62	35	62
5	60	57	41	29	41

Table 2. Effect of current density on the anodic oxidation of p-ethoxy benzyl alcohol.

Sl. No.	Current Density mA/cm^2	Yield %		Time (min)	Current Efficiency% for the formation of p-ethoxybenzaldehyde
		unconverted p-ethoxy benzyl alcohol	p-ethoxybenzaldehyde		
1	20	27	73	98	73
2	30	28	72	58	72
3	40	30	70	43	70
4	50	35	65	35	65
5	60	40	60	29	60

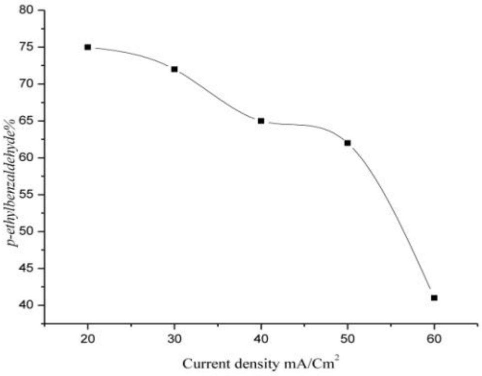


Fig 1: Current Density for p-ethylbenzaldehyde

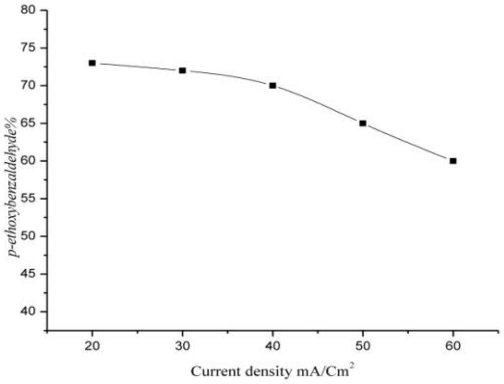


Fig. 2 Current Density for p-ethoxybenzaldehyde

Effect of Charge Passed:

The study of charge passed was carried out for the In-cell electro oxidation of p-ethylbenzyl alcohol and p-ethoxybenzyl alcohol. The time taken for each faraday has given in the Table 3 and 4 and Figure 3 represents the effect of charge passed. The result reveals that the electron donating substituents yields less than the alkyl substituents. Maximum yield of p-ethylbenzaldehyde 85% was reached at a charge of 4F/mole; compare to p-ethoxybenzaldehyde was yield at 75 %. However the minimum charge passed is required to conduct the In-cell electrolysis for the following parameters, so the optimum faraday select for the In-cell electrolysis method as 3F and the corresponding time can be fixed as 87mts as given in the Table 3.

Table 3. Effect of Charge passed on the anodic oxidation of p-ethyl benzyl alcohol.

Electrolysis Conditions: In-Cell Method. Current density = 30 mA/cm^2, Charge Passed: 3F; Substrate: p-ethyl and p-ethoxy benzylalcohol, Anode/Cathode: Pt/Pt (area = 15 cm^2), Electrolyte: 60 mL of aqueous solution of (12%) NaCl and (0.36 M) HCl, Solvent: Dichloromethane (20 mL), Stirring rate: 30 rpm, Cell volume: 120 mL, Type of cell:

S. No.	Charge Passed (F)	Yield %		Time (min)	Current Efficiency % for the formation of p-ethylbenzaldehyde
		unconverted p-ethylbenzyl Alcohol	p-ethylbenzaldehyde		
1	2	30	70	58	47
2	3	20	80	87	53
3	4	15	85	116	56
4	5	16	84	145	56

Table 4. Effect of Charge passed on the anodic oxidation of p-ethoxy benzyl alcohol

S. No.	Charge Passed (F)	Yield %		Time (min)	Current Efficiency % for the formation of p-ethoxy benzaldehyde
		unconverted p-ethoxy benzyl Alcohol	p-ethoxybenzaldehyde		
1	2	30	70	58	47
2	3	28	72	87	48
3	4	25	75	116	50
4	5	27	73	145	49

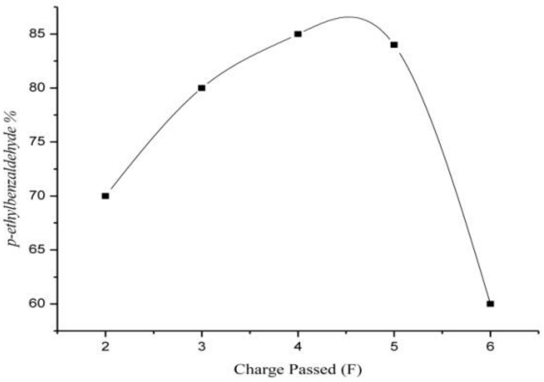


Fig.3 Charge Passed for p-ethylbenzaldehyde

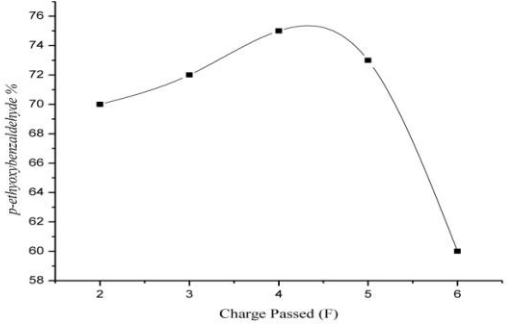


Fig.4 Charge Passed for p-ethoxybenzaldehyde

Effect of solvent

Studies were conducted for both substituted alcohols at room temperature using different solvents. The results are reported in Table 5 and 6. It has been observed that all chlorinated hydrocarbons gave nearly identical results except CH_3CN. Depending upon the polarity index the each chlorinated solvent gave divergent yields, when CH_3CN was used, the reaction took place in homogenous layer, so dichloromethane is considered as an ideal solvent for the oxidation of p-ethyl and p-ethoxybenzyl alcohol due to its low toxicity.

Table 5. Effect of solvents used on the anodic oxidation of p-ethyl benzyl alcohol.

Electrolysis Conditions: In-Cell Method. Current density = 30 mA/cm^2, Charge Passed: 3F; Substrate: p-ethyl and p-ethoxybenzylalcohol,Anode/Cathode:Pt/Pt (area = 15 cm^2), Electrolyte: 60 mL of aqueous solution of (12%) NaCl and (0.36 M) HCl, Solvent: (20 mL) chloroform, Dichloromethane, Carbon tetrachloride Stirring rate: 30 rpm, Cell volume: 120 mL, Type of cell: undivided glass cell, Temperature: 30-34°C.

*CH_3CN = Homogenous system.

S. No.	Solvents	Yield%		Current Efficiency % for the formation of p-ethylbenzaldehyde
		unconverted p-ethyl benzyl alcohol	p-ethylbenzaldehyde	
1	$CHCl_3$	4	96	64
2	CCl_4	6	94	63
3	*CH_3CN	7	85	56
4	CH_2Cl_2	19	95	63

S. No.	Solvents	Yield%		Current Efficiency % for the formation of p-ethoxy benzaldehyde
		unconverted p-ethyl benzyl alcohol	p-ethoxy benzaldehyde	
1	$CHCl_3$	8	92	61
2	CCl_4	10	90	60
3	*CH_3CN	20	80	53
4	CH_2Cl_2	6	94	62

Table 6. Effect of solvent on anodic oxidation of p-ethoxy benzyl alcohol

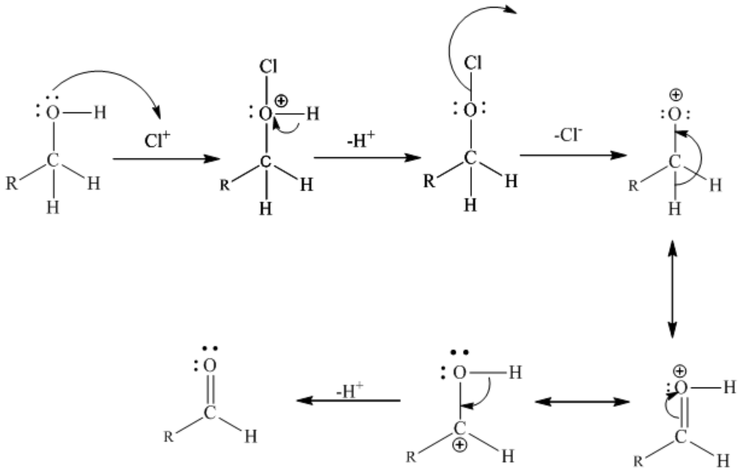
Effect of Recycle Spent Mediator:

Electrochemical reactions were conducted for the oxidation of p-ethyl and p-ethoxybenzylalcohol to their corresponding benzaldehydes under optimized concentration with continuous recycling of NaCl. First portion of the aqueous layer containing redox mediator was taken for the second and third recycling processes. . The results are reported in Table 7. Almost identical yields were obtained (96- 98%) with recycling the NaCl. This reaction has been taken up for scale-up studies, in concluding that the reactions were economically eco-friendly system.

Table 7. Effect of Spent mediator for the anodic oxidation of p-ethoxy benzyl alcohol

Electrolysis Conditions: In-Cell Method. Current density = 30 mA/cm^2, Charge Passed: 3F; Substrate: p-ethoxybenzylalcohol, Anode/Cathode: Pt/Pt (area = 15 cm^2), Electrolyte: 60 mL of aqueous solution of (12%) NaCl and (0.36 M) HCl, Solvent: (20 mL) chloroform, Dichloromethane, Carbon tetrachloride Stirring rate: 30 rpm, Cell volume: 120 mL, Type of cell: undivided glass cell, Temperature: 30-34°C, Recycle 1,2 and 3

S. No.	Recycle Use of Spent Mediator	Yield %		Current Efficiency % for the formation of p-ethylbenzaldehyde
		p-ethyl benzyl alcohol	p-ethylbenzaldehyde	
1	Fresh Sample	15	98.1	65
2	Recycle 1	23	97.5	65
3	Recycle 2	30	97.1	64
4	Recycle 3	26	96.6	64



Scheme2: Plausible Mechanism for the oxidation of alkyl substituents

IV CONCLUSION

In conclusion, the comparative study for the In-cell electrochemical method involving the oxidation of p-ethyl benzyl alcohol and p-ethoxybenzylalcohol to their corresponding benzaldehydes obtained Maximum yield of 94 - 96%. This method constitutes a novel and efficient alternative method over conventional chemical methods. The reactions are carried out under mild condition with a very simple electrochemical setup and present several advantages such as absence of secondary products, and low cost of production. Purity of the product was also consistent during recycling. Thus it seems that this scheme is amenable for scale up as a pollution free process.

V ACKNOWLEDGEMENTS.

The authors thank Dr. K. Kulangiappar, Electro Organic Division, Central Electrochemical Research Institute, Karaikudi-630006, India.

VI. REFERENCES.

[1] N.S. Nandurkar, M.J. Bhanushali, M.D. Bhor, et al. Aluminium Nitrate/Silica Sulfuric Acid/Bromide Ion: As an Effective an Catalytic Oxidizing Media for the Selective Oxidation of Sulfides to SulfoxidesJ. Mol. Catal. A: Chem. 271,142007.

[2] P.R. Likhar, S. Roy, M. Roy, et al. O Metal-Free Catalytic Oxidation of Urazoles under Mild and Heterogeneous Conditions via Combination of Ammonium Nitrate and Catalytic Amounts of Silica Sulfuric Acid .Synlett (2007) 2301.

[3] M.M. Heravi, K. Bakhtiari, H.A. Oskooie, et al. $ZrOCl_2\_8H_2O$ catalyzed one-pot synthesis of 2,4,5-triaryl-1H-imidazoles and substituted 1,4-di(4,5-diphenylimidazol-yl)benzene.J. Mol. Catal. A: Chem. 263 (2007) 279.

[4] Sheldon, A.; Kochi, J. K. Metal Catalysed Oxidations of Organic Compounds; Ruthenium-catalysed aerobic oxidation of alcohols via multistep electron transfer Academic Press: London, 1981.

[5] Hudlicky, M. Oxidations in Organic Chemistry. ACS Monograph Series; A new metal-free protocol for oxidation of alcohols using N,N-dibromo-p-toluenesulfonamideAmerican Chemical Society: Washington, DC, 1990.

[6] Stahl, S. S. Palladium Oxidase Catalysis: Selective Oxidation of Organic Chemicals by

Direct Dioxygen-Coupled Turnove R Angew. Chem., Int. Ed. 2004, 43, 3400–3420.

[7] Musawir, M.; Davey, P. N.; Kelly, G.; Kozhevnikov, I. V.Na-promoted aerobic oxidation of alcohols to ketonesChem. Commun. 2003, 1414–1415.

[8] Cainelli, G.; Cardillo, G. Chromium Oxidants in Organic Chemistry; Heterogeneous Method for the Oxidation of Alcohols under Mild Conditions with Zinc Dichromate Adsorbed on AluminaSpringer: Berlin, 1984.

[9] Lee, D. G.; Spitzer, U. A. Copper Catalyzed Selective Oxidation of Benzyl Alcohol to Benzaldehyde J. Org. Chem. 1970, 35, 3589–3590.

[10] Menger, F. M.; Lee, C. Recent developments in the aerobic oxidation of alcoholsTetrahedron Lett.1981, 22, 1655– 1656.

[11] Reddy, S. R.; Das, S.; Punniyamurthy, T. Polyaniline supported vanadium catalyzed aerobic oxidation of alcohols to aldehydes and ketones Tetrahedron Lett. 2004, 45, 3561–3564.

[12] Iwahama, T.; Yoshino, Y.; Keitoku, T.; Sakaguchi, S.; Ishii, Y. Aerobic Oxidation Reactions Catalyzed by N-Hydroxyphthalimide and Its Analogues J. Org. Chem. 2000, 65, 6502–6507.

[13] Marko, I. E.; Guaiter, A.; Dumeunier, R.; Doda, K.; Philippart, F.; Brown, S. M.; Ureh, Polyaniline/SiO_2 Nanocomposite Catalyzed Efficient Synthesis of Quinoxaline Derivatives at Room Temperature J. Angew. Chem., Int.Ed. 2004, 43, 1588–1591.

[14] Velusamy, S.; Ahamed, M.; Punniyamurthy, T. A Reasonable explanation for the mechanism of photo-promoted chemoselective aerobic oxidation of alcohols using (ON)Ru(salen) complex as catalystOrg. Lett.2004, 6, 4821–4824.

[15] Egami, H.; Onitsuka, S.; Katsuki,Catalytic Activation of Dioxygen by Metal Complexes T. Tetrahedron Lett.2005, 46, 6049–6052.

[16] Martin, J.; Martin, C.; Faraj, M.; Bregeault, M. Nouv. The First Example of Activation of Molecular Oxygen by Nickel in Ni-Al Hydrotalcite: A Novel Protocol for the Selective Oxidation of Alcohol J. Chim. 1984, 8, 141–147.

[17] Schultz, M. J.; Hamilton, S. S.; Jensen, D. R.; Sigman, M.S.Perfluorinated quaternary ammonium salts of polyoxometalate anions:Fluorous biphasic oxidation catalysis with and without fluorous solvents. J. Org. Chem. 2005, 70, 3343–3352.

[18] Haimov, A.; Neumann, R. Selective aerobic oxidation in supercritical carbon dioxide catalyzed by the $H_5PV_2Mo_{10}O_{40}$ polyoxometalate Chem. Commun. 2002, 876–877.

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