



## The role of Ce(IV)/Ce(III) Redox Mediator in Indirect Electrochemical Oxidations

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### Abstract

Voltammetric behaviour of Ce(IV)/ Ce(III) redox couple in sulphuric acid and methane sulphonic acid are compared on glassy carbon electrode. Both media exhibit relatively faster charge transfer kinetics. Voltammetric studies in presence of small concentration of naphthalene and p-xylene indicate that these compounds significantly inhibit the electrochemical oxidation of  $Ce^{3+}$  ion thus justifying the necessity for two stage processes. Optimum experimental conditions achieved for electrochemical oxidation of anthracene, naphthalene and benzene to their corresponding quinones and toluene, p-ethoxy toluene, o-chloro toluene, o, m and p-xylenes, 3, 4 – dimethyl anisole and 2-chloro p-xylene to their corresponding aldehydes are also discussed

Key words: (CeIV)/Ce(III) redox mediator, Indirect oxidation, Methane sulphonic acid medium, cyclic voltammetry.

### Introduction

Indirect electro synthesis using Ce(IV) / Ce(III) and other inorganic redox couples as mediators for organic electro synthesis have been proposed by a number of authors as a highly selective and potentially commercial synthetic route for producing a range of aromatic quinones, aldehydes and ketones. [1-5] The Ce(IV) / Ce(III) redox system in methane sulphonic acid medium has recently received much attention in this area.[ 2-5] This paper presents a broad outline of Ce(IV)/Ce(III)redox mediator in indirect electrochemical oxidation. Recent experimental work covering cyclic voltammetric studies, preparative scale electrochemical oxidation, chemical oxidation of aromatic compounds involving both nuclear oxidation as well as side chain methyl group oxidation carried out in this laboratory are summarised here.

#### Cerous / Ceric mediated electro organic synthesis:

Initial studies on electrochemical generation of  $Ce^{4+}$  as well as oxidation of organic compounds were mainly carried out in sulphuric acid medium. In place of conventional lead dioxide anode dimensionally stable anode have been employed for

electro chemical regeneration [6].  $Co^{3+}$  in nitric acid was compared with  $Mn^{3+}$  and  $Ce^{4+}$  in concentrated sulphuric acid for the chemical oxidation of methyl arenes. The reactivity of the oxidants declines in the order  $Co^{3+} > Mn^{3+} > Ce^{4+}$  [7].  $Ag^+$  ion as an additive in sulphuric acid electrolyte has been shown to improve the current efficiency of  $Ce^{4+}$  generation[8]. The kinetics of chemical oxidation of polycyclic hydrocarbons by  $Ce^{4+}$  and the intermediates involved has been reported[9]. There are some reports that cover the electrochemical oxidation of  $Ce^{3+}$  to  $Ce^{4+}$  exclusively in sulphuric acid [10,11]. Ceric sulphate can be isolated and used as a slurry [11]

A variety of aromatic hydrocarbons have been oxidised using cerous / ceric redox system, though initial studies were confined to electrochemical oxidation of anthracene. Some of the aromatic hydrocarbons which were oxidized using Ce(IV)/Ce(III) redox mediator include p-methoxy toluene (6,12- 14, 16-17 ], toluene [8,15-18 ], p- chloro toluene [16], p- amino toluene[ 16 ], p-cresol [19 ],o-and p-xylenes [15,16,17& 20 ], m-xylene [ 21] and naphthalene [ 22 ,23].

All the studies mentioned above employed sulphuric acid as the medium for  $Ce^{4+}$  /  $Ce^{3+}$  redox system. There is one important limitation in cerous / ceric mediated electroorganic synthesis. The redox mediator is soluble only to the extent of 0.1M in sulphuric acid and other acids. This leads to a

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