



## Electro oxidation of substituted electron–donating benzylic alcohols in a biphasic medium

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### ABSTRACT

A biphasic electrolysis method has been developed for the preparation of aldehydes. Ceric ammonium sulphate (CAS) in aqueous acidic medium is an effective for the electro oxidation of alcohols in dichloromethane to the corresponding carbonyl compounds using graphite electrodes at room temperature. Electro oxidation resulted in high yield (83-99%) of aldehydes from primary alcohols than that of Ex-cell method and CAS was regenerated and reused for further reactions in biphasic electrolysis medium.

**Key words:** Biphasic electrolysis medium; Benzylic alcohols; Ceric Ammonium Sulphate; Electro oxidation; In-Cell method.

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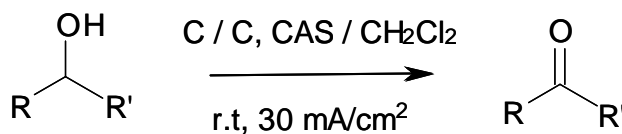
### INTRODUCTION

Aromatic aldehydes and ketones are important chemicals, with applications such as chemical intermediates, pharmaceuticals, dyestuffs and fragrance materials [1-3]. The oxidation of alcohols using transition metal salts [4-11] and polyoxometalates [12] as catalysts has been reported. In the transition metal oxidants, Cr (VI) was found to be most soluble transition metal, possessing the lowest reduction potential and thus the easiest to regenerate electrochemically. On the other hand, it usually 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. Ce (IV) is generally the reagent of choice due to its higher stability and solubility at acid concentrations, which yields excellent selectivities to aromatic carbonyl products [13-21]. A great number of oxidizing agents have been reported for the oxidation benzyl alcohols [22-27].

In biphasic electrolysis, Benzylic and allylic alcohols are selectively oxidised to aldehydes at hydroxide nickel anode are reported [28]. Recently, we developed biphasic electro oxidation of benzyl alcohol mediated by CAS and sodium nitrate in an In-Cell method [29, 30].

In the present work, we have used a non toxic commercially available CAS as electro catalyst for the oxidation of alcohols to corresponding carbonyl compounds using graphite electrodes in perchloric acid (PCA) that is not reported earlier. Because a higher yield was obtained than with those based on indirect anodic oxidation of alcohols and their derivatives catalysed by redox systems [31, 32]. The electrolysis system consists of 60 mL of aqueous CAS (2.3 mmol) and 1.36 M PCA as the aqueous phase and dichloromethane containing the substrate as the organic phase. Under this condition, alcohols were oxidized to the corresponding carbonyl compounds at room temperature in a single compartment cell which resulted in high yields and also required minimum time for the completion of electrolysis (Scheme 1). The advantages of the proposed method are simple reaction conditions (low cell voltage,

undivided cell, and constant current electrolysis with an inexpensive dc-power supply), low cost, easy scale-up and almost no waste problems.



*C* = Graphite electrodes, *CAS* = Ceric Ammonium Sulphate, *R* = Aryl, Substituted aryl, benzyl, *Ph-CH=CH-*, *R'* = *H*

### Scheme1. Electro oxidation of alcohols in biphasic medium

## EXPERIMENTAL SECTION

### Representative procedure for In-Cell method

A solution of cinnamyl alcohol (1.34 g, 10 mmol) in dichloromethane (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 (PCA) was added. Two graphite electrodes (15 cm<sup>2</sup>) 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 conducted galvanostatically at room temperature (2.5 F/mol and current density of 30 mA/cm<sup>2</sup>). The aqueous layer was reused for further reaction. An aliquot was drawn periodically from the organic phase and analysed 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. After the completion of the electrolysis, the lower organic phase was separated, washed with water (2×25 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed by distillation. HPLC analysis of the residue indicated the presence of 99% cinnamaldehyde yield. The crude product was passed through a column of silica gel and eluted with a mixture of ethyl acetate/ n-hexane (1:9) to afford the pure product (95%, 1.2g)

### Representative procedure for Ex-Cell method

A solution of cinnamyl alcohol (1.34 g, 10 mmol) in dichloromethane (20 mL) was taken in a 100 ml beaker. To the above solution, 60 ml of aqueous CAS (2.3 mmol) containing 1.36 M (PCA) was added. Both the phases were stirred with a magnetic stirrer at a rate of 40 rpm. The reaction was allowed to stirrer up to 90 mins. After that the lower organic phase was separated, washed with water (2×25 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed by distillation. The yield of product was noted in HPLC. The yield was obtained lower (70%). than that of In-Cell method. Finally the CAS was regenerated in H-Cell.

## RESULTS AND DISCUSSION

### Ex-Cell Vs In-Cell

Ex-Cell method has some disadvantages like the reactions are carried out in two separated reactors, resulting in an increase of experimental steps and moderate yield (70%). A higher yield was obtained in In-Cell method (98%). Here both anodic and cathodic reactions were carried out in an undivided cell (biphasic medium) and the reusability of CAS was studied for the oxidation of benzyl alcohol (10 mmol) as modal substrate. At the end of the electrolysis, the aqueous phase was reused for further cycle. The results are reported in Table 1. Almost identical yields were obtained (96-98%).

**Table 1: Effect of recycle use of CAS**

| S.No | Amount of CAS (mmol) | Benzaldehyde Yield (%) |
|------|----------------------|------------------------|
| 1    | 2.3                  | 98                     |
| 2    | Reuse 1              | 97                     |
| 3    | Reuse 2              | 96                     |
| 4    | Reuse 3              | 95                     |

Anode/Cathode: Graphite electrodes (area = 15 cm<sup>2</sup>), current density = 30 mA/cm<sup>2</sup>, electrolyte: 60 mL of aqueous solution (concentration CAS + PCA), solvent: Dichloromethane (20 mL). Charge passed: (2.5 F/mol and current density of 30 mA/cm<sup>2</sup>)

In order to expand the scope of the electro oxidation of benzyl alcohol by CAS, we performed the oxidation of various alcohols. The results are put on view in Table 2.

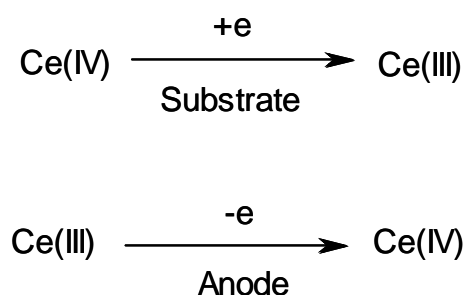
**Table 2. Electro oxidation of benzylic alcohols in a biphasic medium**

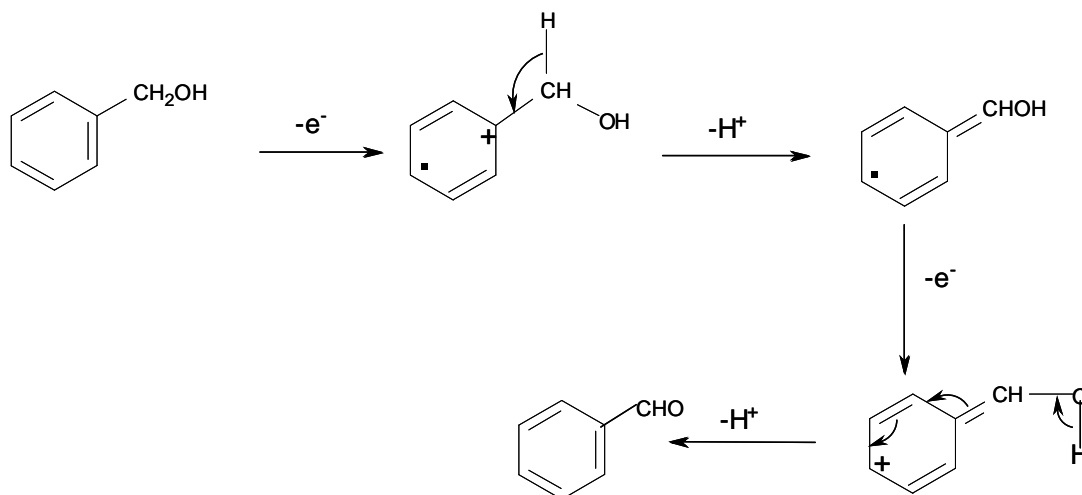
| Entry | Reactant | Product | Yield (%) <sup>a</sup> | Time (min) | Charge Passed (F/mol) |
|-------|----------|---------|------------------------|------------|-----------------------|
| 1     |          |         | 98                     | 90         | 2.5                   |
| 2     |          |         | 95                     | 18         | 1.5                   |
| 3     |          |         | 95                     | 72         | 2.0                   |
| 4     |          |         | 83                     | 72         | 2.0                   |
| 5     |          |         | 99                     | 90         | 2.5                   |

<sup>a</sup> Determined by HPLC

Electron-donating substituents like methyl and methoxy groups (entries 2, 3) on phenyl ring have resulted in good yields to the substituted benzaldehyde with 1.5 to 2.0 F/ mol of current. Biphasic electro oxidation of cinnamyl alcohol was converted into cinnamaldehyde in high yield without disturbing the side chain of C=C double bond. 2-phenylethanol was also more reactive towards oxidation.

A plausible mechanism for the biphasic electro oxidation, based on literature report, is outlined in Scheme 2[33, 34].





**Scheme 2. Mechanism for the biphasic electro oxidation of benzylic alcohols**

### CONCLUSION

To conclude, we have shown that CAS is an effective mediator for the electro oxidation of alcohols in a biphasic medium that smoothly favours oxidation to give corresponding carbonyl compounds selectively in good yields. CAS can also be reused for the consecutive runs with minor decrease in the yield of product. The main advantage of our procedure is that low cost electrodes were employed and separation of product was easy due to biphasic medium.

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