Chapter V

CONCLUSION
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The electrochemical work is performed with the primary intension of formulating eco-friendly and economically viable product selective process as an alternative to conventional chemical process. In the present work selective cathodic reduction of >C=N - bond in oxime, hydrazone, phenylhydrazone and semicarbazone derivatives of benzaldehyde, salicylaldehyde, cinnamaldehyde, acetophenone and benzophenone has been investigated. The following electrochemical parameters have been enabled so as to achieve appropriate electrochemical conditions for product selective process with maximum quantum yield.

Electrode Materials

Cathode - Graphite; Platinum; Nickel
Anode - Graphite; Platinum; Nickel

Solvent

Aqueous - protic (Acetic acid )
Aqueous - Neutral (DMF)
Aqueous - Alkaline (KOH- DMF)
Electrolyte

Sodium acetate / Ammonium acetate

The realization of this project study has been achieved by the following systematic stages.

- An exhaustive literature survey on the cathodic processes prompted to choose and design the theme of the work.

- The experimental part of the work is initiated by the preparation of carbonyl derivatives using conventional methods prescribed in literature.

- The electrochemical studies have been performed independently with Benzaldoxime as the basic reference.

- The working potentials for all the preparative electrolyses have been arrived at by current-potential studies.

- The medium, in which the main investigation is performed, is acidic, using 2M acetic acid solution on Graphite, Platinum and Nickel Cathodes in divided H-Cell. However electrolyses have been observed in neutral (1M sodium acetate) and basic (1M KOH) media with the intension of interpreting the impacts, if any, caused on the nature of the products.

- Assuming 4-electron process to occur 2F/mole/electron of current is passed.
The catholyte solution has been extracted with solvent ether to isolate organic product mixture. Separation of cathodic products is done with column and thin layer chromatographic techniques.

The products have been characterized by co-tlc, wherever possible and identified by nmr spectral analysis.

Vapor phase chromatographic technique is adapted for quantitative analysis.

On Graphite and Nickel, reduction products have been identified as the corresponding 1° amines in major yields and substituted ethylenediamine in significant proportions.

On Platinum, along with 1° amine, hydrazo aromatic compounds have been identified in competitively good yields.

Two different prospective mechanisms – one on Graphite and the other on Platinum – have been suggested.

Cathodic process in acid medium is envisaged to get initiated with a chemical process of protonation leading to the formation of iminium cation, on both the electrodes.

In alkaline medium, electrolysis of water is accomplished as the initial step, subsequently, leading to iminium cation after protonation and elimination.

No characteristic reduction is observed in neutral solutions.

A CECE mechanism in acid medium and an ECEC mechanism in alkaline medium have been proposed.
A 2-electron reduction of iminium ion on Graphite and a 1-electron reduction on Platinum is assumed.

Though iminium cation formation is adjudicated on both the electrodes, ionic supremacy is advocated on Graphite while radical supremacy on Platinum.

The overall cathodic process is visualized as "Adsorption controlled process" on Graphite and "Diffusion controlled process" on Platinum.

The crucial aspects of the proposed mechanism have been substantiated by correlating the experimentally observed fluctuations in working potential values, net conversions realized and comparative quantum yields of various products, with the following factors which are assumed to have influenced these parameters.

- Variations in the aromatic moiety
- Variations in the functional derivative-fragment
- Polarity of the solvent
- pH of the medium and
temperature.

Electroanalytical studies have been carried out only with an intention of substantiating the experimental observations and mechanistic proposals.

Cyclic voltammetric studies, substantially supported with current – potential studies have been exhaustively exploited.

- Cyclic voltammograms with a range of substrates varying in aromatic moiety and in functional derivative –
fragment are obtained on glassy carbon coupled with Ag/Agcl electrode as reference.

- Scans with scan rates 50, 250 and 500 mV/sec and multi scans at 500 mV/sec scan rate in the wide pH range (3, 5, 7, 9 and 12) accomplished for analytical interpretation.

- The correlations of peak potential values from CV with the working potential values obtained from current - potential studies have been observed.

- The shifts in the peak potential values find relevance to the net conversions for various substrates.

- CV obtained in acidic, neutral and alkaline solutions confirm the experimental observation.

- The plots of $i_p$ values against $\sqrt{v}$ values explain the reversible character of the process under taken.

- Scan rate – current plots confirm the ‘absorption controlled process’ on Graphite

- Multi scan CVs indicate the formation of polymeric films- non conducting in the case of Cinnamaldehyde derivative and conducting in the case of Benzophenone derivative.

Electrosynthetic and electroanalytical data generated during the present study have served to initiate an Electroorganic perspective and interpretation for the chemical conversion. The study is conceived to be an initiative towards a concerted approach comprising synthetic and physicochemical aspects of an
organic reaction. Though substantial quantum of data has been obtained, more convergent approach has to be undertaken. Much experimental expeditions involving modified electrode material, ion selective membranes, upgraded electrochemical techniques, widened electroanalytical findings and others are required to achieve product selective and stereo specific electrochemical conversion processes. Much more authentic experimental findings at the laboratory scale must ultimately be extended to the industrial level with futuristic global implications.