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Biphasic electro oxidation of benzyl alcohol mediated by ceric ammonium sulphate in In-Cell method

S. Lawrence[a], C. Christopher[b], A. John Bosco[c], K.Kulangiappar[d],S. Raja[c] and N. Xavier[c]*

[a]*Department of Chemistry, Sacred Heart College, Tirupattur, India*
[b]*Department of Chemistry, Thanthai Hans Roever College, Perambalur, India*
[c]*Department of Chemistry, St.Joseph's College, Tiruchirappalli, India*
[d]*Electroorganic division, Central Electrochemical Research Institute, Karaikudi, India*

ABSTRACT

A bi phase electrolysis method has been developed for the preparation of benzaldehyde. The electrolysis was carried out in an undivided cell using graphite electrodes in the presence of ceric ammonium sulphate (CAS) redox couple. Some experimental conditions affecting the yield for benzaldehyde production such as current density, charge passed, different acids, acid concentration, different solvents and recycle of CAS were studied. The maximum yield for benzaldehyde at room temperature was 98% in In-Cell method under the influence of 1.36 M perchloric acid, 2.3 mmol CAS and at a current density of 30 mA/cm^2.

Key words: Indirect electro oxidation; Bi-phase electrolysis; benzadehyde; ceric ammonium sulphate.

INTRODUCTION

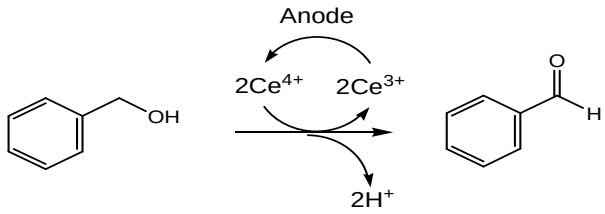
Aromatic aldehydes and ketones are important chemicals, with applications such as chemical intermediates, pharmaceuticals, agricultural chemicals, pulp, paper chemicals, dyestuffs, flavour and fragrance materials [1-3]. The oxidation of alcohols using transition metal salts of V [4], Co [5], Cu [6], Mo [7], Ru [8], Rh [9], Pd [10], Mn, Zn[11], polyoxometalates[12-13] and trialkylammonium halochromates[14-15] as catalysts has been reported. Of the above metal oxidants, Cr (VI) is the most soluble and has the lowest reduction potential and is thus the easiest to regenerate electrochemically. On the other hand, Cr (VI) generally gives the lowest selectivities in the organic oxidations of interest. The manganic ion gives good selectivities but is unstable toward disproportionation, except at very high acid concentrations where both Mn (III) and Mn (II) have low solubilities. The powerful Co (III) ion is also unstable, due to water oxidation. Cerium (IV) is generally the reagent of choice due to its higher stability and solubility at acid concentrations [16], which yield excellent selectivities to aromatic carbonyl products [17-24]. Most of these systems catalyze the oxidation of primary as well as secondary alcohols to give the corresponding aldehydes and ketones. The selective oxidation of primary alcohols to aldehydes is crucial for the synthesis of fine chemicals such as fragrances or food additives [25].

Benzylic and allylic alcohols are selectively oxidised 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 [26].

A general electrochemical method for the selective oxidation of primary and secondary alcohols to carbonyl compounds under anaerobic conditions [mediator, the system $Pd(OAc)_2$-benzoquinone] that prevent the intermediate formation of H_2O_2, which induces side reactions of the products [27]. Other examples of indirect anodic oxidation of

alcohols and their derivatives catalysed by redox systems based on manganese, cerium, chromium, copper ions and nitrate mediator are reported [28-29].

In the present work, a bi phase electrolysis method has been developed for the preparation of benzaldehyde. Bi phase liquid/liquid systems offer some advantages over single phase methods, in that the aqueous phase containing the spent redox mediator may be easily separated and passed over an electrode to regenerate the active redox species, and product separation is also simplified. The electrolysis was carried out in an undivided cell using graphite electrodes in the presence of redox couple Ce^{4+}/Ce^{3+}. The maximum yield of 98% benzaldehyde production at room temperature was achieved. The sequence globally representing benzyl alcohol oxidation is as follows:



Scheme.1. Proposed electrochemical oxidation mechanism of benzyl alcohol

MATERIALS AND METHODS

Electrochemical oxidation of Benzyl alcohol (In-Cell method)
An Aplab power source was used as the direct current source for the electrolysis. Deionised water was used for preparation of electrolyte. A beaker type glass cell (100 ml capacity) equipped with a magnetic stirrer was used for the electrolysis and two platinum sheets of 15 cm^2 area were used as the anode and the cathode. The reaction was monitored by HPLC using a SHIMADZU LC-8A column (250 mm×4.6 mm) as the stationary phase. The eluent consisted of acetonitrile/water (80:20) at a flow rate of 1 ml/min. Samples were analysed at a wavelength of 254 nm with a UV detector. Authentic sample of benzaldehyde and benzoic acid were used to calculate the peak areas of all the experimental products for yield calculation.

A solution of benzyl alcohol (1.04 g, 10 mmol) in chloroform (20 ml) was taken in a single compartment electrolytic cell. To the above solution, 60 ml of aqueous CAS (2.3 mmol) containing 1.36 M perchloric acid (PCA) was added. The aqueous upper phase acted as the supporting electrolyte. Two platinum electrodes were placed in the aqueous phase without touching the organic phase but very close to the interphase. The organic phase alone was stirred with a magnetic stirrer at a rate of 40 rpm in such a way that the organic layer does not touch the electrodes. The electrolysis was carried out at room temperature. The electrolysis was conducted galvanostatically at a current density of 30 mA/cm^2 was passed. An aliquot was drawn periodically from the organic phase and analysed by HPLC. After the completion of the electrolysis, the lower organic phase was separated, washed with water (2×25 ml), dried over anhydrous Na_2SO_4 and the solvent was removed by distillation. HPLC analysis of the residue indicated the presence of 98% benzaldehyde yield (1.02g) along with 1% unconverted benzyl alcohol.

RESULTS AND DISCUSSION

3.1 Eelectrochemical oxidation of Benzyl alcohol
Bi-phase electrolysis is one where the electrolyte and the substrate are present in different phases. Bi-phase electrolysis is advantageous than the homogenous electrolysis because in the homogenous system less selectivity is observed due to substrate gets oxidised on the surface of the electrode giving mixture of products. When electrolysis occurs, electrolytically generated species travels from aqueous phase to organic phase and attacks the substrate. The products obtained in bi-phase electrolysis will not be the same as in the homogenous electrolysis. In the homogenous electrolysis the products are non-selective. If the bi phases are made into emulsion by vigorous stirring, then this type of electrolysis is called emulsion electrolysis [30, 31]. In the electrochemical oxidation of benzyl alcohol, the following parameters were studied and the results are reported:

3.2 Effect of current density
Indirect electrochemical oxidation of benzyl alcohol was carried out in an undivided cell at a current density from 30 to 75 mA/cm^2. Table 1 and Figure 1 show the effect of current density on product yield and current efficiency. At low current densities it takes a long time for the oxidation of benzyl alcohol to benzaldehyde. High current densities

resulting in decrease in yield of product. Hence the optimum current density for the indirect electrochemical oxidation of benzyl alcohol is 30mA/cm^2.

Table 1: Effect of current density

S.No	Current density (mA/cm^2)	Benzaldehyde Yield (%)	Current efficiency (%)
1	30	90	67
2	45	89	66
3	50	88	65
4	60	86	64
5	75	82	61

Anode: Platinum (area = 15 cm2), cathode: platinum (area = 15 cm2), current density = 30 mA/cm2, electrolyte: 60 ml of aqueous solution of CAS (9.5 mmol) and Nitric acid (2.6 M), solvent: chloroform (20 ml), stirring rate: 20–40 rpm, cell volume: 100 ml, type of cell: undivided glass cell, temperature = room temperature.

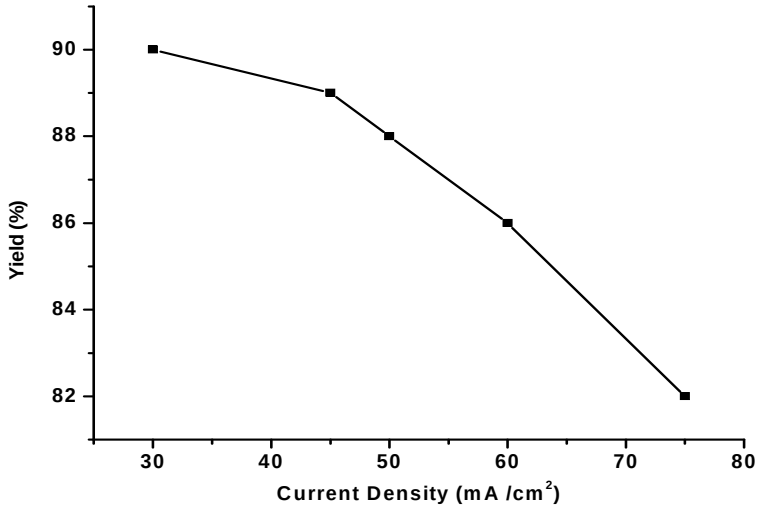


Figure.1: Effect of current density on benzaldehyde yield

3.3 *Effect of charge passed*

In indirect electrochemical oxidation of benzyl alcohol at optimum conditions, 95% of benzaldehyde and 3% of unconverted benzyl alcohol was obtained after passing 2.5 F charge per mole of benzyl alcohol. The curves in Figure 2 shows relative quantities of benzyl alcohol, benzaldehyde as a function of charge passed on indirect electrochemical oxidation of benzyl alcohol. The maximum concentration of benzaldehyde is reached at a charge of 2.5 F/mole. There is no increase in the product yield beyond this charge, as shown in Table 2.

Table 2: Effect of charge passed

S.No	Charge passed (F)	Benzaldehyde Yield (%)	Current efficiency (%)
1	1.5	91	68
2	2.0	90	67
3	2.5	95	71
4	3.0	93	69
5	3.5	93	69

Anode: Platinum (area = 15 cm2), cathode: platinum (area = 15 cm2), current density = 30 mA/cm2, electrolyte: 60 ml of aqueous solution Of CAS (9.5 mmol) and Nitric acid (2.6 M), solvent: chloroform (20 ml), stirring rate: 20–40 rpm, cell volume: 100 ml, type of cell: undivided glass cell, temperature = room temperature.

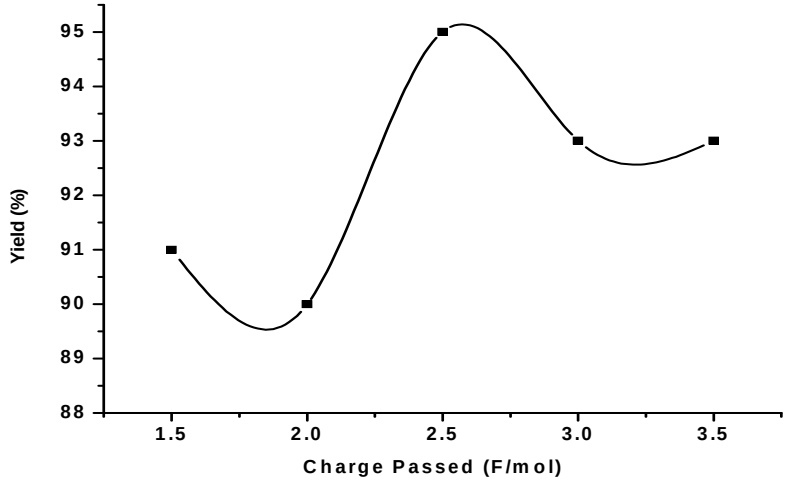


Figure.2: Effect of Charge passed on benzaldehyde yield

3.4 Effect of CAS concentration

The effect of CAS concentration on the oxidation of benzyl alcohol was studied from the range 2.4 mmol to 9.5 mmol. The results are reported in Table 3. Almost identical yields were obtained (94-95%). Hence 2.4 mmol CAS was chosen as the optimum concentration.

Table 3: Effect of cerium concentration

S.No	Cerium concentration (mmol)	Benzaldehyde Yield (%)	Current efficiency (%)
1	9.5	95.4	71.5
2	7.1	94.9	71.1
3	4.7	95.9	71.9
4	2.4	95.7	71.7

Anode:Platinum (area = 15 cm2), cathode: Platinum (area = 15 cm2), current density = 30 mA/cm2, electrolyte:60 ml of aqueous solution Of CAS and Nitric acid (2.6 M), solvent: chloroform (20 ml), stirring rate: 20–40 rpm, cell volume: 100 ml, type of cell: undivided glass cell, temperature = room temperature.

3.5 Effect of acids

Indirect electrochemical oxidation of benzyl alcohol was carried out in an undivided cell at various acids and Table 4 shows the effect of various acids on product yield and current efficiency. Hence the suitable acid for the indirect electrochemical oxidation of benzyl alcohol is PCA. The oxidant capacity of CAS increases in the presence of the acids in the following order $HClO_4$>HNO_3>H_2SO_4>HCl.

Table 4: Effect of Acids

S.No	Acids	Benzaldehyde Yield (%)	Current efficiency (%)
1	$HClO_4$	96.9	72.6
2	HNO_3	95.7	71.7
3	H_2SO_4	94.1	70.5
4	HCl	55.4	41.5

Anode: Platinum (area = 15 cm2), cathode: platinum (area = 15 cm2), current density = 30 mA/cm2, electrolyte:60 ml of aqueous solution Of CAS (9.5 mmol) and solvent: chloroform (20 ml) and different acids (10 ml), stirring rate: 20–40 rpm, cell volume: 100 ml, type of cell: undivided glass cell, temperature = room temperature.

3.6 Effect of Acid Concentration

Acid concentration is another important parameter in the redox mediated indirect oxidation. Studies were conducted to observe the effect of PCA concentration on the oxidation of benzyl alcohol to benzaldehyde. The results are reported in Table 5. Almost identical yields were obtained (93-97%). It is observed from the table that oxidation of

benzyl alcohol to benzaldehyde is favoured with the use of minimum acid concentration of around 1.36 M PCA. At lower acid concentration, the ceric ion is produced in the slurry form due to lower solubility. 1.36 M PCA concentration appears to be the optimum acid concentration.

Table 5: Effect of acid concentration

S.No	Acid Concentration (M)	Benzaldehyde Yield (%)	Current efficiency (%)
1	2.13	96.9	72.6
2	1.94	96.9	72.6
3	1.74	93.7	70.2
4	1.55	94.3	70.7
5	1.36	95.9	71.9

Anode:Platinum (area = 15 cm2), cathode: Platinum (area = 15 cm2), current density = 30 mA/cm2, electrolyte: 60ml of aqueous solution of CAS (2.4 mmol) and PCA, solvent: Chloroform (20 ml), stirring rate: 20–40 rpm, cell volume: 100 ml, type of cell: undivided glass cell, temperature = room temperature.

3.6 Effect of solvent

Studies were conducted at room temperature using different solvents. The results are reported in Table 6. It is observed that dichloromethane and chloroform gave nearly identical results. Even though carbon tetrachloride gave quantitative yield, dichloromethane is considered as an ideal solvent for the oxidation of benzyl alcohol due to its less toxicity.

Table 6: Effect of solvent

S.No	Solvent	Benzaldehyde Yield (%)	Current efficiency (%)
1	CH_2Cl_2	95.9	71.9
2	$CHCl_3$	96.0	72.0
3	CCl_4	98.6	73.9

Anode: Platinum (area = 15 cm2), cathode: platinum (area = 15 cm2), current density = 30 mA/cm2, electrolyte: 60ml of aqueous solution Of CAS (2.4 mmol) and PCA (1.36 M), solvent: chloroform (20 ml), stirring rate: 20–40 rpm, cell volume: 120 ml, type of cell: undivided glass cell, temperature = room temperature.

3.8 Effect of various anodes

The behaviour of various anode materials on the indirect electrochemical oxidation of benzyl alcohol was studied using platinum and graphite as electrodes. From the Table 7 it is observed that the best yield was obtained using graphite as electrodes.

Table 7: Effect of various anodes

S.No	Anode	Cathode	Benzaldehyde Yield (%)	Current efficiency (%)
1	Platinum	Platinum	96.0	72.0
2	Graphite	Graphite	98.1	73.5
3	Graphite	Platinum	97.6	73.2
4	Platinum	Graphite	85.1	63.8

Current density = 30 mA/cm2, electrolyte: aqueous 60ml of aqueous solution Of CAS (2.4 mmol) and PCA (1.36 M), solvent: Dichloromethane (20 ml), stirring rate: 20–40 rpm, cell volume: 100 ml, type of cell: undivided glass cell, temperature = room temperature.

3.9 *Effect of recycle use of CAS*

A few reactions were conducted for the oxidation of benzyl alcohol to benzaldehyde under optimized concentration with continuous recycling of CAS. The results are reported in Table 8. Almost identical yields were obtained (96-98%) with recycling the CAS. This reaction has been taken up for scale-up studies.

Table 8: Effect of recycle use of CAS

S.No	Amount of CAS (mmol)	Benzaldehyde Yield (%)	Current efficiency (%)
1	2.3	98.1	73.5
2	Reuse 1	97.5	73.1
3	Reuse 2	97.1	72.8
4	Reuse 3	96.6	72.4

Anode: Graphite (area = 15 cm2), cathode: Graphite (area = 15 cm2), current density = 30 mA/cm2, electrolyte: 60ml of aqueous solution Of CAS and PCA (1.36 M), solvent: Dichloromethane (20 ml), stirring rate: 20–40 rpm, cell volume: 100 ml, type of cell: undivided glass cell, temperature = room temperature.

CONCLUSION

In conclusion, an electrochemical method involving the oxidation of benzyl alcohol to benzaldehyde in 98% yield with the current efficiency of 74% by bi-phase electrolysis 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, low cost of production, high conversion and yield.

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