Chapter I

INTRODUCTION
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1.1 ELECTROORGANIC INITIATIVE

Electroorganic chemistry is a multidisciplinary science overlapping the vast fields of organic chemistry. Historically, synthetic electroorganic chemistry made its debut in 1801 with the electrochemical oxidation of alcohol \(^1\). The electroorganic synthesis was performed by Michael Faraday (1834). It was the anodic decarboxylation of acetic acid in aqueous medium. Henry Kolbe (1849) electrolyzed fatty acids and half-esters of dicarboxylic acids and established the practical basis of electroorganic synthesis. Near the end of the 19\(^{th}\) century, various electrolytic industrial processes emerged, mostly reductive, stimulated by the pioneering works of Kolbe, Haber, Fichter, Tafel and other notable contemporaries who expanded the foundation of organic electrochemical technology.

Several works have been compiled \(^2-7\) detailing the many electroorganic reactions that have been discovered over the years. Various aspects of organic electro chemistry have been covered by earlier publications \(^8-10\).
A Faraday society discussion, review's such as polarography of organic compounds, the reduction of aromatic hydrocarbons, the reactions of carbanions, the oxidation of organic compounds, the oxidation of aromatic hydrocarbons and amines, the Kolbe reaction, Electrosynthesis, cyclization reaction, and solvents and electrolytes are major areas worth mentioning in the field of electroorganic synthetic works.

The concept of 'Controlled potential electrolysis' had a great impact on modern electroorganic synthesis. The current density, current duration and electrode material are important only in so far as they determine the electrode potential and its changes in the process of electrochemistry. Subsequently considerable data had been accumulated by 1940 as documented by Fichter in his excellent monograph. It is in the last few decades that electroorganic chemistry has assumed a character distinct from usual electrochemistry, which occupies a well defined position in inorganic chemistry. During 1955 -65, great efforts were made to introduce electrochemical concepts into synthetic organic chemistry.

It is increasingly apparent that the electrochemical method offers the most convenient general technique for generating ion radicals. The study of these interesting species is fast becoming a new frontier for organic chemists. However majority of organic chemists were still unaware of its potentiality. Only a few pioneering synthetic chemists took full advantage of the novel and versatile methods of electrochemistry. Much has been learnt about the reaction pathways of cation radicals, carbonium ions or uncharged radicals.
formed at the cathode, through product isolation, polarography \(^8,28\), coupled electroanalytical and spectroscopic techniques \(^{29}\) and a host of other methods.

Apart from the advances in the field of electrosyntheses made in 1970’s, various other novel concepts and methodologies for organic synthesis were developed during this period. These include the concept ‘dipole inversion’ which is of vital importance and has been widely accepted \(^{30}\). For example, it is possible to generate a cationic species in a basic medium or anionic species in an acidic medium and to obtain nucleophilic attack at the \(\alpha\)-position of a carbonyl group. In such ways, the potentiality of electrosyntheses can be expected to have a profound impact on research in organic chemistry in the 1980’s.

Cell design and scale-up including dimensionally stable anodes, electroanalytical studies to elucidate the mechanisms of electroorganic reactions, the effect of absorption and diffusion controls on the electrode reactions, functionalization of organics, electro generation of unusual valence states, electro initiated polymerization, electro bio-chemical processes and environmental control by electrochemical methods have subsequently gained increasing attention by electroorganic researchers.

Electrosynthetic reactions began to attract much attention among synthetic chemists due to their high-energy efficiency and cleanliness with its wide applications spread into all fields of organic chemistry \(^{31}\). Strong emphasis on the elucidation of product compositions being replaced to some extent by greater investment in designing more acceptable electrolysis systems and optimizing the electrolysis conditions to obtain high yields of the desired
products. In this sense, electroorganic synthesis in the 1970’s was able to emerge from its infancy and be more fully assimilated into routine synthetic organic chemistry.

More recent developments in electroorganic chemistry have been covered by Adams. The importance of the newer analytical techniques to identify the reaction products is not to be underestimated; a detailed knowledge of the identity and amounts of the products still provides the least ambiguous information about the course of the reaction. Great progress in the understanding of fundamental mechanisms of electrochemical reactions has been achieved during the last few decades in parallel with the spectacular advances of electroanalytical and spectroanalytical methodologies and the commercial availability of the relevant instruments.

1.2 SIGNIFICANCE OF ELECTROCHEMICAL STUDIES

Electroorganic chemistry is now a rapidly growing field compared to the relative dormancy prior to the last decade. The ‘black-magic’ associated with the field is disappearing and being replaced by a sound mechanistic basis. The significance of electrochemical synthesis is even more formidable.

- Electroorganic synthesis can be inherently pollution free at the process site.
- Precise control of the electrode potential, and hence of product selectivity is easily attainable when required.
- Electrochemical reactions do not require thermal energy to overcome activation barriers, and hence are applicable to thermally sensible
compounds. The driving force is the electrode potential.

- The reducing or oxidizing energy and the reaction rate may be increased or decreased to any extent by simply varying the electrode potential. This certainly avoids the high temperature - high pressure experimental conditions employed. Eg., in the catalytic hydrogenation route.

- Electrochemistry should be considered when there is no known chemical procedure; thus there are many products which have only been synthesized electrochemically.

- Stoichiometric amounts of oxidants and reductants are not required and their by-products are thus avoided. This has interesting implications, when one considers the current pressure to avoid pollution by discarded by-products.

- Some chemical oxidizing or reducing agents, although available at cheaper rates, pose a formidable pollution problem. The zinc and Iron sludge from chemical reduction routes, for example, are likely to face stiffer public resistance in the years to come.

- Electrochemical routes either avoid the use of such reagents or recycle them effectively in indirect electrochemical processes thus providing a clean and pollution free alternative route. In this connection, many conventional redox reactions have the possibility of being ‘catalytic’ if the redox product can be easily reconverted in situ to the starting reagent by electrolysis.

- Although the cost of most materials has increased steadily over the years,
the cost of electricity has remained remarkably stable, and is thus becoming an even more attractive reagent for large-scale reactions.

- Electrochemical synthesis, by its very nature, and by ease of instrumentation, is eminently suitable for continuous and automatic operations, another industrially attractive feature.

- Although many oxidizing and reducing agents employed in the chemical processes are cheaper ones, some costly reagents such as lithium aluminum hydride are required for some specific reductions, such as the reduction of Anthranilic acid to o-Aminobenzyl alcohol. The same process may be cost effectively achieved by electrochemical processing.

- Number of unit operations may be less in electrochemical process when compared to a chemical process.

- Even in chemical processes where a competitive chemical process exists, the electrochemical process may consume less energy when compared to the chemical ones.

- Quantitative monitoring of the course of the reactions by coulometry, using electronic/ electrochemical coulometer is unsurpassed compared to most other general synthetic techniques. The current itself is the measure of the rate of reaction.

- When a multifunctional molecule is oxidized or reduced, electrochemical route can show selectivity which is not easy to achieve by other means. For example, in a molecule containing - Br and >C=0 groups, -Br species may be eliminated keeping >C=0 group intact \(^{32}\).

- Petrochemical feed-stocks are becoming increasingly costly and scarce.
Electrochemical routes are being developed to use non-conversional feed stocks such as carbon dioxide, coal and lignin.

- Some specific organic synthetic reactions can be carried out by electrochemical means alone. Anodic fluorination and other anodic substitution reactions and electrochemical reduction of Phthalic acid to Dihydrophthalic acid are some examples of such processes.
- There are some specific occasions where very high purity of products is required. In such occasions, the electrochemical routes are the invariable options.
- Electrochemical method is the suitable one for small scale production. Even the tonnage chemicals can be manufactured in small quantities for captive use to reduce transportation and inventory costs and
- Useful and desired products on both cathodic and anodic electrodes can be produced by electrochemical method only.

The electrochemical reactions make significant contributions to organic synthesis either in the laboratory or on an industrial scale. These methods have the potential for developing more ‘green’ chemical synthesis. Over recent years, modern investigations have clarified the mechanisms of important organic electrochemical reactions. Progress has also been made in controlling the reactivity of intermediates through either radical or ionic pathways. The electrochemical routes may be found more economical as well if a cheaper raw material can be utilized or if, by using electrochemistry, a continuous operation is facilitated.
1.3 ELECTROCHEMICAL PROCESSES

Electrochemical reactions are performed in reactors known as electrolytic cells or electrolyzers and are commonly referred to as cell reactions. All overall cell reactions are necessarily the result of two half-cell reactions, the cathodic and the anodic. These reactions take place simultaneously and involve transfer of electrons at the electrode-solution interface.

\[
\begin{align*}
A + e^- & \rightarrow C & \text{Cathodic} \\
B - e^- & \rightarrow D & \text{Anodic} \\
A + B & \rightarrow C + D & \text{Overall cell reaction}
\end{align*}
\]

Overall cell reaction can proceed either spontaneously or by imposing on the cell a certain external electrical potential or a driving force. Because of inhibiting thermodynamic or kinetic factors, most organic cell reactions are not spontaneous. Therefore they must be driven by an imposed potential.

1.3.1 Classification

The fundamental events in electroorganic reactions are shown schematically in the following steps. The organic substrate R, is considered to undergo an electron transfer reaction (electro-reaction) as a primary step in the overall electrochemical reaction. This primary electron transfer (ET) reaction is defined as a direct reaction if the electron exchange takes place directly between the electrode and the organic substrate. If the organic substrate undergoes the primary electron exchange via a mediator, the reaction is indirect. Direct ET reactions are typical heterogeneous reactions. Indirect
reactions may be either homogeneous or heterogeneous, depending on whether the mediator is dissolved in the solution or immobilized physically or chemically on the electrode surface.

I. **Direct Reactions**

   a. **Anodic Reactions**

   \[
   \begin{align*}
   \text{R} & \rightarrow \text{R}^{\bullet+} \quad \text{anode} \\
   \text{R}^{\bullet+} & \rightarrow \text{R} + \text{R}^{2+} \quad \text{disproportionation} \\
   \text{R}^{\bullet+} & \rightarrow (\text{R R})^{2+} \quad \text{dimerdication} \\
   \text{N}^- & \rightarrow (\text{R N})^* \quad \text{Nucleophilic addition} \\
   -e & \rightarrow \text{R}^{2+} \quad \text{dication} \\
   -E^+ & \rightarrow \text{R}^* \quad \text{radical} \\
   -E^+,-e & \rightarrow \text{R}^+ \quad \text{carbonium ion} \\
   -E^+ & \rightarrow \text{R}^{\bullet} \rightarrow \text{RR} \rightarrow \text{dimmer}
   \end{align*}
   \]

b. **Cathodic Reactions**

   \[
   \begin{align*}
   \text{R} & \rightarrow \text{R}^{\bullet-} \quad \text{cathode} \\
   \text{R}^{\bullet-} & \rightarrow (\text{RR})^{-2} \quad \text{dimmer dianion} \\
   \text{E}^+ & \rightarrow (\text{RE})^* \quad \text{electrophilic addition} \\
   e & \rightarrow \text{R}^{2-} \quad \text{dianion} \\
   \text{R}^{\bullet-} & \rightarrow \text{R} + \text{R}^{2-} \quad \text{disproportionation} \\
   -N^- & \rightarrow \text{R}^{\bullet-} \rightarrow \text{RR} \rightarrow \text{dimmer} \\
   -N^-,-e & \rightarrow \text{R}^- \quad \text{carbanion}
   \end{align*}
   \]

II. **Indirect or Mediated Reactions**

   \[
   \begin{align*}
   \text{M} & \rightarrow \text{M}^{\bullet+} \quad \text{Cathode} \\
   \text{M}^{\bullet+} & \rightarrow \text{R} \rightarrow \text{R}^{\bullet-} + \text{M} \\
   \text{M} & \rightarrow \text{M}^{\bullet+} \quad \text{anode} \\
   \text{M}^{\bullet+} & \rightarrow \text{R} \rightarrow \text{R}^{\bullet+} + \text{M}
   \end{align*}
   \]
From a purely synthetic perspective, organic electrode reactions are perceived as heterogeneous chemical processes involving transfer of electrons in the overall mechanistic reaction scheme.

a. Symmetrical Couplings

Anodic Addition

\[ \text{Anodic Addition} \]

\[ 2 \text{ } \text{ } - 2 \text{ e}^- + 2 \text{ Nu}^- \rightarrow \text{Nu} \text{ } \text{ } \text{Nu} \]

Cathodic Addition

\[ \text{Cathodic Addition} \]

\[ 2 \text{ } \text{ } - 2 \text{ e}^- + 2 \text{ E}^- \rightarrow \text{E} \text{ } \text{ } \text{E} \]

Anodic Elimination

\[ \text{Anodic Elimination} \]

\[ 2 \text{ RE } - 2 \text{ e}^- \rightarrow \text{RR } + 2 \text{ E}^+ \]

Cathodic Elimination

\[ \text{Cathodic Elimination} \]

\[ 2 \text{ RNu } + 2 \text{ e}^- \rightarrow \text{RR } + 2\text{Nu}^- \]

b. Unsymmetrical Couplings

Anodic

\[ \text{Anodic} \]

\[ \text{R } - \text{ e}^- + \text{XY } \rightarrow [\text{RY}]^+ + \text{x}^+ \]

Cathodic

\[ \text{Cathodic} \]

\[ \text{R } + \text{ e}^- + \text{XY } \rightarrow [\text{RX}]^+ + \text{Y}^- \]
1.3.2 E and C Processes

The reaction mechanisms of electroorganic reactions are henceforth composed of at least one electron transfer steps at the electrode as well as proceeding and follow up bond breaking, bond forming and / or structural rearrangement steps \(^{34, 35}\). Most electrooxidation of organic compounds proceed in a step fashion through the loss of electrons by electrolysis [E process] and subsequent chemical reaction [C process] \(^{36}\). In the E process, desired reactive species are selectively produced and in the C process, the reactivity of the intermediates are controlled by designing a situation in which they are directed in the desired ways. The importance of the C process is therefore clear as even starting from the same reactive intermediate, it is possible to obtain widely desperate results by changing the constituents of the electrolysis media. In other words, the fate of the reactive intermediates is always affected by the solvents, electrolytes, additives and electrodes. Most of the electrochemical reactions involving organic compounds do not terminate in the E process. But the reactive intermediates further undergo chemical reactions leading eventually to stable products after substitution, elimination, addition, degradation, recombination, fission or rearrangement reactions \(^{37-39}\).

For a substrate [S-H], an ECEC mechanism may be proposed as

\[
[S-H] \xrightarrow{\text{E}} [S-H]^* \xrightarrow{\text{C}} [S]^* \xrightarrow{\text{E}} [S]^+ \xrightarrow{\text{C}} [S-H] \\
\]

Today’s concept of electroorganic synthesis is necessarily an extension of that of classical electrode reactions and embraces all chemical and physical phenomena involved in the electrolysis system.
The E process in electroorganic synthesis comprises all the possible electron transfer process which may exist not only around the electrode surface but also in the diffusion layer or even in the bulk solution.

In order to classify the various mechanisms of organic electrode reactions, a specific nomenclature has been developed. It is often extended in an informal way to accommodate particular reaction features and one may find additional or deviant symbols.

Usually, however, electron transfers at the electrode are denoted by ‘E’, while chemical steps, not involving the electrode, are denoted by ‘C’. The electron transfer may further be characterized as ‘E\(_r\)’, ‘E\(_{qr}\)’ or ‘E\(_i\)’ in the reversible, quasi-reversible or irreversible cases. It is usually not indicated how transport occurs. If the ‘C’ step is a dimerization, the symbol ‘D’ is common while an electron transfer between two species in a solution is denoted as ‘SET’ (solution electron transfer).

For more complex mechanisms, picturesque names such as square, ladder, fence or cubic schemes have been selected. In redox polymer films, additional transport of counter ions, solvation and polymer reconfiguration are important and four dimensional hyper cubes are needed to describe the reactions.

The E and C processes can very well be controlled by distinctly different parameters. The E processes are controlled by maintaining constant potential where the potentials are externally controlled by means of the applied voltage through a potentiostat or by maintaining constant value of current density.
throughout the electrolysis. The C processes are dependent on the microscopic reaction sites under which electrogenerated active species come in contact with the solvents, electrolytes, additives, etc., to undergo subsequent chemical reactions. Hence the control of the C process depends on optimizing the functions including the solvents, electrolytes, additives, electrode materials, current density, pH and temperature.

Modern electroorganic synthesis characteristically prefers on the product selectivity. A careful provision of electrolytic conditions and system can lead to product selectivity. The difference from the traditional reagent based organic reactions is that the solvent-electrolyte-electrode system and the electrolysis conditions such as current density, potential, pH, etc., play an important role in the outcome of the C process.

The electroanalytical method is conveniently classified on the basis of current control or potential controlled electrolysis. Alternately, the electrochemical techniques can also be distinguished depending on the stationary or non stationary diffusion of mass transportation.

1.3.3 Physical Principles in Electrosynthesis

The electrical double layer or the electrified interface between an electrode and a solution is the “innermost essence” of electrochemistry. Only a pictorial, simple representation of the electrical double layer can be made in order to discuss most simply its practical significance in electrosynthetic work.
The structure of the double layer is sometimes the most influential factor in the outcome of the reaction, as in the electrohydrodimerization of acrylonitrile, and in stereochemical reactions in which the electrode surface is covered with chiral compounds. A recent review about the electrical double layer has been presented by Parsons 45.
a. Thermodynamic Aspects

The fundamental thermodynamic equation in electrodic reactions is the well-known Nernstian equation.

\[ E_e = E_e^o - \frac{RT}{nF} \ln Q \]

The electrode potential expresses the energy of the electrons in the electrode in contact with the electrolysis medium \(^{33,46}\). When the electrode is negative, it has an excess of electrons and when positive, an excess of positive charges. Thus the electrode potential affects the energy required to add electrons to the electrode or remove electrons from it. It is important to understand the difference of the sign(- or +) of electrode potential and the sign of the half-cell reaction. The Nernst's equation in connection with a simple reversible electrodic organic reaction is represented as

\[ O + n \, e^- \quad \xrightarrow{ \text{Cathodic partial current} } \quad -i \]

\[ +i \quad \xrightarrow{ \text{Anodic partial current} } \]

The Nernstian equation may be written in the usual practical form.

\[ E_e = E_e^o + \frac{RT}{nF} \ln \frac{C_O}{C_R} \]

Where \( C_O \) and \( C_R \) are concentrations of the oxidized and reduced terms of the redox couple \( O/R \).

b. Kinetic Aspects

Electrochemical reaction rates are generally expressed as current-potential \((i-E)\) relationships. The most simple and practical current-potential
relationship is Tafel’s (1905) empirical equation.

\[ \eta = a \pm b \log i \]

In most practical synthetic applications electrolysis is carried out of relatively high positive or negative electrode potentials. That is at potentials far from the equilibrium potential. Under such potentials, only one of the exponential terms is practically significant. Thus at high anodic or cathodic potentials, the limiting forms expressed in the following equations are derived from the general equation. These limiting forms represent the detailed Tafel equation as derived from the theoretical considerations.

\[ \log i_{\text{anodic}} = \log i_o + \frac{\alpha A n F}{2.3 R T} \eta \]

\[ \log i_{\text{cathodic}} = \log i_o + \frac{\alpha C n F}{2.3 R T} \eta \]

At very low overpotentials, another limiting form derived by expanding the exponentials.

\[ i = i_o \frac{n F}{R T} \eta \]

1.4 ELECTROCHEMICAL PARAMETERS

Electrolytic processes characteristically are controlled and affected by many parameters, some of which are mechanical, electrical and chemical and a combination of thereof. The realization of electroorganic synthesis depends heavily on the proper application and control of those variables.
The following experimental variables are of importance for the outcome of an organic electrosynthesis

### 1.4.1 Cell Design

The design of an electrolysis cell, operating within the constraints can be extremely simple or quite complex depending on the requirements of the actual system under investigation. Chemical engineering concepts are now widely employed in electrochemical process. The industrial application in the past could be attributed to the absence of electrolytic cells suitable for competitive process design. Two causes can be found to account.

(I) Suitable engineering materials made it difficult to construct a cell, capable of standing up to the testing process-requirements. The suitable synthetic polymers construct rigid and light cells that are not subject to corrosion and solvent attack.

(II) Due to lack of good engineering design, batch electrolytic cells were on the whole unable to compete with the more sophisticated continuous chemical reactors.

Of course, the overall objective of process development can be achieved by optimizing a number of valuable parameters. Highest yield and current efficiencies must be achieved in the electrochemical process. The amount of product produced per ampere hour measured by space time yield ($Y_{st}$)

\[
Y_{st} = \frac{\text{Amount of product produced}}{\text{Time of electrolysis} \times \text{cell volume}}
\]

Specific electrode area ($A_s$) and high electrode area volume ratio ($A_e$) also
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contribute to high space time yield and higher productivity.

\[ \text{As} = \frac{\text{Electrode area}}{\text{cell volume}} \]
\[ \text{Ae} = \frac{\text{Electrode area}}{\text{electrode volume}} \]

The ohmic voltage drop in the anolyte or catholyte can be minimized by
minimum spacing of the electrodes. Uniform current density distribution on the
electrode surface is another requirement to ensure product selectivity.

The continuous operation of the cell usually gives a number of
advantages - first, better current efficiencies and second steady state process.
It is possible to work at a fixed electrode potential.

Based on energy and production considerations, an ideal electrolytic cell
should satisfy the following requirements \(^{48,49}\). The cell should be operated at a
voltage very near to the theoretical voltage.

- The electrode should be dimensionally stable and the designs of the
  same should facilitate minimum losses in current efficiency.
- Provision for easier separation of anodic and cathodic products should
  be made.
- Adequate circulation of the electrolytes should be maintained to realize
  uniform concentration within the cell and
- At a given volume, it is always advantageous to have the maximum
  electrode area.

A wide variety of electrochemical cells have been designed. Beaker type
undivided and H-type divided cells of monopolar or dipolar configurations
consisting 2D as well as 3D electrodes where the electrodes as well as
electrolytes may be stationary or dynamic have been developed. An excellent
comprehensive book and a number of classical reviews by experts\textsuperscript{50-55}, on cell designs and electrode geometry are available.

In general the cells have been grouped under two main types, namely, batch and flow cells.

(I) \textbf{Batch Cells} - in which the electrolyte remains inside the cell throughout the experiment, have in the past constituted the majority of laboratory electrolytic cells. Due to lack of good engineering design, batch electrolytic cells were on the whole unable to compete with the more sophisticated continuous chemical reactors.

(II) \textbf{Flow Cells} - in which, with circulating electrolyte, have in recent years found increasing application for synthetic purpose. Electrolyte continuously flows though the cell. A diaphragm is introduced into an electrolytic cell when it is necessary to keep the contents of the anodic and cathodic sides of the cell separate. This condition arises when

- The starting material and/or products of the electrode process being investigated could be destroyed by reaction and/or contaminated with reaction products of the counter electrode.
- It is required to maintain different electrolyte compositions at the anode from those at the cathode.
- There is a need to exercise careful control of pH in the vicinity of the working electrode.

\textbf{Undivided Cell}

The undivided cell is one in which the electrolyte, solvent, starting materials and products have equal contact with both electrodes. Mostly glass
beaker is used as a cell with solid electrodes, the anode and cathode may be simply draped over opposite sides of the beaker. Electrical connections can be conveniently made with alligator clips, using care not to allow electrolyte to touch them. A magnetic stirrer can be used for agitation. The simple undivided cell is always more desirable for large scale synthesis from both technical and economic aspects.

**Divided Cell**

A two compartments or divided cell is mostly required for best result, in which a semipermeable barrier is interposed between anode and cathode. For micro scale amount, the divided H-cell is useful and is readily available from commercial sources. These have low space-time yields and energy losses.

**Cell Dividers**

Most electroorganic systems require the use of separate chambers for anolyte and catholyte. A suitable barrier material called ‘cell divider’ is used for that purpose. It is interposed between anode and cathode. The ideal divider must be selected according to the following requirements.

- It must be permeable to ions, preferably impermeable to other species.
- It must be stable to the electrolytic medium at the temperature of the electrolysis.
- It must be continuous and mechanically strong enough to withstand any pressure differences encountered.

The divider separates the system into two chambers, one in which the anolyte comes into contact only with anode and the other in which the catholyte
contacts only the cathode. The membrane type cell dividers made of this polymeric material offer better selectivity and less diffusion of neutral species, but are less chemically resistant than the ceramic type.

The most frequently used cell dividers are made of refractory materials, such as ceramics or fritted glass of various porosities. They have excellent chemical resistance, but have less selectivity with respect to diffusion of solvent, starting material, products and electrolyte. Depending upon the diaphragm-two types of dividers are used:

(I) Permeable membrane composed of porous matrix and

(II) Semi permeable or ion exchange membranes consist of a resin material.

Refractory material, cellophane, ion exchange resins are some of the diaphragms, being employed in electrochemical process.

1.4.2 Electrodes

Electrode material plays a crucial role in the electrode process. The selection of the electrode was made mainly on the basis of the electrode potential range available, within which the electrolyte-solvent did not undergo electrolysis. However, the catalytic features of the electrodes and their designs must also be taken into account when selecting a particular electrode material \(^{56,57}\). The greatest stimulus for research in electro catalysis has come from the search for cheaper catalytic electrode material \(^{58,59}\). An electrode process involves at least three steps.
1. Adsorption of reactant (chemical step)

2. Charge transfer (electrochemical step)

3. Desorption of products (chemical step)

The characteristics of the electrode becomes more important as the changes occur around the electrode during electrolysis are influenced by electrode potential and the structure of the double layer at the electrode, which is itself being affected by electrode potential\textsuperscript{60-62}.

The nature of the electrode used for electrolysis is therefore becoming a key variable, to the extent that adsorption and double layer effects may play a role in a given system. The electrode may have a profound influence on the system and could, in fact, change the entire nature of the product\textsuperscript{63}. Choice of a suitable electrode will be restricted by its stability under electrolysis conditions. The useful potential range for a particular electrode depends on the electrode and on the medium.

The role of the cathodic material in the electrosynthesis of organic compounds has been well discussed\textsuperscript{64}. The direct electron transfer from the cathode to the organic compound takes place predominantly at \textit{sp} metals such as Pb, Hg, Sn, Ga, Tl, Zn, Cd, Bi, Al, In etc., and it is known that the highest hydrogen over potential is exhibited by these \textit{sp} metals. The absorption of hydrogen on the \textit{sp} metals does not occur. The use of the \textit{sp} metals also favors the production of anion radicals and radicals, and their secondary chemical reactions lead to hydrodimerization, cathodic coupling, and the formation of organometallic compounds.
In contrast, the lowest hydrogen over potential is observed on d metals with the maximum degree of occupancy of the outer d orbitals of metals such as Pt, Ru, Ni, Pd, Rh, Fe, Co, Re, etc. in which hydrogen atoms are readily absorbed. Such hydrogen atoms sorbed on the d metals cathode surface act as a hydrogenating agent.

The electroreduction of a Ketone to the corresponding carbinol without forming pinacol as a by-product can be conducted at platinized Platinum, Raney Nickel, or other electrodes having electrocatalytic characteristics. Purely catalytic reactions that either do not take place electrochemically or are realized with great difficulty on account of the need to reach potential that are too negative, are possible at these d metals.

The preparative electroreduction of Nitrobenzene, Phenyl-hydroxylamine, Azoxybenzene, Azobenzene, and Hydrazobenzene at copper and Raney Nickel electrodes in neutral and basic aqueous methanolic solutions affords Aniline in 80-100% yields\(^65, 66\). The effect of Ni, Cu, Pb, Cu - Hg, and Pb - Hg electrodes for the reduction of m-Chloronitrobenzene, yielding 3, 3' – Dichloroazobenzene in around 90% yields, has been well investigated\(^67\). Surface effects of glassy carbon electrode have been observed on responding aromatic carbonyl compounds. The interaction between acidic surface functional groups on glassy carbon electrode and the aromatic carbonyl group such as Benzil has been noticed\(^68\).

When selecting an electrode for a particular electrolysis, it should possess the following properties.

- It should be a good conductor.
- When possible, the surface should be an effective catalyst for the reaction.
- It should not suffer from chemical or electrochemical attack and it should usually be of rigid construction.

a. Platinum

Platinum has been the most widely used anode material for electroorganic reactions. On the other hand, at cathodic potential or with strong reducing agents, hydrogen will be adsorbed on the surface. It is similar, if not exactly analogous, to catalytic hydrogenation, with hydrogen being generated electrolytically from water. In neither case do these effects prevent the use of Platinum for electrolysis except that they should be taken into account when considering mechanisms or when examining results of voltammetry. Polarization determination will show the hydrogen oxidation as a transient. The platinized electrode (deposition of finely divided Platinum) has an extremely high surface area and is sufficiently rugged to withstand. In fact, bright Platinum itself is often subjected to platinization to increase its surface area and catalytic activity. The overvoltage of Platinum cathode is 0.3V.

The relatively high cost of Platinum defers the use of the bulk metal in large scale applications. This problem is often overcome by deposition of finely divided Platinum on base metal. Platinum electrodes are liable to bring about one-electron oxidations, and are available for holding a cation radical or radical cage. For industrial scale electrolysis, Platinum plated Titanium electrodes are often used.
b. Graphite

Graphite is porous and consists of interconnecting carbon crystals which make up 70 to 90% of the total volume of the material. Both carbon and Graphite are porous to some extent, which may be an advantage if high surface area is desired, but porosity may also cause problems due to clogging with insoluble residues. Carbon paste electrodes have been described in detail by Adams. The over voltage of Graphite cathode is 0.8V.

There are various types of Graphite manufactured which differ from each other in the method of fabrication and temperature treatment. They are chemically resistant and reasonably good conductors.

A form of Graphite known as pyrolytic Graphite, although at present expensive has the desirable properties of being impervious to liquids and gases and inert to most forms of chemical attack. Pyrolytic Graphite has been used successfully in a number of organic electro chemical investigations.

Other Graphite materials, such as ‘glassy’ carbon and a similar material called vitreous carbon, are available but have been little used as anodes. They are slightly porous and therefore may suffer degradation similar to that of the more common graphite. Graphite is employed as a counter electrode to eliminate the formation of anode corrosion products which could plate out on the cathode.

c. Nickel

Nickel is a useful cathode material. It is relatively inert in acidic media and having moderately high hydrogen over voltage. The over voltage of Nickel
cathode is 0.6V. It may be bright plated onto most metal substrates, and is hard
and abrasion resistant. It may be useful as an anode material only in alkaline
media. It is available in sheets, rods, and powder, in addition to a porous form.

1.4.3 Electrolytic Media

Electrolyte media consists normally of a solvent for the organic reactions
and a supporting electrolyte to enable the current to pass through the medium
without too great an ohmic resistance. In some cases, the reactant or a solvent,
or a combination of the two, may be sufficiently conducting to avoid the need
for a supporting electrolyte. This can be important since the recovery of
products from the reaction mixture will be considerably easier.

The selection of a suitable reaction medium can be made on the
grounds of at least four criteria.

(i) Solubility of reactant
(ii) Range of electrode potential
(iii) Suitability for a desired reaction path and
(iv) Degree of conductivity.

The solvent and electrolyte perform important functions in electrolytic
work, and should be selected only after considering several factors. The
general considerations to be applied to the selection of solvent and electrolyte
may be summarized as follows.

- Stability towards electrolysis conditions
- Solubility of starting material
- Conductivity
• Reactivity toward products of intermediates
• Ease of purification and separation
• Adsorption
• Toxicity and ease of handling.
• High dielectric constant to ionize the electrolyte.

In some cases the solvent or electrolyte itself can be chosen purposely to participate in the reaction. Proton availability can also be an important factor, particularly when carbanions or radical anions are involved.

The suitable choice of a solvent and an electrolyte is essential for product – selective electrolysis. The behavior of cationic species in a catholyte is directly related to the product – selectivity in electro reduction. Tetraalkyl ammonium ions play an important role in a variety of electro reduction reactions.

The cathodic formation of Tetraalkyl ammonium amalgams has been recognized at mercury electrodes. The formation of Tetraalkyl ammonium graphite lamellar compounds are known to form electrochemically. Tetraethylammonium tetrafluoroborate can be electrochemically reduced to ethane and ethylene at -1.44V (vs SCE) in a DMF – BU₄NBF₄ (0.1M) – (C) system. Absorption behavior of o-Aminobenzoic acid on the mercury surface from the three different electrolytes, i.e., NaCl (0.1M), NaNO₃ (0.1M), and Na₂SO₄ (0.05M), has been investigated in aqueous media. Electroreduction of Benzaldehyde using reduced Silver bound on SPE (Solid Polymer Electrolyte) electrode brings about very good selectivity in formation of Benzyl alcohol.
a. Solvents

Aqueous Solvents

Suitable choice of the solvent is very important in almost every instance for obtaining product selectivity. Water itself is used as a solvent and also mixed aqueous organic solvents are used to carry out effective electrolysis. Difficulties encountered with aqueous media can be two fold. First, when quantities of non-ionic organic solvents are used in sufficiently high concentrations to ensure the required solubility. Conductivities are often too low. Second, particularly in anolytes, reaction of the solvent at the electrode is sometimes difficult to avoid.

Aqueous electrolytes are simply prepared by the dissolution of solvent, supporting electrolyte and reactants in triply distilled water. If particularly accurate kinetic studies are contemplated, further purification of the distilled water and additionally, pre-electrolysis might be employed.

Non-Aqueous Solvents

Many non-aqueous solvents are far more effective than water in dissolving organic reactants. Generally, the solvents other than water come into the category of non-aqueous solvents. The use of non-aqueous solvents in electrochemistry has increased dramatically over the past 20 years as interest in organic systems has grown. This subject has been reviewed in a chapter by Mann. Some of the non-aqueous solvents which find wide application in this field are Acetonitrile, Ammonia, Pyridine, THF, DMF, DMSO, etc.,
b. **Supporting Electrolytes**

The electrolyte usually exhibits good conductivity. Their prime function is to provide the source of ions to conduct current across the cell. In general, electrolytic media of high conductivity are desirable. Many electrolytes have a tendency to form ion pairs at high concentrations in organic media. The ability of certain electrolytes to adsorb on the electrode and to influence the double layer structure can play a key role in determining the course of the reaction. In some cases, the electrolyte may be chosen to serve as a buffer when acids or bases are formed during electrolysis and the electrolyte may also be chosen to serve as a reactant.

The supporting electrolyte may actually participate in an electrode process by attacking intermediate species or alter product distribution by changing the acid–base character of the solution \(^{88}\).

The criteria for selection of a suitable electrolyte are as follows

(I) Must dissolve and ionize in solvent

(II) Must be inert to starting materials, intermediates and products

(III) Must be inert over the potential range of interest

(IV) Should be easily removed on product work-up

The examples for cationic and anionic electrolytes are as follows:

**Cations:** Tetra alkyl ammonium salts, ammonium salts, alkali metal cations

**Anions:** Perchlorates, halides, Tetra phenyl borates, acetates, sulfonates.
1.4.4 Solvent - Electrolyte - Electrode Combination

The Solvent-Supporting Electrolyte–Electrode Combination (SSE) plays one of the most important roles for the synthetic result of an organic electrode process. The SSE system must be chosen as per the following criteria.

1. It should possess good solvent properties with respect to the substrate, as it serves as a medium for the reaction.

2. It should have good conductivity for the electric current. That is, the solvent should have reasonably high dielectric constant and the supporting electrolyte be present in fairly high concentration (0.1M) and

3. It may serve as a source of reactant in the chemical processes following electron transfer.

The anodic and cathodic limit of a particular SSE depends on an electrochemical process involving either solvent or supporting electrolyte. In acetonitrile, the anode limit is dependent on the nature of the anion and cathodic limit on the nature of the cation.

Anions can be ordered in series of increasing resistance towards anodic oxidation as

\[ \text{I}^- < \text{Br}^- < \text{Cl}^- < \text{NO}_3^- < \text{CH}_3\text{COO}^- < \text{ClO}_4^- < \text{BF}_4^- < \text{PF}_6^- \]

and cation in series of increasing resistance towards cathodic reduction.

\[ \text{Na}^+ < \text{K}^+ < \text{R}_4\text{N}^+ < \text{Li}^+ \]

In aqueous or aqueous-organic SSEs, the accessible potential range is dependent on the electrochemical oxidation and reduction of water with formation of oxygen and hydrogen respectively. The potential at which these processes take place are different for different electrode materials\(^4\). The
anodic limit for aqueous systems moves to more anodic potentials in the series.

\[ \text{Ni} < \text{Pb} < \text{Ag} < \text{Pd} < \text{Pt} < \text{Au}. \]

and cathodic limit moves to more cathodic potential in the series

\[ \text{Pd} > \text{Au} > \text{Pt} > \text{Ni} > \text{Cu} > \text{Sn} > \text{Pb} > \text{Zn} > \text{Hg} \]

Thus to perform a reduction of difficultly reducible substance in a water containing system, one would normally prefer a metal like Pb, Zn or Hg where as for difficult oxidations, Au or Pt would be the anode material of choice. In non-aqueous SSEs, the choice of the electrode material is not critical from this point of view.

Generally, inert SSEs tend to favour coupling reaction between two or more substrate molecules whereas those with nucleophilic or electrophilic properties favor substitution or addition reactions. As an example, the anodic oxidation of Durene \(^{89}\), on Platinum can be controlled to give substitution product only, in a strongly nucleophilic SSE, and coupling product only, in non – nucleophilic SSE. In SSEs of intermediate nucleophilicity, both types of products are formed.

Even if a consideration of macroscopic properties of the SSE many times is useful as a first approximation for predicting the outcome of an unknown electroorganic reaction, it must be borne in mind that the composition of the electrolyte at the electrode surface and its immediate vicinity might be completely different from that of the bulk of the solution. Current theory \(^{37,90}\) assumes that the electrode surface is covered by an absorbed layer of ions and neutral molecules during electrolysis. The thickness of this layer, the electrical double layer is of the order of 10A. The region between the electrical double
layer and the bulk of the solution is denoted as the diffuse layer (50-100A in thickness) in which concentrations gradually change from those of the double layer to those of the bulk of the solution. Since the electron transfer process necessarily must take place with the substrate molecule situated very close to the electrode surface, and short lived intermediate formed will undergo further chemical reactions in a medium with properties differing from those of the bulk of the solution.

The ions of the SSE can exert a powerful influence on the chemical follow-up reactions. For example, in the anodic oxidation of hexamethyl benzene in acetonitrile – water in the presence of different supporting electrolytes, different product distribution is observed. Acetamidation and hydroxylation at the side chain occur. It is observed at an anode potential, being kept the same, use of tetrabutyl ammonium perchlorate favours 95% Acetamidation, while tetrabutyl ammonium fluroborate favours 95% hydroxylation. This indicates the possibility that some species of the SSE is available in much higher or lower concentration at the electrode solution interface, which may decide the product distribution.

Having chosen the solvent, a suitable supporting electrolyte, which is soluble in the solvent, is to be selected in such a way that the resultant solution may have adequate conductivity. In general, the desirable solubility expected for an electrolyte is in the range of 0.05 – 0.3M and under such conditions, the solution should exhibit a usable current-density. The actual procedures of electroorganic synthesis can involve various electrolytes which include not only stable strong electrolytes, but frequently also electrolytically
labile electrolytes. For example, most halide salts as well as some acids and bases can be oxidized through electrolysis to give reactive species, i.e., halonium ion or molecular halogen, which may react with substrates or solvents to yield a variety of *in situ*-generated active species and products which are otherwise inaccessible \(^{93,94}\).

When the electrolysis is carried out with electrolyte NaNO\(_3\), the electrooxidation of nitrate ion provides [NO\(_3\)]\(^-\) by one electron oxidation on the anode and this radical may abstract a reactive hydrogen atom from the substrate \(^{95}\). A sandwich type arrangement such as electrode substrate-electrolyte can also be realized which function like an 'electrolyte push-electrode pull' electron transfer system \(^{96}\).

A reasonable choice of suitable electrolysis solvent cannot be expected without due consideration of what combination of electrolyte, electrode material and additive will be best for achieving the desired product-selectivity in relation to the chemical nature of the substrate. In other words, adequate selection of the above variables is closely related with the nature of the desired functionalization of the substrate. The solvent-electrolyte system required for electroorganic synthesis is quite different from that employed in conventional electrochemical measurements. In electroorganic synthesis, emphasis should be placed on the C process which may settle the fate of active intermediates stemming from the E process. As a result, most efforts have tended to concentrate on finding the best suited solvent-electrolyte-electrode system, so that various possible combinations of such variables have been examined experimentally. On the contrary, the aim of the latter investigation centres on
the establishment of a theoretical basis and its applications to the analysis of electrode reactions, on the basis of measurements of various parameter such as oxidation potential, current, scanning rate etc.,

1.4.5 Substrates

The substrate must be reducible or oxidizable within the accessible potential range (-3.3 to +3.7v). This is best done by studying the electrochemical behavior of the compound using any of the simple voltammetric techniques, for a cathode reaction at Mercury cathode and for an anodic reaction at the Platinum.

As anodic electronic transfer occurs from the HOMO of the substrate, groups which raise the energy of this molecular orbital will lower their oxidation potentials. These are the same groups that stabilize cationic centers inductively and/or by conjugation. Example: alkyl, aryl, alkoxy, hydroxyl, amino and halogen. On the contrary, since the cathodic electron transfer occurs to the lowest empty molecular orbital, substituents which lower the energy of this molecular orbital will raise reduction potentials. These are the electron withdrawing substituents such as nitro, carbonyl, cyano etc., which stabilize carbanionic centers.

1.4.6 Temperature

Normally, temperature should have little effect on the electron–transfer part of an electroorganic reaction but these are not major effects with moderate excursions. The conductivity of most electrolytes will increase with increasing
temperature. An increase in cell temperature has the distinct advantage of shortening electrolysis periods. Only in rare cases, does the product composition change considerably with temperature.

1.4.7 Concentration

Normally, it is desirable to utilize the highest concentrations of starting material and electrolyte within the constraint of solubility. Higher currents and hence greater rate of production of product can usually be attained. However, several other factors should also be considered in assessing the effect of concentration on a particular reaction. In organic electrochemical reactions, the first step is often the formation of a relatively highly reactive, and perhaps unstable, intermediate such as radical or ion. As such, this intermediate can decompose, react with solvent or condense with another species. Decomposition or reaction with solvent follows first order kinetics. On the other hand, condensation is usually second order and will be relatively more effective at higher concentrations. Thus, the distribution of the products from parallel reactions of this type may be expected to depend on concentration.

1.4.8 pH

The pH of the electrolysis solution plays a decisive role in determining the nature of the electrochemical product. This may have an effect on the starting material or its electrochemical products. Earlier studies on electrochemical Oxidation and cathodic reduction demonstrate the effectiveness of pH variation on various aspects of electron transfer processes.
α, β - unsaturated ketones are reduced on a Mercury or Glassy carbon electrode, leading to various products such as saturated ketones, unsaturated alcohol, hydrodimers, organomercuric derivatives and others, depending on the type of substrate, reaction medium, pH, the applied potential etc.,

It has been suggested that the electro reductive hydrodimerization of 2-cyclopenten-1-one follows two different radical – radical coupling pathways to from its hydrodimer in basic media under the different pH values, electroreductive dimerization of 3-buten – 2-one, benzalacetone and benzalacetophenone, has been investigated. Electrochemical modulation of self-doped sulfonated polyaniline is shown to provide electronic control of pH and enzyme activity in the vicinity of the electrodes.

1.4.9 Additives

Certain additives have been utilized to increase yield and efficiency in some electrochemical processes. These so called oxygen and hydrogen carriers have been used in aqueous media. Their action, in these cases result from a mechanism, referred to as electro regeneration. These materials are potential oxidizing or reducing agents, where the following mechanism may be applicable.

\[
\text{Substrate} + \text{O} \xrightarrow{\text{fast}} \text{product} + \text{R [chemical ]}
\]

\[
\text{R} \xrightarrow{\text{fast}} \text{O} + \text{e}^{-} \text{ [Electrochemical]}
\]
Where O and R are oxidized and reduced forms of the additive respectively. This scheme is reminiscent of catalysis, since the rate of product formation may be increased without the destruction of the additive. Notable examples of this effect are the electro chemical oxidation of Anthracene to Anthraquinone, promoted by Cerium salts $^{107}$, in the oxidation of Toluene to Benzoic acid by Chromium salts $^{102}$ and m-Phenoxy toluene to m-Phenoxy Benzaldehyde by Ceric trifluoro acetate $^{103}$.

1.4.10 Agitation / Rotation

Because electrolysis is a heterogeneous reaction, mass transport of material toward and away from the electrode is an important consideration. In most cases, it will be desirable to agitate the solution in order to speed up mass transport. The most common and convenient practice is to stir the bulk of the solution. But, it is not the most effective and a definite stationary boundary layer around the electrode will persist. Alternately, the electrolyte is made to circulate, by means of an external pump. More effective stirring can be achieved by moving the electrode itself, such as with rotating or vibrating electrodes.

In some cases, it may be desirable to prevent disruption of the depletion region, in order to take advantage of the high concentration gradients at the electrode surface. For example, if a desired reaction involves a second order process (EE Process) between reactants, the higher concentrations near the electrode may result in better yield of the product.
1.4.11 Electrode Potential

The electrode potential is the most important electrolysis variable, since it essentially controls the type of the reaction and its rates. Many compounds undergo only a single-election-transfer reaction, so that electrode potential becomes important only in governing the rate of the reaction. When more than one electron-transfer reaction is possible, proper control of electrode potential is crucial and is the basis for the high selectivity of the electrolysis process. Though a good number of electrode reactions are available, to illustrate the influence of electrode potential on the product selectivity, the anodic oxidation of phenol may be considered. At lower anodic potentials (0.8 - 0.9V vs SCE), phenol undergoes dimerization through Cyclohexadienone radical to give 4.4’- Diphenols, whereas at slightly higher potentials (0.9 - 0.95V vs SCE) p-Benzoquinone is formed through Cyclohexadienyl cation 104.

1.5 ELECTROCHEMICAL TECHNIQUES

Many electrode reactions have been performed successfully in an undivided cell which is a simple beaker type apparatus. As a matter of fact, numerous electroorganic reactions have been carried out in undivided cells equipped with 2 electrodes, a thermometer, a gas outlet and a magnetic stirrer.

For small scale experiments in the laboratories run 1 – 10g of substrates, compact DC suppliers are commercially available which can be operated at a standard output of 0.5 to 2.5A/0-35V. These are connected with ammeter and voltmeter in series. A magnetic stirring system is convenient and is used in almost all cases. The reference electrodes are installed through the
wall of the cell through a luggin capillary in order to monitor the operating potential.

Electro chemical measurements commonly involve the three variables namely electrode potential (E), current density (i) and time (t). In order to investigate the relationship between any pair of these variables, the potential of the working electrode is measured against a reference electrode. A third electrode called counter electrode, to complete the electric circuit is required. The investigation of these parameters can be made by the application of steady and non-steady signals to the cell. If the signal applied to the cell is a controlled current, then the method is described as galvanostatic and if the signal to the working electrode is a controlled electrode potential, then the technique is described as potentiostatic.

Both galvanostatic and potentiostatic techniques can be used to obtain the current voltage and time characteristics of an electrode reaction.

1.5.1 Galvanostatic Method

The galvanostatic method is probably unique in chemical kinetic measurements in which the reaction is forced to proceed at a given rate by the application of a steady current. The free energy of activation changes to fit this rate. Thus in this method, a known current is applied to the cell and the resulting variation in electrode potential is observed.

The galvanostatic method is the oldest method used for investigating electrochemical reactions; but since the advent of potentiostatic control apparatus, its application has declined. A better method of obtaining
galvanostatic action is to use electronic control of the current from a power supply. Measurements are usually made by both increasing and decreasing current density values.

1.5.2 Potentiostatic Method

In a potentiostatic experiment, the electrode potential of the working electrode is controlled and the resulting current is observed. This control in the electrode potential can be achieved by an instrument known as potentiostat.

The potentiostatic method has several advantages over the galvanostatic method, and these are listed as follows:

- The potentiostat is useful for investigating parallel electrode reactions,
- In the study of anodic reactions electrode potential regions often exist where a passive oxide film is formed which will stop the electrode process. Potentiostatic control can prevent entering this region.
- Both techniques will produce identical polarization curves. But the sigmoid characteristic can only be reproduced by potentiostatic control.

1.5.3 ELECTROCHEMICAL PROCESS DEVELOPMENT

– LABORATORY SCALE PREPARATIONS

Preliminary preparative works may be initiated using the electrodes and the medium selected. A few preparative experiments would indicate whether the electrodes really influence the reaction process. The optimum conditions
are chosen as the ones which give the best yield (moles of the product x 100 / moles of the reactant used up) and current efficiency (charge required theoretically x 100 / charge consumed experimentally). Deposited electrode and even a few closely related electrode materials may also be tried for obtaining better yield and efficiency.

The first major decision to be taken is whether or not to use a diaphragm to separate the anode and cathode compartments. If the product formed at one electrode is likely to be destroyed at the other electrode, divider becomes necessary. However, it is always advisable to see if the diaphragm can be avoided, because it is much easier and economical to devise and operate an undivided cell. If a diaphragm is a necessity, then the choice for it must be made. A variety of materials, such as unglazed porous ceramic pot, cloth, paper, asbestos and the like have been employed as membrane materials. At present, a number of ion exchange membranes like Nefion cation exchange membranes are being employed. Optimizing the proper medium, composition is another important objective in preparative scale experiments. Since organic compounds are generally poorly conducting, addition of large quantities of such reactants in a single step itself might cause an increase in cell resistance as well as electrode poisoning. Stepwise addition may be resorted to in such occasions. The temperature range, at which the preparative work is to be carried out, is another important experimental parameter. Temperature in fact can have a number of effects in an electrochemical process. It would increase the chemical reaction rate as well as diffusion rate. It would enable melting of a solid reactant and enhance its mixing with the solvent. It would also result in
volatilization of chemicals. If the reaction intermediates is a gas, higher temperature would enhance its loss. Hence it is always necessary to optimize the correct temperature, taking into consideration all these favorable and adverse effects.

1.6 ELECTROANALYTICAL TECHNIQUES

In electroorganic synthesis, the nature of the reactions depends on both the chemical and electrochemical pathways, possible for a given system. It can be done in the way of understanding these mechanisms and directing the reaction to desired result by careful analysis of the identity and quantity of the products formed. Many aspects of electroorganic reactions cannot be inferred directly from product analysis. Phenomena such as the formation of unstable intermediates, multi-step electron transfer, potential dependent adsorption, competing electrolytic reaction and so on can only be made ‘visible’ by the proper application of suitable voltammetric experiments. In recent years, a number of powerful electroanalytical techniques, such as current-potential studies, polarography, linear sweep voltammetry, cyclic voltammetry, coulometry, chrono-potentiometry and controlled potential electrolysis have come to exist.

1.6.1 Current-Potential Studies

The current passing through an electrolysis cell is the measure of the rate of electrolytic reactions occurring at the electrodes. Electrode potential measurements and voltage measurements across circuits in which small
currents are flowing, require the use of a voltameter, which draws essentially zero current. Usually a vacuum tube voltmeter (VTVM) is employed to monitor the potentials maintained.

The plots of electrode potential and the current density or current for the solvent and the solution systems provide useful and essential information on the electrolytic processes. The shifts in the polarization curves corresponding to the substrates chosen are often exploited to offer interpretation on the mechanistic routes of the processes undertaken.

The ampere-voltage relations for the solvent and the solutions containing the substrate and electrolyte/supporting electrolyte could be graphically represented to obtain polarization curves and their corresponding decomposition potentials. The deviation from the regular trend in the relations within the polarization curve and any shift in between the polarization curves may well be utilized for appropriate interpretations to fix the experimental conditions like the compatibility of the solvent-electrolyte-electrode combinations, the maximization in the working potential levels, the feasibility of the electrode process etc and to substantiate the mechanistic pathways.

1.6.2 Polarography

It is an important electroanalytical tool. The technique is capable of high reproducibility and accuracy, and although the detailed theory is quite complex, the results can be expressed on relatively simple form \(^{106}\).

Polarography is the measurement of the current that flows in solution as a function of an applied voltage. The actual form of the observed 'polarographic
wave' depends upon the manner in which the voltage is applied and on the characteristics of the working electrode. The working electrode is often a Dropping Mercury Electrode (DME), the polarographic curve is a current-voltage curve showing the dependence of the current, passing through the system. On the voltage applied to the electrodes, or on the electro chemical potential of the dropping electrode.

The most important aspect of polarographic waves which gives information concerning the nature of the electron-transfer process involved is the shape and position of the wave itself.

One of the most revealing occurrences in the polarographic behavior of certain compounds is the appearance of more than one wave. This indicates that the electron-transfer reaction is comprised of separate steps, and for controlled potential electrolysis. In general, whenever the two steps are distinguishable polarographically, they also ought to be separable by controlled potential electrolysis. The electrolysis are usually carried out at the potential between the two waves, two distinct cases are possible.

1. The first wave diminished and the second wave remains the same.
2. Both waves diminish. This indicates that the intermediate product is unstable.

1.6.3 Linear Sweep Voltammetry

Linear sweep voltammetry differs from polarography in two aspects.

1. The electrode is stationary
2. Sweep rates are much faster.
The first difference permits one to use electrode materials other than mercury, and hence, for this reason alone, Linear sweep voltammetry (LSV) is a much more generally applicable tool, although somewhat more complex to analyze quantitatively, than polarography. The instrumentation required is, in principle, the same as for polarography. In practice, however, since the sweep rates are generally much faster, special instruments for generating the sweep and displaying the results are usually used.

In this case, the sweep is initiated after a specified time has elapsed from the start of the formation of the drop. In general, however, solid electrodes, usually planar in shape, are used, and in such cases, all the precautions necessary for working with solid electrodes must be employed. In practice, a linear potential sweep is applied to the working electrode, and the current vs time is displayed on an appropriate device, in the presence of an electro active material which undergoes reversible electron transfer in a single step.

The simple system, a reversible electron transfer at a planar electrodes, was solved independently by Randles and Sevcik using different approaches. The peak current at 25°C could be shown to be equal to

$$i_p = 272 \times n^{3/2} AD^{1/2} C_0 \times v^{1/2}$$

Where,

Ip is the peak current(mA), n is the number of electrons, A is the area of electrode (cm²), D is the diffusion co-efficient(cm²/sec), C₀ is the concentration (millimoles/litre), v is the sweep rate(V/sec)

In many organic systems, the course of the reaction can be quite
complex, with various intermediates and electron-transfer steps possible. Many of these details may be seen via LSV, particularly with the triangular wave technique. Many such systems were analyzed by Nicholson, Shain and Polcyn \(^{110-114}\), including multistep electron transfers, both reversible and irreversible cases where intervening chemical reactions are occurring, and combinations thereof. The features characteristic of each can in most cases be determined by the way the peak currents and potentials vary with sweep rate.

The linear sweep voltammetry has the following advantages.

1. Unlimited choice of electrode materials.
2. Wide range of time scale.
3. Ability to respond to intermediate products.
4. Model systems can be described analytically.

### 1.6.4 Cyclic Voltammetry

Cyclic voltammetry is the most widely used electro chemical technique and is frequently used for the characterization of a redox system. It can provide information about the number of redox states, as well as qualitative information about the stability of these oxidation states and the electron transfer kinetics. There are also simple models that can be used to calculate the rate of electron transfer and the rate of chemical reactions coupled to the electron transfer for simple systems. However, these simple models cannot be used for more complicated systems. Since the effects of this simulation can help quantitative studies (eg. mechanistic investigations) in cyclic voltammetry, it can be useful for investigating the electro chemical mechanisms of real redox systems.
Cyclic voltammetry is similar to linear sweep voltammetry\textsuperscript{115-117}, except for the potential scans from the starting potential to the end potential, then reverse from the end potential back to the starting potential. In cyclic voltammetry the direction of the potential is reversed at the end of the first scan. Thus, the wave form is usually of the form of an isosceles triangle. This has the advantage that the product of the electron transfer reaction that occurred in the forward scan be probed again on the reverse scan. In addition, it is a powerful tool for the determinations of formal redox potentials, detection of chemical reactions that precede or follow the electrochemical reaction.

The complex wave form composed of two isosceles triangles. The voltage is first held at the initial potential where no electrolysis occurs and hence no Faradic current flows. As the voltage is scanned in the positive direction, the reduced compound is oxidized at the electrode surface. At a particular set value, the scan direction is reversed and the material that was oxidized in the outward excursion is then reduced. Once the voltage is returned to the initial value, the experiment can be terminated. However a further voltage excursion takes place to more negative (more reducing) values. This may be useful in probing for other species present in the sample or for investigating any electroactive products formed as a result to the first voltage excursion.

Cyclic voltammetry is a type of potentiodynamic electrochemical measurement. In this experiment the working electrode potential is ramped linearly versus time like linear sweep voltammetry. Cyclic voltammetry takes the experiment a step further than linear sweep voltammetry which ends when
it reaches a set potential, the working electrode’s potential ramp is inverted. This inversion can happen multiple times during a single experiment. The current at the working electrode is plotted versus the applied voltage to give the cyclic voltammogram trace. Cyclic voltammetry is generally used to study the electrochemical properties of an anolyte in solution $^{118,119}$.

In Cyclic voltammetry, the potential is measured between the reference electrode and the working electrode and the current is measured between the working electrode and the counter electrode. This data is then plotted as current ($i$) vs potential ($E$). The forward scan produces a current peak for any anolyte that can be reduced through the range of the potential scanned. The current will increase as the potential reaches the reduction potential of the anolyte, but then tails off as the concentration of the anolyte is depleted close to the electrode surface. If the redox couple is reversible then when the applied potential is reversed, it will reach the potential that will re oxidize the product formed in the first reduction reaction and produce a current of reverse polarity from the forward scan. This oxidation peak will usually have a similar shape to the reduction peak. From this the redox potential and electrochemical reaction rates of the compounds are obtained.

The peak current for a reversible process is given by the Randles-Sevcik equation.

$$i_p = 2.69 \times 10^5 n^{3/2} A D_o^{1/2} v^{1/2} C_0$$

Where

- $i_p$ = peak current (A)
- $n$ = number of electrons transferred per molecule
- $A$ = electrode surface area (cm$^2$)
- $D$ = diffusion coefficient (cm$^2$/s)
C = concentration (mol / cm$^3$), \( v = \text{scan rate (Volt} / \text{s)} \)

The relationship for the reverse scan in the cyclic voltammogram is given by,

\[
E = E_i - 2 V \lambda + V t
\]

Where,

\( \lambda \) is the time at which the potential is reversed.

\( E \) is the initial electrode potential.

The method uses a reference electrode, working electrode and counter electrode which in combination are sometimes referred to as a three-electrode setup. The combination of the solvent, electrolyte and specific working electrode material determines the range of the potential. Common materials for working electrodes include glassy Carbon, Platinum and Gold. A regular working electrode has a radius within an order of magnitude of 1mm.

The cells employed in cyclic voltammetry require provisions for a working electrode, inert gas purge and auxiliary electrode, a reference electrode and thermostatic maintenance. It is desirable to minimize solution resistances by keeping the supporting electrolyte concentrations up to at least 0.1M in solvents such as Acetonitrile, DMF and Methanol and higher in solvents of lower dielectric constants$^{120}$. The accessible potential range depends upon the selection of the solvent and the supporting electrolyte. Increasing interest has been shown in this technique, as it helps in analyzing the reaction process occurring at the electrode. This fact has initiated several workers towards fundamental electrochemical studies$^{121-123}$. 

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1.6.5 Coulometry

For Coulometry, a macro working electrode is employed \cite{116,124}. The working electrode placed in a separate compartment to prevent interference from the reaction occurring at other electrodes. A controlled potential is applied to the working electrode and \( i - t \) response recorded until the current drops to zero. Controlled potential Coulometry is principally used to confirm the overall number of electrons transferred in the electrode reaction. This can be done simply by plotting \( i - t \) and estimating the area under the curve. From knowledge of the balance reactant material, the current yield of the products can be calculated.

1.7 MECHANISMS OF ORGANIC ELECTRODE REACTIONS

The electrochemical reactivity of organic compounds are usually concerned with the act of electron transfer and its potential dependence, with the orientation and adsorption of reactants, intermediates, and products at the electrode surface and with the possibility of uptake of more than one electron in the 'act' of reduction \cite{5,6,7}.

Examination of the behavior of a dilute solution of the substrate at a small electrode is preliminary step towards electrochemical transformation of an organic compound. The electrode potential is swept in a linear fashion and the current recorded. This experiment shows the potential range where the substrate is electro active and information about the mechanism of the electrochemical process can be deduced from the shape of the voltammetric response curve \cite{125}. 

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1.7.1 Investigation of Electrode Reaction Mechanisms

Two extreme forms of mechanistic investigations in organic electrochemistry are frequently applied.

1. **Qualitative** analysis has the main objective of confirming a given mechanistic hypothesis by rejection of conflicting alternatives. This may be applied to single elementary steps, the intermediates, or how the steps are linked together.

2. **Quantitative** analysis relies on a highly probable mechanistic hypothesis and determines as many as possible kinetic, thermodynamic, and/or transport parameters for the various steps. This is often a complex problem, since the values of the parameters are usually correlated, their relation to experimental data is nonlinear, and the data contain artifacts and statistical errors\(^ {126,127}\).

Both types of mechanistic analysis are supported by the instrumental techniques.

1.7.2 Mechanistic Analysis

In general, for a mechanistic analysis, as many facts as possible of the investigated electrode reaction should be taken into account and the various experimental parameters be varied as widely as possible. Among these are

*Time scale*: This is particularly important for kinetic studies and the determination of rate constants.
Concentration: The dependence of results on concentration indicates chemical reactions of an order higher than unity.

Presence of Reagents: Formation of intermediates may be proven by their reaction with intentionally added reagents, for example, nucleophiles to quench electrogenerated carbonium ions. Characteristic changes are expected, for example, peaks in CV may disappear.

Usually, the experimental results are compared with the theoretical model stimulations. Again, it is important to consider wide ranges of experimental conditions that have to be adequately modeled using a single set of parameters. Generally comparison is enabled with the following methodologies.

Data Transformation: Suitable transformations of the experimental data lead to straight lines (e.g. Anson plot in Chrono Coulometry) or similar simple curves (semi-integration or differentiation)\(^{128}\).

Feature Analysis: The experimental curves exhibit features (viz. peaks in CV) that change characteristically with the experimental conditions. The results are usually compared to working curves\(^{110}\) or surfaces\(^{129,130}\).

Full Curve Analysis: Global analysis of experimental and theoretical data is applied by comparing entire curves. This is used to great advantage in simulation procedures\(^{131,132}\).

Though certain experimental hazards are to be avoided in any investigation, especially in electroorganic mechanistic studies, the following factors are to be addressed with concern.

- **Background currents**: are current components related on the ET of
substrates or products, but rather to impurities or are caused by non-Faradic processes (charging of the double layer). They are at least approximately corrected by subtraction of a blank curve recorded in the electrolyte without substrate.

- $iR$ drop is caused by the resistance $R$ between the reference and the working electrode in a three-electrode cell. It is particularly awkward in low-conductivity electrolytes and distorts curves in a nonlinear way. Compensation in commercial instruments is often possible, and procedures for correction have also been given $^{133,134}$. However, it is best to avoid an $iR$ drop by increasing conductivity or decreasing distance between reference and working electrodes.

1.8 CATHODIC SYNTHETIC PROCESSES

Great many cathodic reactions have been carried out on the micro scale, all these decades of electroorganic synthetic research. Mechanisms of the cathodic reactions have been dealt with exhaustively for a considerable extent. Cathodic processes involving organometallic compounds, nitrogen heterocyclic and electro initiated polymerizations are some of the unique areas of contributions to electroorganic research.

The electroreduction procedures provide a variety of active reaction species by the electron-transfer from cathode to substrate. The active species are expected to be the anion radical $[S]^{\cdot-}$, dianion $[S]^{2-}$, radical $[S]^{\cdot}$ and anion $[S^-]$. 

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Electron transfer process

<table>
<thead>
<tr>
<th></th>
<th>Active species</th>
</tr>
</thead>
<tbody>
<tr>
<td>S + e⁻</td>
<td>S⁻⁺</td>
</tr>
<tr>
<td>S⁻⁺ + e⁻</td>
<td>S⁻²⁺</td>
</tr>
<tr>
<td>S⁺ + e⁻</td>
<td>S⁺⁺</td>
</tr>
<tr>
<td>S⁺⁺ + e⁻</td>
<td>S⁻⁺⁺</td>
</tr>
</tbody>
</table>

The active intermediates [S]⁻⁺ and radical [S]⁺⁺ are generally derived from aromatics, alkyl halides, aromatic halides, carbonyl and active methylene compounds, etc., by 1 or 2–electron reduction around the cathode, while the anion [S⁻⁻], and dianion [S]⁻²⁺ species may arise from disulfides, alkyl halides, haloketones, hetero atom-containing compounds, etc., by one-or two–electron additions at the cathode.

Electroreduction of organic compounds proceeds in a stepwise manner through electron uptaking at the cathode (E process) and subsequent chemical reaction (C process).

Organic compounds (substrates) are converted firstly into electron – enriched active species by electron-uptaking (an electron donation
process) which then undergo a series of electron – transfer and chemical reactions to yield products.

\[
\text{Substrate (S)} \quad \rightarrow \quad \text{Active Species} \quad \rightarrow \quad \text{Product (P)}
\]

\[\text{Electrode (E)} \quad ||\quad \text{Electron Donation} \quad ||\quad \text{Electron – Transfer (E)} \quad & \quad \text{Chemical Reaction (C)}\]

The electron donating process to the substrate (S) involves either a direct electron – transfer from the cathode or an indirect electron transfer from electronegatively activated materials (Mediator). Eg., electrogenated anion radicals, anions, radicals and low-valent metal complexes.

The fate of the active species, ie., \([S]^{-}, [SH]^+, [SH]^−\) etc., is always affected by solvents, electrolytes, additives, electrode materials, etc., in which their interactions in electrolysis media provide a variety of chemical potential surfaces.

Electrochemical reduction of aromatic nitro compounds have been tried and established as early as 1951\textsuperscript{136,137}. As a matter of fact it is perhaps the most studied electroorganic reaction for its complexity in reaction and its industrial importance \textsuperscript{138}.
The literature survey indicates reports on quite a considerable extent of cathodic processes on a wide range of organic molecules. Electrochemical parameters, synthetic aspects and the impacts of certain experimental variables on the electrode process have been exemplified in these works.

The reduction of both aliphatic and aromatic nitro, nitroso and other azo compounds mostly in divided cells were observed to have influenced by electrode material, pH of the medium, electrolyte and other electrolytic parameters. Early workers demonstrated the fact that the electrochemical process has its supremacy felt by way of better yields in comparison to the chemical route.

Two typical examples of one electron transfer reactions in conventional chemical organic synthesis are the Brich reduction and the Grignard reaction

\[
\text{Birch reduction: } \text{Birch liq.\text{NH}_3} \text{-40°C} + \text{Na} \rightarrow \left[ \text{Birch} \right]^- + \text{Na}^+ \\
\text{Grignard reaction: } \text{RX} + \text{Mg} \rightarrow \left[ \text{Pair } \cdot \text{RXMg}^- \right] \rightarrow \text{RMgx}
\]

In electrolytic cells the ET reactions would be effected by direct ET from the cathode to the organic molecule,
Investigations on the electrochemical processes on nitrogenous heterocyclic compounds and polynitro compounds have also been reported\(^{152-159}\).

Reports on cathodic reduction on organic halides and on their electroanalytical aspects attract much attention. Wawzonek and other exploited the electrochemical routes to generate carbenes and benzynes form organic halides\(^{160,161}\). The mechanistic interpretations on the selective reduction under controlled potential in non aqueous media have been attempted on the basis of polarographic wave patterns for carbon - halogen bonds and for certain poly halides\(^{162-164}\). Stereochemical approach on electro reduction on 2, 4-Dibromo pentanes has initiated such similar studies on other organic molecules\(^{165}\).

It is quite interesting to observe the reports on electro reduction in aromatic rings\(^{152,166}\). The concept of solvated electron has been conceived in the visualization of aromatic radical anions. The mechanistic route is envisaged as

\[
e^{-} \text{(cathode)} + \text{solute} \rightleftharpoons e^{-} \text{(solvent)}
\]

which is analogous to the situation with alkali metals in liquor ammonia\(^{167,168}\).

\[
\begin{align*}
    n - \text{BU}_4\text{N}^+ + e & \xrightarrow{\text{Hg}} n - \text{BU}_4\text{N} \ldots \ldots e_s^- \\
    n - \text{BU}_4\text{N} \ldots e_s^- + \text{benzene} & \rightarrow \text{(benzene)}^- + n - \text{BU}_4\text{N}^+ \\
    \text{(benzene)}^- + \text{solute} & \rightarrow \text{H}
\end{align*}
\]
In cases of electrolytic reduction of olefinic and acetylenic compounds, some useful information have been derived. The radical anions of enecarboxylates are found to show nucleophilicity on the carbon atom. Carbon-carbon bond formation has been reported from suitably placed alkyl bromides and from compounds containing carbonyl functions \(^{169,170}\).

Anomalous reactions have been reported for some butenolides, leading to unprecedented mode of cyclization \(^{171-173}\). At the advent of electroorganic mechanistic revelations, some of the existing mechanistic proposals have been revised. One mechanism for intermolecular hydrocyclization of enecarboxylates was originally thought to involve nucleophilic addition of the enecarboxylate radical anion on the Ketone function. Subsequently an ECE mechanism has been prompted for such a change \(^{174}\).

\[
\begin{align*}
-\text{CH = CH – COOMe} + e^- & \rightleftharpoons -[\text{CH = CH – COOMe}]^{+}\leftarrow H^+ \\
\text{e}^- & \downarrow \\
-\text{CH – CH}_2 – \text{COOMe} & \rightleftharpoons -\text{CH – CH}_2 – \text{COOMe}
\end{align*}
\]

Kinetic and physico-chemical aspects of electroreduction provided by earlier workers serve as the authentic support to evolve convincing mechanistic interpretations. The molecular orbital approach towards the behavior of molecules under electrolytic conditions, esr coupled electrolytic studies, polarography, chronopotentiometric studies pulse radiolysis carried out on quite a considerate extent of organic system lay a strong foundation for the evolution of synthetic works \(^{175-179}\). The linear relationship between \(\log(K_{tr})\) and \(E_D^0\) over

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a wide range of reaction rates have been corroborated with the dissociative
electron transfer between the radical anion and the bond under
dissociation$^{180-182}$. Such interpretations lead to convincing proposals for
electrochemical path ways$^{183}$.

It is quite interesting to note the mechanistic interpretations brought out
in the case of electron transfer process in aryl halides. It has been envisaged
that electron transfer and bond dissociation need not be concerted as
conceived in most of the dissociate electron transfer reactions. The existence
of $\pi$ radical anion intermediate of the substrate has been demonstrated with
scan rate variation studies of cyclicvoltammetry in aprotic solvents. At fast
scan rates, reversible electron transfer has been demonstrated. At slower scan
rates, the anodic peak height has fallen and a second reversible electron
transfer has been assumed, due to the formation of radical anion.

$$
\begin{align*}
\text{Ar}X + e^- & \rightleftharpoons [\text{Ar} - X]^+ \\
[\text{Ar} - x]^+ & \xrightarrow{Kr} \text{Ar}^+ + x^-
\end{align*}
$$

Ar$^+$ + solvent $\rightarrow$ ArH + [solvent]$^+$.

Such radical anion is believed to abstract after dissociation to form a radical,
abstracts a hydrogen atom from the solvent, leaving a solvent radical. These
proposals have been substantiated by the kinetic studies$^{184-190}$.

These synthetic and physicochemical studies reported on the range or
organic molecules under electrochemical environment, accomplish healthy
initiatives, in a number of electroorganic synthetic research.
1.9 ELECTROLYTIC REDUCTION OF \( >C = O \) BONDS

In general, aldehydes are found to undergo easier reduction than Ketones, which are in turn easier than acids, amides and esters. The products from the reduction of carbonyl compounds have been observed to be depended on nature of cathode and pH of medium.

Zuman and co-workers\textsuperscript{191-196} have published a series of papers on the reduction of aldehydes and ketones to carbinols and pinacols. A detailed reduction scheme for aryl alkyl ketones at mercury cathodes in protic media was presented\textsuperscript{191,196} and the different mechanisms involved in acid solution, at intermediate pH and in alkaline solution were contracted.

The nature of the electrode has a pronounced effect on the product obtained from the reduction of carbonyl compounds. For example, Acetone \([1]\) With a lead cathode under acid conditions affords 2-Propanol \([2]\) and Pinacol \([3]\)

\[
\begin{align*}
\text{CH}_3 - C - \text{CH}_3 & \xrightarrow{\text{Pb}} \xrightarrow{+2e} \text{CH}_3 - C - \text{CH}_3 + \text{CH}_3 - C - \text{CH}_3 \text{CH}_3 \text{CH}_3 \\
\end{align*}
\]

Leonard\textsuperscript{197} reported that the reduction of p-Amino aceto phenone in aqueous acid on a Mercury cathode afforded the corresponding alcohol while reduction on a Tin cathode gave the Pinacol as the major product. It was also observed that the reduction of Michler ketone yielded the Pinacol with a Copper cathode, while both the alcohol and the Pinacol were formed in equal amounts when Nickel was used as the cathode\textsuperscript{198}.
The pH of the medium may have an affect on the starting material or its electrochemical product. The reduction under acidic conditions should be carried out at low temperature; otherwise the pinacol product may be prone to rearrange to the corresponding Pinacolone\textsuperscript{199}. Aromatic aldehydes may also form Benzoins\textsuperscript{200}.

The reduction of aldehydes and ketones can afford the corresponding hydrocarbons\textsuperscript{201}.

\[
\text{CHO} \xrightarrow{\text{Pb, Hg, THF, H}_2\text{SO}_4} \text{CH}_3
\]

In some cases, a so called “catalytic cathode” such as Cadmium has been used. Under such conditions, Acetaldehyde was reduced to Ethane\textsuperscript{202}. The formation of hydrocarbon products in appropriate solvents allows the incorporation of Deuterium in molecules.

The potential of the electrode may also affect reduction. For example, in the reduction of Benzil\textsuperscript{203}, \textit{cis-} trans isomerization takes place.

As for the mechanism of the carbonyl reduction, the reduction of aldehydes and ketones in aprotic solvents, (eg., DMF) exhibit two one-electron polarographic waves\textsuperscript{204}.

\[
R\text{C} = 0 + e \xrightarrow{\text{First wave}} R\text{C} - O^2
\]
The appearance of a second wave, at a more negative potential is attributed due to the addition of second electron to negatively charged species, the ketyl radical anion. The observed separation of two waves prompts about the stability of such Ketyl radical and the availability of proton in the medium. The aromatic ketyl radicals have sufficient stability to be detected by ESR spectroscopy.

In aqueous medium, the mechanism of reduction of aldehydes and ketones has been extensively discussed. Under acidic conditions, two 1-electron polarographic waves are observed.

The dimerization or further reduction of the ketyl radical, depends on applied potential. Thus, under macro scale conditions, with reduction at the
plateau of the first polarographic wave, the main product is the Pinacol, while reduction at the plateau of the second wave affords the corresponding alcohol $^{209}$.

The carbonyl group is both a good electrophore and an activating group. It can therefore participate in a great variety of intermolecular and intramolecular electrochemical bond formations. Hydrogens on α-carbons to carbonyl are easily abstracted by electrogenerated bases; and hydroxyl groups on such carbons are cathodically replaced by hydrogen. Electrolytic reduction of aldehydes affords hydrodimerization products by a one-electron reduction process. Formaldehyde is thus dimerized to glycol. A pilot-plant process developed for the production of 4, 4'-Dihydrobenzoin from p-Hydroxy Benzaldehyde $^{210}$. The electrolysis was performed in an aqueous 2M Sodium hydroxide solution at a Mercury cathode.

\[
\begin{align*}
2 \text{CHO} & \xrightarrow{2e, 2H_2O/Hg} \text{HO-CH - CH - OH} + 2 \text{OH}^{-}
\end{align*}
\]

Recently, Shono reported an electroreductive cyclization method using γ and δ cyanoketones $^{211}$. Bukhtiarov and coworkers $^{212}$ reported that aliphatic ketones undergo electroreductive splitting of C-H bonds at transition metals as cathodes (Pt, Ni, Fe, Co) in aprotic solvents containing quaternary ammonium salt as electrolytes. Hydrogen is produced at the cathode while the anions may react in various ways depending on the composition of the electrolysis medium.
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An interesting electro reduction of α-hydroxy aldehydes was recently reported\textsuperscript{213}. The electrolysis is carried out in buffered (pH 7) aqueous solution at 20^\circ C. Bases and hydroxyl groups on such carbons are cathodically replaced by Hydrogen.

Little and coworkers\textsuperscript{214} reported an electroreductive intramolecular cyclization involving ketonic or aldehydic groups. The electrolysis is carried out in a divided cell in acetonitrile water solution using a mercury cathode.

Electro hydrodimerizations of cyclohexanones give the glycol and the hydroxyl ketone products, Pletcher and Lain\textsuperscript{215} demonstrated that electro catalytic reductions of carboxyl compounds are possible at Graphite cathodes modified by electro deposited Ni\textsuperscript{2+} ions. Thus Benzaldehyde and Acetophenone were reduced to their corresponding alcohols and hydrocarbons (mixed products) by electrolysis in acidic ethanol-water solutions containing 0.01M Ni\textsuperscript{2+} ion. Some Hydrogen also is evolved in this electrolysis.

Electro catalytic reduction of aldehydes affords hydridimerization products by a one-electron reduction process. Formaldehyde is thus dimerized to glycol\textsuperscript{216}. This is also an example of the activating influence of the carbonyl group on the \(\text{C-OH} \) bond to the carbonyl.

\[
\begin{align*}
\text{CH}_3 & \quad | \quad \text{C} - \text{C} - \text{H} + 2 \text{C} + 2 \text{H}^+ \\
\text{OH} & \quad | \quad \text{O} \\
\text{H}_3 \text{C} - & \quad \text{C} - \text{C} - \text{H} \\
\text{CH}_3 & \quad | \quad \text{C} - \text{C} - \text{H} \\
\text{H}_3 \text{C} - & \quad \text{C} - \text{C} - \text{H} \\
\text{OH} & \quad | \quad \text{O} \\
\text{CH}_3 & \quad | \quad \text{C} - \text{C} - \text{H} \\
\end{align*}
\]
The electrochemical reduction of aldehydes and ketones has not been restricted to simple molecules and the yield of the product is often about 50%. An important application of electrochemical reduction lies in its use for the preparation of reactive compounds such as the Cyclopropanediol \(^{217}\).

**1.10 CATHODIC REDUCTION OF CARBONYL DERIVATIVES**

The electrochemical reduction of Carbon-Nitrogen double bonds was reviewed by Lund \(^{218}\). The carbon-nitrogen double bond in imines is reduced at less negative potentials than the corresponding carbonyl function. Also imine radical anions are more basic than carbonyl radical-anions. Imines with at least one phenyl substituent on the carbon-nitrogen double bond are sufficiently stable for examination in aprotic solvents and reversible one-electron reduction of benzaldehyde anil \(^{219}\), or benzophenone anil \(^ {220}\). Under ordinary conditions, reduction of these imines in Dimethyl formamide is a 2-electron process.

Preparative scale reduction of oximes at a Mercury or Lead cathode in acid solution has been used in the conversion of the carboxyl function to amine. Originally 30-50% Sulphuric acid was used as solvent \(^{221}\). Aliphatic and aromatic oximes give amines in 64-86% yields \(^{222}\). Aromatic ketoximes are also reducible in alkaline solution and Acetophenone oxime has been converted to 1-phenylethylamine in a Tri-potassium orthophosphate solution \(^ {223}\). The reduction of oximes in acid solution is tolerant of any other substituents as indicated by a number of examples \(^ {224},^{225}\).
Large-scale reduction of Phenyl hydrazones at Mercury or Lead in ethanolic Hydrochloric acid or 30-50% Sulphuric acid results in cleavage of the nitrogen-nitrogen bond yielding aniline and the amine corresponding to the original carbonyl compound. Benzaldehyde phenylhydrazone give one 4-electron wave, the half-wave potential of which varies with pH. The reduction of Phenylhydrazones using sodium amalgam under alkaline conditions saturates the carbon nitrogen double bond to give the N-alkyl, N-phenylhydrazines.

Lund has examined the reduction of oximes and semicarbazones in alkaline solution. The actual aim was to seek the reduction of oximes to Hydroxylamines in a similar way to the reduction of a semicarbozone to the Hydrazine via the hydrazone. Benzaldehyde oxime was found to give between 6 and 28% of Benzyl hydroxylamine, depending upon the pH. The other product might be Benzyamine. The mechanism of the reduction is not certain and the relative roles of the unprotonated and three protonated forms of the oxime were discussed.

An 87% yield of N-Benzyl semicarbazide was obtained from of the reduction of Benzaldehyde semicarbazone in strongly alkaline solution. In acid solution; the product was Benzyamine. These results confirmed that protonated substituted hydrazones and oximes do not have hydrazones or hydroxylamines as reductive intermediates except in alkaline solution. The reduction of hydroxylamine and some N- and O- substituted derivatives was investigated polarographically by Heyrovsky and Vavricka. It was found that the only protonated cationic form was reduced. N-Substituted derivatives also...
caused catalytic hydrogen evolution.

The mechanism of imines which affords the corresponding amines, resembles that of carboxyl compounds. Since imines are intermediates in the reduction of oximes.

Under acidic condition, imines exhibit two one-electron waves which merge at higher pH values. The half wave potential of the first wave is pH dependent, thus the over-all mechanism.

**Low pH**

\[
\begin{align*}
\text{C} = \text{NH} + \text{H}_3\text{O}^+ & \quad \overset{\text{equilibrium}}{\rightleftharpoons} \quad \text{C} = \text{NH}_2 + \text{H}_2\text{O} \\
\text{C} = \text{NH}_2 + 1\text{e} & \quad \overset{1\text{st wave}}{\rightarrow} \quad \text{C} - \text{NH}_2 \\
\text{C} - \text{NH}_2 + 1\text{e} & \quad \overset{2\text{nd wave}}{\rightarrow} \quad \text{C} - \text{NH}_2
\end{align*}
\]

**High pH**

\[
\begin{align*}
\text{C} = \text{NH} + 1\text{e} & \quad \rightarrow \quad \text{C} - \text{NH} \quad \overset{\text{H}^\oplus}{\rightarrow} \quad \text{C} - \text{NH}_2 \\
\text{C} - \text{NH}_2 + 1\text{e} & \quad \overset{\text{H}^\oplus}{\rightarrow} \quad \text{C} - \text{NH}_2
\end{align*}
\]

The reduction of oximes consumes four electrons to afford the corresponding amines. Their reduction occurs at more positive potentials with a decrease in the pH values of the medium, indicating that the reduced species is
the protonated oxime. Under acidic conditions imines and not hydroxylamines are believed to be the intermediates in the reduction of oximes, since the reduction of Hydroxylamine would occur at a more negative potential.

The over-all reduction is

**Low pH**

\[
\begin{align*}
\text{C} &= \text{NOH} + \text{H}^+ \\
\text{C} &= \text{N} + \text{OH}_2
\end{align*}
\]

\[
\begin{align*}
\text{C} &= \text{NOH}_2 + 2e + \text{H} \\
\text{C} &= \text{NH} + \text{H}_2\text{O}
\end{align*}
\]

\[
\begin{align*}
\text{C} &= \text{NH} + \text{H} \\
\text{C} &= \text{NH}_2 \xrightarrow{+2e} \text{CH} - \text{NH}_2
\end{align*}
\]

**High pH**

\[
\begin{align*}
\text{C} &= \text{NOH} \xrightarrow{=} \text{C} &= \text{NO}^- + \text{H}^+ \\
(\text{difficult to reduce})
\end{align*}
\]

\[
\begin{align*}
\text{C} &= \text{NH} + 2e + 2\text{H} \\
\text{C} &= \text{NH}_2
\end{align*}
\]

The intervention of imines in the reduction of oximes is consistent with the observation described for the reduction of Benzaldehyde oxime.

Under the appropriate reaction conditions the syn- and anti-forms of oximes exhibit different reduction behavior. Thus, under basic conditions, only
the syn-isomer exhibits a polarographic wave. Therefore, it may be possible to separate the syn- and anti- isomers by electrochemical reduction.

1.11 FUTURISTIC TRENDS ON ELECTROORGANIC PROCESSES

- The high level of activity in this field established in recent years has continued, as can be seen by the large number of papers.
- Although to investigate minor variations on established reactions and to look for model systems with intermediates conveniently studied by electrochemical methods.
- Several interesting new areas are being opened up, and in particular there has been some movement towards the study of less active molecules.
- Even for the commercially established processes, new cell designs may be developed.
- Continuous efforts would be made to replace or regenerate costly redox reagents by electrochemical means.
- To learn and utilize non-aqueous solvents in industrial electro organic processes would continue.
- The electrochemical kinetics should be investigated and the nature and yields of both major and minor products determined.
- Paired electro synthesis where both cathodic and anodic processes are utilized for the preparation of electro chemicals\textsuperscript{231}, is receiving renewed attention\textsuperscript{232,234}. One approach is to produce useful products at both the electrodes.
A wide range of chemicals is now being prepared on a few metal, metal oxide and carbon electrodes only. However, attempts are now directed towards synthesizing specific electrode materials attached with inorganic, organic and organometallic electrocatalysts by means of covalent linkage of electro adsorption. These electrodes can specifically catalyze the desired electrochemical processes alone. These types of ‘catalyst-bound electrodes’ are termed as ‘chemically modified electrodes’\textsuperscript{235}. In the near future, one may expect the use of these electrodes in electrosyntheses of stereospecific and optically active compounds\textsuperscript{236}. 

Electroorganic synthesis using solid polymer electrolyte [SPE] cell is another direction which promises highly energy efficient, with practically no $i_R$ drop, electrochemical route\textsuperscript{237-239}. 

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