

MEDIATED ELECTROSYNTHESIS OF *p*-TOLUALDEHYDE FROM *p*-XYLENE USING CERIC METHANE SULPHONATE

K JAYARAMAN, S KRISHNAMOORTHY, V DEVADOSS, R KANAKAM SRINIVASAN
AND S CHIDAMBARAM

Central Electrochemical Research Institute, Karaikudi - 630 006, INDIA

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Mediated electrosynthesis using Ce^{3+}/Ce^{4+} redox system offers a clean and facile route for the production of several important aromatic carbonyl products. Use of methane sulphonic acid medium for the generation of ceric ion has made cerium mediated electrosynthesis practical for the commercial production of aromatic carbonyl products. In this paper, results are presented for the electrochemical generation of $Ce(IV)$ in methane sulphonic acid medium and the oxidation of *p*-xylene to *p*-tolualdehyde using different solvent media. Under optimised conditions, 90-95 % selectivities have been achieved for the synthesis of *p*-tolualdehyde.

Keywords: *p*-tolualdehyde, mediated electrosynthesis, Ce^{3+}/Ce^{4+} , redox system.

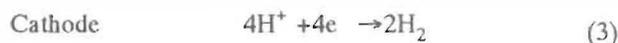
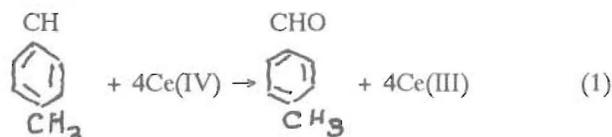
Aromatic aldehydes find wide applications as intermediates in the production of pharmaceuticals, flavouring chemicals etc. and the development of an electrochemical process for the production of aromatic aldehydes is of considerable interest in industrial electro-organic synthesis. While the direct oxidation process is hampered by poor product selectivity, difficulties associated with product isolation, deactivation of electrodes etc., indirect electrochemical oxidation using electrogenerated metal oxidants offers a clean and facile route for the production of aromatic aldehydes.

Mediated or indirect electrosynthesis is basically a cyclic process involving electrochemical generation of a redox agent and the use of the agent to effect a chemical reaction. Several mediators such as chromous/chromic, manganous/manganic, cerous/ceric etc., have been employed in the oxidation of alkyl aromatics and the electrolytic regeneration of these redox reagents have also been investigated. Among the metal oxidants, cerium(IV) is generally the reagent of choice due to its higher stability and solubility at all acid concentrations and yields excellent selectivities to aromatic carbonyl compounds [1]. Among the cerium salts, use of cerium methane sulphonate has several advantages over other anions, such as high stability towards oxidation, high selectivity for a wide range of substrates, high

solubility of ceric and cerous ions and poor nucleophilicity [2,3].

p-tolualdehyde is widely used in the perfumery industry and also finds application as polymer-additive. The objective of the present studies is to conduct preliminary voltammetric studies on the oxidation to optimise process condition for the generation of ceric from cerous and chemical oxidation of *p*-xylene using ceric methane sulphonate.

The reactions involved in the indirect electrochemical oxidation process are as follows



EXPERIMENTAL

Linear sweep voltammetric studies were carried out on the electrochemical generation of ceric methane sulphonate using a single compartment 50 cc capacity glass cell with platinum

electrode of area 0.19 cm^2 at a sweep rate of 2 mV/sec . Platinum foil and a saturated calomel electrode were used as counter and reference electrodes respectively. Cerium concentration was varied from 20-500 mM in 2 M - methane sulphonic acid. All readings were recorded at $303 \pm 1 \text{ K}$.

Wenking potentiostat (Model 75L, FRG), Scan generator (VSG 72 FRG) and Rikadenki recorder (X-Yt) were used.

Preparative studies on the generation of ceric methane sulphonate were carried out in a divided cell using cation exchange membrane (Nafion 423) as the diaphragm. Platinum was used as anode and stainless steel as cathode. The cell contents were stirred by a glass stirrer. Electrolysis was conducted at constant current conditions. Current efficiency for the Ce(III) oxidation was calculated by estimating total cerium and ceric content in the electrolyte before and after electrolysis. All chemicals used were of technical grade and deionised water was used for preparing the electrolyte. Total cerium and ceric content were estimated periodically during the course of electrolysis using FeSO_4 and ferroin as indicator.

Chemical oxidation studies were carried out in a glass reactor kept in a thermostatically controlled heating bath. Oxidation of the p-xylene was conducted with the ceric ion fully dissolved or with suspensions of ceric methane sulphonate complex.

p-xylene was dissolved in an organic solvent and the organic phase was added to the ceric solution. Reaction was

conducted till there was no more ceric in the aqueous phase. After the reaction, the phases were separated and the aqueous phase was extracted with the organic solvent. The combined organic phases were dried over anhydrous sodium sulphate and distilled to recover the solvent and separate the product. The concentrations of the product and the unconverted substrate were analysed by HPLC using Shimatzu LC-8A. HPLC analyser with CLS-ODS column with methanol as mobile phase with UV detector. The flow rate was 2 ml/minute . The retention time for p-toluadldehyde was around 3.643 minutes. After the product isolation, the aqueous phase was charged to the electrochemical reactor for regeneration of cerium(IV).

RESULTS AND DISCUSSION

Voltammetric studies

Platinum oxide formation is a well known occurrence at high anode potentials and can affect the study of reaction kinetics of Ce(III) oxidation. The procedure of Kuhn and Randle [4] was hence followed to obtain a constant reproducible oxide layer. The electrode was initially cleaned by polarizing it negatively to remove any existing oxides. The electrode was then held at a positive potential ($+ 1.6 \text{ V}$) for 15 minutes to create a reproducible oxide layer. Steady state polarisation studies were carried out on this platinum surface.

Fig. 1 shows the linear sweep voltammograms (LSV) obtained for the oxidation of Ce(III) to Ce(IV) in methane sulphonic acid (MSA) medium. It is seen that in the absence of any Ce(III) the oxide film formation takes place between 1.1 V to 1.2 V and oxygen evolution takes place at 1.5 V

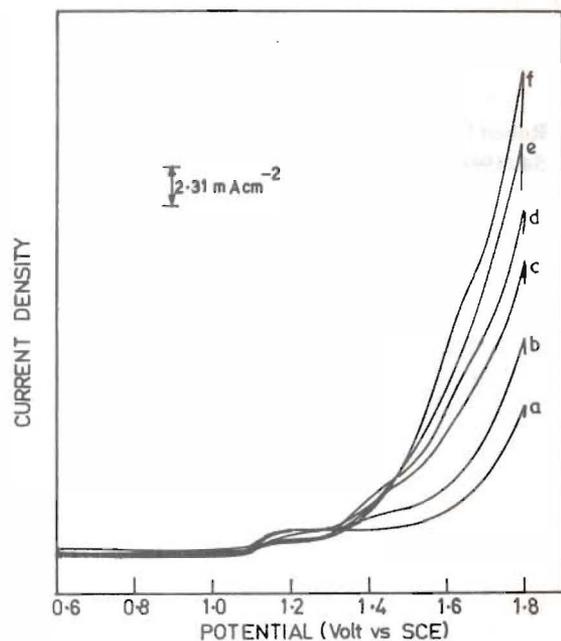


Fig.1: Linear sweep voltammetry (LSV) of Pt in (a) $2 \text{ M CH}_3\text{SO}_3\text{H}$ (b), (c), (d), (e) & (f) are (a) + 50, 200, 300, 400 & 500 mM Ce(III) solution. $v = 2 \text{ mV.S}^{-1}$

TABLE I:

Electrochemical oxidation of Ce(III) to Ce(IV) in methane sulphonic acid
 Anode : Pt
 Cathode : Stainless steel
 Anolyte : 2 M methane sulphonic acid
 Catholyte : 1 M methane sulphonic acid
 Temperature : $303 - 313 \text{ K}$

Con. of Ce(III) M	C.D A.dm ⁻²	Ce(IV) M	Output	
			Ce(III) M	Current efficiency (%)
0.35	3.5	0.27	0.08	56
0.47	3.5	0.39	0.08	76
0.80	9.0	0.55	0.25	65
0.80	9.0	0.70	0.10	65
1.20	10.0	0.83	0.35	68
1.20	10.0	1.01	0.12	72

TABLE II:
Chemical oxidation of p-xylene using Ce(IV)
methane sulphonate
Temperature: 303 - 333K

Expt. No.	Ce(IV) M	Concn of MSA M	Solvent	Conversion %	Selectivity %
1	0.60	1	Dichloro ethane	89.9	97.8
2	0.55	2	-do-	87.4	95.0
3	0.61	4	-do-	81.0	88.0
4	0.70	2	Acetonitrile	82.8	90.0
5	0.53	2	Cyclohexane	79.1	86.0

Conc: Concentration in M

MSA: Methane sulphonic acid

vs SCE. Fig. (b), (c), (d), (e) etc. show the LSV in presence of varying concentration of Ce(III) and it is seen that Ce(III) oxidation takes place from 1.3 V to 1.5 V vs SCE which is more pronounced at higher concentration of Ce(III) and is followed by oxygen evolution beyond 1.5 V. However the peaks are not well defined. This explains the high current efficiencies achieved with higher concentration of Ce(III) in preparative scale studies. However the oxidation of cerous to ceric is not a simple reaction and is reported to proceed through a complex involving the formation of an intermediate species [4].

Electrochemical oxidation of Ce(III) to Ce(IV)

Electrochemical oxidation of Ce(III) to Ce(IV) was conducted at varying current densities and Ce(III) concentrations, with both fresh solution and solution obtained after chemical oxidation of p-xylene. The results are reported in Table I. It is seen that the current efficiency for oxidation was 60-70 % and ceric concentration upto 1.0 M can be generated at higher current densities with good current efficiencies.

Chemical oxidation of p-xylene

Oxidation of p-xylene was conducted with homogeneous solution of ceric methane sulphonate or with suspensions of the ceric salt in MSA. Studies were conducted with varying concentrations of MSA and different solvents and the results are reported in Table II. It is seen that 90-95 % selectivities were obtained for p-tolualdehyde at 80-90 % conversions. After chemical oxidation, the aqueous phase containing cerous methane sulfonate was regenerated in the electrochemical reactor and the regenerated ceric solutions were used for chemical oxidation.

CONCLUSION

An indirect electrochemical method has been developed for the oxidation of p-xylene to p-tolualdehyde using ceric methane sulphonate. Preliminary voltammetric studies were conducted, to study the oxidation of cerous to ceric in methane sulphonic acid medium. Process optimisation studies were conducted to optimise the conditions for the electrochemical generation of ceric and 65-75 % current efficiencies were achieved for the oxidation. Chemical oxidation of p-xylene using ceric methane sulphonate yielded p-tolualdehyde with 80-90 % conversions (based on isolated yield of product). As compared to direct electrochemical oxidation or catalytic oxidation technique, the indirect electrochemical process will be a facile and clean technology for the production of p-tolualdehyde. Further developmental studies are in progress.

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