Effectiveness of Ceric Naphthalene Sulfonate on Controlled Indirect Electrooxidation of Aromatic Side Chain at Platinum

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The effect of complexation of Ce(IV) as ceric naphthalene sulfonate, on the oxidation of side chain in hydroxy-, amino- and nitro-toluenes at platinum electrode is explored. Partial oxidation due to complexation could be achieved. The products, characterized by IR and PMR, are identified to be aldehydes in acidic range and dimer in the alkaline medium. Mechanisms for these anodic conversions are proposed.

Key Words: Electrooxidation, Toluenes, Ce(IV).

INTRODUCTION

Direct[1-4] and redox mediated[5] electrooxidations of aromatic side chains have been dealt exhaustively. In particular, regioselectivity in direct electrooxidations[6,7] and usage of metal ions in indirect electrooxidations[8,9] are of some importance.

The oxidation power of Ce(IV) is reported to be dependent on the nature of the medium, the anions present and temperature[10-12]. While Ce(IV) in sulfuric acid brings about oxidation only at elevated temperatures, the corresponding nitrate and perchlorate could effect the required change at the laboratory temperature[13-15]. Further, the oxidation power of Ce(IV) was found to decrease due to coordination, especially with sulfate anion or water as ligand[16-18]. Thus complexation enables to bring about controlled oxidation of aromatic side chains, which otherwise not possible with other redox systems. These ideas led to explore the effectiveness of ceric naphthalene sulfonate (CNS) in its compatibility for organic systems, in its controlled oxidation power even at room temperature and in its current efficiency. Ceric naphthalene sulfonate is chosen in this study, also for its cost effectiveness, easier method of production and its ease in dissolution into the partial aqueous media.

p-Cresol, *p*-toluidine and *p*-nitrotoluene are subjected to indirect electrooxidations with CNS as electron carrier, in acidic and alkaline pH solutions at platinum electrodes. The influences of substituents on the products yield are investigated.

EXPERIMENTAL

p-Nitrotoluene (Ottokemi), *p*-toluidine (Burgoyne) and *p*-cresol (SDS) were purified by distillation[19]. Ceric naphthalene sulfonate was obtained by refluxing 5 g of sodium α-naphthalene sulfonate (Riedel) in 40 mL of dilute sulfuric acid. The bright yellow crystalline solid is recrystallized from 1:1 ethanol-water mixture. It is introduced in an electrolytic cell by dissolving in acetic acid followed by neutralization with drops of NH_4OH.

The purities of the samples were characterized by their b.p. and refractive indices and confirmed by TLC. A transistorized power supply (Systronics-163) and divided H-cell with G4 sinter were employed. The working potentials were measured as cell voltages.

The preparative electrolyses were performed at the potential corresponding to redox potential value of Ce(IV)/Ce(III) electron transfer process, with 2 M solution of CH_3COOH/NaOH having 0.1 M substituted toluenes and 0.01 M CNS in the anolyte. The duration of electrolysis was fixed, for an assumed $2e^-$ process. Whenever concomitant decrease in the current was observed, brief reversal of polarity or pulsing to zero volt was executed[20,21]. The product mixture was extracted with ether, and resolved by TLC using benzene with drops of petroleum ether as eluent. The products were characterized by co-TLC, physical constants, chemical tests and confirmed by IR and PMR. The product yields were obtained from the GLC studies.

RESULTS AND DISCUSSION

The complexation of Ce(IV) with α-naphthalene sulfonate has a decreasing effect on its oxidizing power. The non availability of vacant *d*-orbitals in cerium, due to complexation renders difficult, the temporary accommodation of electrons to be absorbed from the aromatic π-electrons. This is evident by the fact that only substituted aldehydes and not acids are formed, under these experimental conditions.

The decomposition potential studies prompt that it is the oxidation of Ce(III) that controls the electrode process irrespective of the aromatic compound employed in the system. Even when a very low concentration (0.01 M) of Ce(IV) is provided in the system in comparison to a considerably higher concentration of substrate (0.1 M), there is no unreacted substrate as observed from TLC. Obviously this must be possible by the regeneration of Ce(IV) by the anodic oxidation of Ce(III). The co-TLC chromatograms reveal aldehydes in the acidic range, dimer and traces of aldehyde in weakly basic medium and only the dimer in strong basic conditions.

The coordinated Ce(IV) abstracts an electron from the aromatic π-electrons to yield a radical ion as envisaged in earlier works[16,22,23]. The cation radical may eliminate a proton from the side chain or attacked by any nucleophile. The loss of proton in an acid solution can very well be justified by considering the electrical field by which the relieved proton can drift towards the cathode.

The radical ion assumes the most probable orientation **1** and **2** (**Scheme -I**). Acid medium favours the aci-form of the nitro substituent and enhances its -M influence which destabilizes the cation radical **2** to a greater extent than **1**. Similarly the protonated amine group loses the mesomeric influence on the cation radical **2**. On the other hand phenols in alkaline solution, stabilizes the radical ion **2** by its phenolate form.
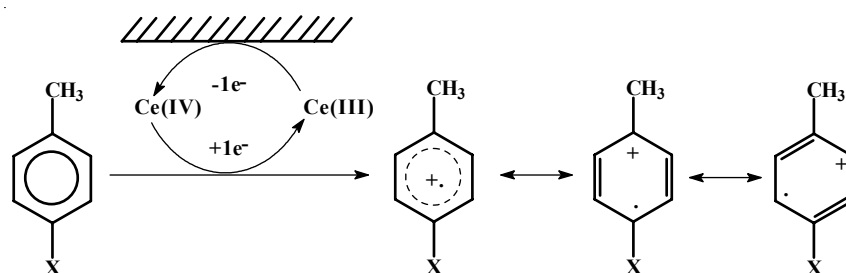
Scheme-I

The cation radical **1**, loses a proton from the side chain, leaving a radical which subsequently undergo oxidation with CNS, ultimately leading to the formation of aldehydes (**Scheme-II**), as observed in earlier similar situations[16,24]. Further oxidation of aldehyde to acid gets ceased because of the fact that the deactivated Ce(IV) by its complexation would have lost the power to abstract an electron from such a ring.

In alkaline solution, the radical ion **2** is attacked by OH⁻ followed by either dimerization or oxidation to hydroxylated products (**Scheme-III**). However, the hydroxylated derivatives have been observed in traces.

The extent of products, as obtained from GLC, stands to strengthen the above proposal. The descending orders of aldehyde yield in the case of acidic pH and dimer yield in alkaline pH are

Aldehyde: *p*-nitrotoluene > *p*-toluidine > *p*-cresol

Dimer: *p*-cresol > *p*-toluidine > *p*-nitrotoluene

The above order seems to be dependent on the comparative stability of carbonium ion (**1a**) for aldehyde. But the trend in dimer formation is likely to be controlled by steric factor. To draw further conclusive decisions on the present study, works on electroanalytical parameters are being attempted.
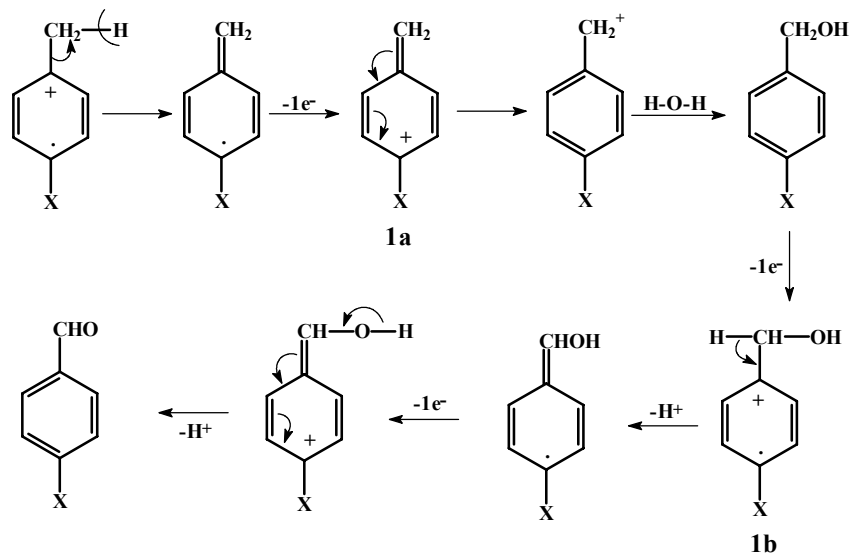
Scheme-II
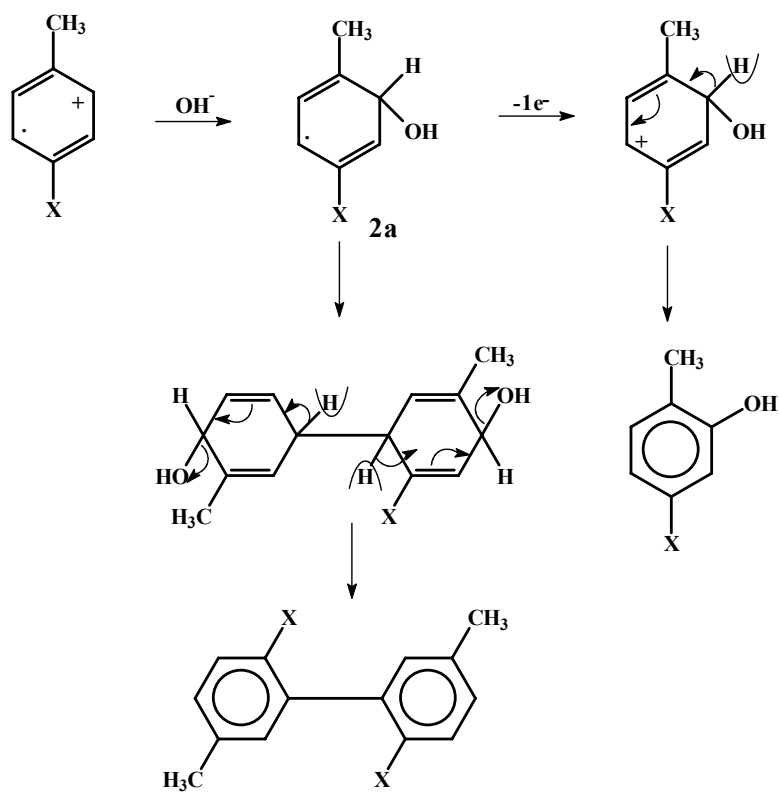
Scheme-III

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