Chapter IV

RESULTS and DISCUSSION
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4.1 POLARIZATION STUDIES

The preparative electrolyses for the systems under consideration have been performed galvanostatically. The working potentials for these systems were arrived at by current – potential studies. It has been ascertained that the decomposition potential for the solution containing the substrate under study fell before the decomposition potential for the solvent – electrolyte – electrode combination chosen for that particular run. The sudden fluctuation in the current flow occurring for the solution before the decomposition potential for the solvent system indicates electron transfer process taking place for some reason other than for the decomposition of the electrolyte.

The current-potential values for various systems studied reveal a supportive trend towards the possible involvement of specific centres in electron transfer process, at Platinum and Graphite (Table 4.1 to 4.12). When the current-potential values are represented in a graphical mode, useful revelations have emerged (Graph.4.1 to 4.12).
The working potential of the system under consideration seems to have direct relation to the ease or difficulty in electron addition to the substrate or any other species in the electrolytic system.

It has been observed that irrespective of the electrode material employed, in the aqueous protic medium, there are shifts in the working potentials for Oximes, hydrazones, phenylhydrazones and semicarbazones of Benzaldehyde (Ia), Salicylaldehyde (IIa), Cinnamaldehyde (IIIa), Acetophenone (IVa) and Benzophenone (Va). The operating potentials follow the same pattern as detailed below.

<table>
<thead>
<tr>
<th>S. No</th>
<th>Electrode</th>
<th>WORKING POTENTIAL V</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(Ia)</td>
</tr>
<tr>
<td>1</td>
<td>Pt</td>
<td>-1.5</td>
</tr>
<tr>
<td>2</td>
<td>C</td>
<td>-1.4</td>
</tr>
<tr>
<td>3</td>
<td>Ni</td>
<td>-1.6</td>
</tr>
</tbody>
</table>

The order is observed to be

With respect to Oximes

\[ \text{IIa} > \text{IIIa} > \text{IVa} > \text{Ia} > \text{Va} \]

with respect to electrode material

\[ \text{Pt} > \text{C} > \text{Ni} \]

The observed order in the case of oximes may be interpreted on the basis of the fact that the ease of addition of electrons has relevant correlation to the polar or field effects exist in these systems. It seems that systems having a tendency to release electron towards nitrogen, either mesomerically or inductively, obviously tend to require more potential for the addition of electron...
to the system. This indirectly suggests the probable reaction centre for the electron transfer, to be nitrogen.

![Chemical Structure](image)

In Salicylaldoxime (IIa), the more pronounced +M influence of the – OH group at the ortho position in conjugation with the electronic system surrounding nitrogen, does not favour the acceptance of external electrons to its ambit. In order to effect the addition of electron to this molecule, at the cathodic region, extra potential is needed to overcome the adverse influence of the phenolic group. In the case of Cinnamaldoxime (IIIa), it is the resonance effect due to the double bond in conjugation. The extent of adversity to the addition of electron is more by mesomeric influence than by resonance effect, in this case. Consequently, cathodic reduction occurs in Cinnamaldoxime, at a lower potential, in comparison to the Salicylaldoxime. While +I effect of –CH₃ group holds the responsibility for the higher potential in Acetophenoneoxime, it is the electron draining character of phenyl group in Benzophenoneoxime renders that system more susceptible towards cathodic process.

For any given substrate, the potential required for electron transfer between the electrode and the species, is found to be influenced by the electrode material too. In the present study, the cathodic process is greatly felt easily at Nickel electrode while at Platinum and Graphite it was somewhat observed at in higher potentials.

\[ Pt = C > Ni \]
In other words, the transfer of electron from the electrode to the species in the electrolytic solution is easier in Nickel than at Platinum or Carbon. It is quite justifiable from the fact that the release of electrons from the electrode material is depending on the type of electronic level of the electrode material from which the electron gets transferred. This observation is very much in conformity with the characteristics of the electrode material towards their behavior in electrochemical situations. The direct electron transfer from the cathode to the organic compound takes place predominantly from $sp$ metals, like Al, Sn, Hg and Pb. Further, highest hydrogen over potential is exhibited by these $sp$ metals.

A similar trend has been observed in the case of hydrazone, Phenylhydrazone and semicarbazone derivatives of these substrates, as well.

It is also to be noted that among these derivatives for any one substrate, there is slight variation in the working potentials in the following ascending order of potentials required (Table 4.13).

$$\text{semicarbazones} < \text{oximes} < \text{phenylhydrazones} < \text{hydrazones}$$

The sequence in the order can well be justified by invoking the influences of field effects exerted by the fragments in the functional groups, on the reaction centre to be assumed later.

\[
\begin{align*}
\text{–CH} = \text{N} & \quad \text{– CH} = \text{NH} - \text{NH}_2 & \quad \text{– CH} = \text{NH} - \text{NH} \rightarrow \phi \\
\end{align*}
\]

\[
\begin{align*}
\text{– C} = \text{NH} \rightarrow \text{C} \rightarrow \text{NH}_2
\end{align*}
\]
Table – 4.13 Polarisation studies - Working Potential

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>Pt</td>
<td>Ni</td>
<td>C</td>
</tr>
<tr>
<td>1.</td>
<td>Benzaldehyde</td>
<td>-1.4</td>
<td>-1.5</td>
<td>-1.4</td>
<td>-1.3</td>
</tr>
<tr>
<td>2.</td>
<td>Salicylaldehyde</td>
<td>-0.8</td>
<td>-0.8</td>
<td>-1.0</td>
<td>-0.6</td>
</tr>
<tr>
<td>3.</td>
<td>Cinnamaldehyde</td>
<td>-1.0</td>
<td>-1.0</td>
<td>-1.1</td>
<td>-0.9</td>
</tr>
<tr>
<td>4.</td>
<td>Acetophenone</td>
<td>-1.2</td>
<td>-1.2</td>
<td>-1.5</td>
<td>-1.1</td>
</tr>
<tr>
<td>5.</td>
<td>Benzophenone</td>
<td>-1.8</td>
<td>-1.8</td>
<td>-1.6</td>
<td>-1.8</td>
</tr>
</tbody>
</table>

The Carbonyl polarization present in Semicarbazone may enhance the residual positive charge on the protonated nitrogen in the aqueous protic media, thereby enabling the addition of electrons from the electrode, more comfortably. Hence the electron transfer from the electrode to the system occurs at lower potentials in comparison to that required for oximes. The more pronounced mesomeric influence of the adjacent nitrogen in hydrazones may
warrant more effort and potential for adding the electron, demanding potentials higher than required for oximes. The presence of electron sink, viz., phenyl ring in the vicinity of the reaction centre may enhance the electron acceptability at the reaction centre to a greater extent than hydrazones but to a lesser extent than in semicarbazones. Hence the working potentials for phenylhydrazones are in between oximes and hydrazones.

4.2 CATHODIC PROCESS

The carbonyl derivatives under study have been observed to undergo cathodic reduction both under acidic and alkaline conditions. There seems to be emphatic variations in the nature of products, formed under different conditions. The electrode material plays an important role in deciding the course of the reaction and thus the nature of product mixture. However there are concrete fluctuations in the extents of forming these varied products. In addition to the nature of cathodic material, exerting major impacts on the product formation, the cell design as divided and undivided, the nature of the solvent employed as aqueous and non aqueous, and the pH of the electrochemical system as acidic, neutral and alkaline have indelible impacts in their own way on the course of product formation.

a. Oximes

Benzaldoxime is taken to be the reference substrate with reference to which oximes of other Carbonyl compounds have been analysed.
Oximes of Benzaldehyde, Salicyaldehyde, Cinnamaldehyde, Acetophenone and Benzophenone, when subjected to electrochemical reduction, have been observed to form the corresponding amines as major product, irrespective of the nature of electrode, solvent and pH employed for the experimental condition. However, other products like hydrazo compounds, diamine derivatives, hydroxylamines, nitriles and $2^\circ$ amines have been found either in small yields or traces depending on the differing experimental conditions.

The variations in the mixture of products are mainly felt with different electrode materials. Dimerization is observed mainly on Platinum surface while Nickel surface favours completely hydrogenated products. The details of the main products formed by the cathodic process on oximes are provided in the following flow chart.
As an emphatic observation, the oximes of ketonic compounds, viz., Acetophenone and Benzophenone, give rise to $2^\circ$ amines along with regular products.

\[
\begin{align*}
\phi & \quad \text{C} = \text{N} - \text{OH} \\
& \quad \rightarrow \quad \phi \quad \text{CH} - \text{NH}_2 + \phi - \text{NH} - \text{CH}_2 - \text{CH}_3 (\phi) \\
(\phi)\text{H}_3\text{C} & \quad 1^\circ \text{amine} \\
& \quad \rightarrow \\
(\phi)\text{CH}_3 & \quad 2^\circ \text{amine}
\end{align*}
\]

The cell design accomplishes its own impact on the formation of products. The observed products in all the earlier mentioned circumstances have been realized when electrolyses were carried out in divided cells. On the other hand, when electrolysis was performed in undivided cells, along with regular anodic and cathodic products, oximes are found to yield corresponding nitriles too, in a considerable proportion, especially in neutral conditions at Platinum

\[
\begin{align*}
\text{Ar} - \text{CH} = \text{N} - \text{OH} & \quad \xrightarrow{\text{undivided cell}} \quad \text{Ar} - \text{CN} \\
& \quad \text{MeOH} / \text{NaOAc} / \text{Pt}
\end{align*}
\]

The formation of $1^\circ$ amines in major proportions has been observed in basic ranges too, especially at pH = 9.

\[
\begin{align*}
\text{Ar} - \text{CH} = \text{N} - \text{OH} & \quad \xrightarrow{\text{H}_2\text{O} / \text{KOH} / \text{C}} \quad \text{Ar} - \text{CH}_2 - \text{NH}_2 \\
& \quad \text{pH} = 9
\end{align*}
\]

b. Hydrazones and Phenylhydrazones

With hydrazones and phenylhydrazones, electrochemical behavior very similar to that for oximes, are observed. However, variations in working potentials have to be accomplished. Although similar product formations were
encountered, liberation of ammonia in the cases of hydrazones and formation of aniline in the cases of phenylhydrazones has been noticed significantly.

c. Semicarbazones

The electrochemical behavioral patterns for semicarbazones are very much the same as that of oximes, but with liberation of urea in electrolytic solution.
4.3 PRODUCT ANALYSIS

During the chromatographic separation and identification of the organic portion of the catholyte, tentative inferences are drawn on the basis of the polarities, correlated to the probable products.

The individual products have been characterized by appropriate chemical tests, physical parameters and spectral data. Most of the products are confirmed by the pmr spectral studies (Fig. 4.3.1 to 4.3.17)

1. Benzylamine (Fig. 4.3.1)
\[ \delta \text{ppm}: \begin{align*} &8.77(t): \text{NH}_2; 3.91(t): -\text{CH}_2 - \text{NH}_2; 7.31 - 7.06(m); \textbf{Ar} \\ &7.31 - 7.06(m); \textbf{Ar} \\ &7.06 - 6.73(m); \textbf{Ar} \\ &6.73 - 6.53(m); >\text{CH}=\text{CH}_2; 6.53(d): -\text{CH}=\text{CH}_2; 6.32(m); >\text{CH}=\text{CH}_2 \end{align*} \]

2. 2- Aminomethylphenol (Fig. 4.3.2)
\[ \delta \text{ppm}: \begin{align*} &9.83(s): \text{Ar} - \text{O}-\text{H}; 8.77(t): \text{NH}_2; \text{CH}_2; 7.09 - 6.73(m); \textbf{Ar} \\ &7.09 - 6.73(m); \textbf{Ar} \\ &6.73 - 6.53(m); >\text{CH}=\text{CH}_2; 6.53(d): -\text{CH}=\text{CH}_2; 6.32(m); >\text{CH}=\text{CH}_2 \end{align*} \]

3. 3 – Phenylprop-2-en-1- amine (Fig. 4.3.3)
\[ \delta \text{ppm}: \begin{align*} &7.39 - 7.24(m); \textbf{Ar}; 6.53(d): -\text{CH}=\text{CH}_2; 6.19(m); >\text{CH}=\text{CH}_2; 5.12(t): \text{CH}_2 - \text{NH}_2; 3.32(m); >\text{CH}=\text{CH}_2 - \text{NH}_2 \end{align*} \]

4. 1 – Phenylenethanamine (Fig. 4.3.4)
\[ \delta \text{ppm}: \begin{align*} &7.3 - 7.14(m); \textbf{Ar}; 4.08(m): -\text{CH} - \text{NH}_2 \\ &4.08(m): -\text{CH} - \text{NH}_2 \end{align*} \]

5. Diphenylmethanamine (Fig. 4.3.5)
\[ \delta \text{ppm}: \begin{align*} &7.29 - 7.06(m); \textbf{Ar}; 5.19(t); >\text{CH} - \text{NH}_2; 2.0(m) - \text{CH} - \text{NH}_2 \end{align*} \]

6. 1, 2, - Diphenylethane – 1, 2 – diamine (Fig. 4.3.6)
\[ \delta \text{ppm}: \begin{align*} &7.32 - 7.12(m); \textbf{Ar}; 2.0(d): \text{NH}_2; 4.52(m) - \text{CH} - \text{NH}_2 \end{align*} \]
7. 1, 2-Di (2-Hydroxyphenyl) ethane – 1, 2 – Diamine (Fig. 4.3.7)

$\delta_{ppm}: 9.83(s)\: \text{Ar–O–H} \quad 7.05–6.77(m)\: \text{Ar};
4.52(m): >\text{CH} - \text{CH}_2–\text{NH}_2$

8. 1, 6-Diphenylhexa–1,5–diene–3, 4–diamine (Fig. 4.3.8)

$\delta_{ppm}: 8.81(d): -\text{NH}_2 – \text{CH}<; 7.33–7.24(m): -\text{Ar};
6.53 (q); -\text{CH} – \text{CH} = \text{CH} \quad 6.19(m) \quad >\text{CH} - \text{CH}_2–\text{NH}_2;
\quad |$
3.57 (d); Ar – CH = CH.

9. 2, 3-Diphenylbutane–2, 3–diamine (Fig. 4.3.9)

$\delta_{ppm}: 7.26–7.13(m): -\text{Ar}; 2.0 (s): -\text{NH}_2; 1.48 (s): -\text{CH}_3$

10. 1, 1, 2, 2 - Tetraphenylethane–1, 2–diamine (Fig. 4.3.10)

$\delta_{ppm}: 7.26 – 7.12 (m) : \text{Ar}; 2.0 (s): -\text{NH}_2$

11. N, N– Dibenzylhydrazine (Fig. 4.3.11)

$\delta_{ppm}: 7.31–7.06(m): \text{Ar}; 3.91(d); \text{Ar–CH}_2–\text{NH};
2.0(m): \text{CH}_2–\text{NH–NH}$

12. N, N – Bis (2-Hydroxybenzyl)hydrazone (Fig. 4.3.13)

$\delta_{ppm}: 9.83(s): \text{Ar–O–H}; 7.04–6.83(m): \text{Ar};
3.91(d): -\text{NH} – \text{CH}_2– \text{Ar}; 2.0 (m): -\text{NH} – \text{NH} – \text{CH}_2$

13. N,N’ –Dicinnamylhydrazine (Fig. 4.3.13)

$\delta_{ppm}: 7.33–7.24(m): \text{Ar}; 6.53(d): \text{Ar–CH}=\text{CH};
6.19(m): >\text{CH}=\text{CH}_2–\text{CH}_3; 
3.32(q): >\text{CH}–\text{CH}_2–\text{NH};
2.0(m): -\text{CH}=\text{NH–NH}$

14. N, N – Bis (1-phenylethyl)hydrazine (Fig. 4.3.14)

$\delta_{ppm}: 7.32–7.12(m): \text{Ar}; 4.08(m): -\text{CH}_2–\text{NH};$
$\quad |$
2.0(m): \text{CH–NH–NH}, 1.36(d): >\text{CH–CH}_3$
15. N, N’ – Bis (diphenylmethyl)hydrazine (Fig. 4.3.15)

$\delta_{ppm}: 7.29–7.06 (m)$: Ar; $5.19 (d)$: C–CH–NH;

$2.0 (m)$: CH-NH-NH

16. N–Methyl benzylamine (Fig. 4.3.16)

$\delta_{ppm}: 7.31–7.25 (m)$: Ar; $3.81 (d)$: Ar-CH$_2$–NH–;

$2.47 (d)$: -NH-CH$_3$; $2.0 (m)$: -CH$_2$–NH–CH$_3$

17. N–Benzylhydroxylamine (Fig. 4.3.17)

$\delta_{ppm}: 7.31–7.06 (m)$: Ar; $3.91 (d)$: -CH$_2$–NH–;

$2.0 (m)$: CH$_2$–NH; $1.98 (m)$: NH–OH

4.4 MECHANISM

The behavioral patterns of organic molecules are of unique character under the electrical field. The molecular behavior under electrochemical environment is markedly different from that under chemical conditions. The orientation of the reactant molecules, their threshold energy level, the nature of reaction intermediates and the other connected aspects of a chemical reaction under electrical stimulation are quite different from their analogs under the chemical activities. They behave in a disciplined way under the electrical field. Therefore the electrochemical conversions are construed to be ‘Controlled chemical conversion’. Such an identical approach has been exhaustively dealt with in earlier reports of Weinberg $^5$ and in reviews of electroorganic reactions by swann $^7$ and in the specialized review of specific reactions of electrochemical interest $^{249-255}$.
Though electrochemical reduction on carbonyl compounds both analytical and preparative aspects have been reported in the earlier literature, not much report on the mechanistic interpretations are available. More specifically on the derivatives of carbonyl compounds, only discrete reports on their anodic and cathodic behaviors are available \(^{219,223,254-260}\). Polarographic behaviors of certain carbonyl derivatives \(^{261,262}\), impacts of electrode materials \(^{263}\) and solvents \(^{223,264}\), the stereochemical aspects \(^{265}\) and nature of products formed \(^{266, 267}\) are some of the aspects dealt with by earlier workers on the cathodic reduction of carbonyl derivatives and that of \(>\text{C} = \text{N}\) bonds in some isolated molecules. A corroborative approach and further comprehensive insight into the mechanistic aspects on the electro reduction of carbonyl derivatives are very much needed so as to enable more accommodative initiatives in this area of electrochemical processes.

In the present study, cathodic reductions on carbonyl derivatives – oximes, hydrazones, phenylhydrazones and semicarbazones of selective aromatic aldehydes and ketones have been mainly dealt with and that too on Platinum, Graphite and Nickel. Based on the type of products formed at these electrode surfaces, different mechanisms have been contemplated.

A. At Graphite Electrode

Graphite electrodes are known for their porosity and hence providing larger surface areas for reacting molecules. The surface activity of the Graphite material enables adsorption of reacting molecules and intermediate species. It has been authentically reported by earlier workers of the ability of
adsorbing most of the aromatic molecules on the surface of Graphite, to a greater extent than on Platinum\textsuperscript{36,268,269}.

The cathodic process of carbonyl derivatives on Graphite are accomplished as ‘Adsorption controlled’ electrolysis process in which the surface of the electrode plays an active role. The electron transfer and the possible chemical reactions are assumed at the electrical double layer.

In the present work, oximes, hydrazones, phenylhydrazones and semicarbazones of chosen aromatic aldehydes and ketones have been subjected to cathodic process in aqueous medium at acidic, neutral and basic conditions. It has been observed that no substantive electrode process occur in neutral conditions irrespective of the electrodes used. The cyclic voltammetric studies endorse this view that no such characteristic peaks or deviations are observed in the reverse sweep in neutral pH. (Fig. 4.6.13). This observation prompts to assume the participation of aqueous solvent in acidic and alkaline conditions.

With these experimental findings as a backdrop, the mechanism for the cathodic behavior of Benzaldoxime at Graphite cathode has been contemplated.

The protonation of oxime is assumed as the initiative step which occurs in a reversible slow step at the electrode surface. The protonated oxime, subsequently, may eliminate a water molecule in a reversible chemical step to form an Iminium ion I [Scheme.1].
Though the availability of proton for such a process is very much justified in the acidic solutions, it must be possible in alkaline conditions too by the electrolytic decomposition of water. The formation of iminium ion I can further be justified by the fact that such positive ion can be stabilized under electrolytic conditions by the cathodic potential. As such the above equilibrium may favor to shift towards the formation of iminium ion.

Further, it has been reported in the polarographic investigations carried out on N and O-substituted hydroxylamines that it was only the protonated cationic form that was reduced. Subsequently, an EC or ECEC mechanism may be visualized for the furtherance of the reaction. The iminium ion may involve in the electron transfer process in which 2-electron reduction may occur to form an anionic species II which can accept a proton to result in the corresponding Imine [Scheme 2]
The electron transfer and addition of proton may occur in a concerted way, specifically at Graphite electrode as the process is assumed to be an ‘Absorption controlled process’.

Imines are considerably stable, especially under alkaline conditions. However, in protic environment they undergo further protonation and a 2-electron transfer to yield ultimately corresponding 1° amines [scheme 3] through an immonium ion III and carbanion IV.

![Scheme 3](image)

The proposition of formation of iminium ion I and the subsequent ECEC process is further endorsed by a crucial observation that the same 1° amine is formed as the major product when hydrazone, phenylhydrazone and semicarbazone of Benzaldelyde are subjected to electrolyses, of course at varied working potentials. The formation of ammonia in the case of hydrazones, aniline in the case of phenylhydrazones and urea in the case of
semicarbazone in the catholyte solution, further favors this proposal of the mechanistic route. [ scheme 4].

Similar such approaches have been noticed by the earlier workers \(^{262,270-273}\). The protonation followed by the electron transfer process of the cation has been proposed in a number of electrochemical reduction processes on heterocyclic compounds containing \(>C = N\) – bonds. Such N–N cleavages under electrolytic conditions, for hydrazones and phenylhydrazones have been reported by earlier workers. The electroreductive cleavage of the N–N bond in hydrazone has been investigated in an aqueous ethanolic solution with Britton-Robinson buffer in acidic medium to give \(2, 2'\) – Dipyridylketone via the corresponding Ketimine \(^{274}\) with the liberation of ammonia. Under similar conditions, p-Hydroxybenzaldehyde isonicotinyl hydrazone is found to undergo electro reductive cleavage leading to the corresponding imine along with Nicotinamine \(^{275}\). This is a supportive evidence for the liberation of urea when semicarbazones are cathodically reduced. Similarly, the liberation of aniline has been established in the electrolytic cleavage studies on p-tolyl derivatives of Phenyldrazones of the heterocyclic system at the working potential of \(-1.6V\) vs SCE \(^{276}\). In all these studies the formation of imines has been established.
Electroanalytical and Electrosynthetic Studies – Carbonyl Derivatives

\[ \text{Scheme: 4} \]
TABLE: 4.14  PRODUCT DISTRIBUTIONS AT GRAPHITE ELECTRODE

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Substrate</th>
<th>Working potential V [ vs SCE]</th>
<th>Net conversion (%)</th>
<th>Product Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Amine</td>
<td>Hydrazo</td>
</tr>
<tr>
<td>1</td>
<td>Oxime</td>
<td>-1.4</td>
<td>37</td>
<td>90</td>
</tr>
<tr>
<td>2</td>
<td>Hydrazo</td>
<td>-1.5</td>
<td>30</td>
<td>90</td>
</tr>
<tr>
<td>3</td>
<td>Phenylhydrazo</td>
<td>-1.4</td>
<td>29</td>
<td>80</td>
</tr>
<tr>
<td>4</td>
<td>Semicarbazone</td>
<td>-1.5</td>
<td>34</td>
<td>85</td>
</tr>
</tbody>
</table>

* amine  ** urea

The reduction of some oxaziridines in aqueous alcohol was identified with the formation of the gem – amino alcohol by hydrogenation of the nitrogen – oxygen bond. This initial product, identified by its polarographic behaviour, loses water or amine, the former being faster at low pH and the latter being favoured above pH 4. The azomethine compound which was formed by loss of water, was reduced to amine in a second wave and at higher pH, the carboxy compound formed by loss of amine was reduced to the alcohol. The amine and alcohol as final products were identified after controlled potential electrolysis [277].

It is to be observed that the survey of the influence of cathode material for the electro reduction of >C = N - bonds in general and nitriles in particular, reveals the catalytic activity enabled in the cases of Raney Nickel and Carbon...
cathode. Along with the influence of current density, the electro catalytic activity of these electrode materials was found responsible for electrochemical reduction of nitriles to the corresponding $1^\circ$amines$^{278}$. The electro catalytic hydrogenation at Ni / C system has been reported to proceed effectively in aqueous protic systems$^{279}$ while the use of Pd-C cathode was noted for its slow and selective hydrogenation in considerably good yield$^{280}$.

B. At Platinum Electrode

Contrary to Graphite electrode, the surface activity of Platinum material under electrochemical environment is more conducive for electron transfer and has lesser tendency to adsorb organic molecules. The lowest hydrogen overpotential is observed on ‘d’-metals with maximum degree of occupancy of the outer ‘d’ orbitals in which hydrogen atoms are readily absorbed. This observation renders Platinum electrode with such outer ‘d’ orbital configuration to accumulate hydrogen atoms in the micro layers around it. Though this characteristic enables Platinum to be an effective hydrogenating agent chemically, under electrical field in protic aqueous solvents, the electron transfer from the electrode to the substrate material occurs in stages. That perhaps is the reason for the occurrence of mostly 1-electron processes at Platinum electrode, especially with respect to organic substrate molecules. Platinum is observed to favor formations of radical and radical ions under electrical fields and hence favoring dimerization or polymerization to occur in the diffused layer and effective hydrogenation at its surface$^{65, 281-287}$. Cathodic
process is assumed to be 'Diffusion controlled' at Platinum while it is 'Adsorption controlled' at Graphite.

The mechanisms for the cathodic reductions of chosen carbonyl derivatives are contemplated based on the above considerations of the characteristics of Platinum material. Similar to the behavior of these derivatives on Graphite, their cathodic treatments at Platinum surface yielded, in addition to the $1^\circ$ amine, hydrazo aromatics and N : N' – Diphenylethylenediamine.

The formation of Iminium ion $\text{I}$ as per scheme 1 is proposed to be formed due to chemical protonation of oximes in the protic medium under the organized electrical field. At the observed working potential, slightly higher than the reduction potential required on Graphite, the iminium cation $\text{I}$ may either preferentially undergo 1- electron reduction to form a radical $\text{V}$, or with difficulty undergo 2 - electron reduction to give the Iminium anion $\text{II}$ as described in scheme 2.

\[ \text{C} = \text{N} \rightarrow \text{CH} = \text{N} \]
\[ \text{C} = \text{N} \rightarrow \text{CH} = \text{N} \]

$\text{I}$

The radical $\text{V}$ thus formed may dimerize to yield Diazo compound $\text{VI}$, which after protonation and delocalization may result in a dication $\text{VII}$.
subsequent 4- electron transfer followed by protonation, a hydrazo aryl derivative VIII may ultimately be formed. [Scheme 5]

With regards to the formation of the Hydrazo derivatives from oximes, electroreduction has to be assumed to follow electron transfers in two stages – a 1- electron process followed by a chemical protonation and a 4-electron process in an ECE mechanistic route.

The above proposal finds its authentic support from the cyclic voltammetric studies executed for this system. The cyclic voltammogram obtained at Platinum cathode shows two responses in its reverse sweep – one
at the lower reduction potential of -0.8V with lower $i_{pc}$ value and the second with a higher $i_{pc}$ value at a higher reduction potential of -1.28V. The peak current values correspond to 1-electron involvement at a lower potential and 4-electron involvement at a higher potential.

The formation of such radicals under similar conditions at Platinum surface has been reported for some similar functionalities. For instance, polarographic reports of aryl diazo compounds have revealed such two reduction waves. The first wave was correlated with the formation of a free radical and the second wave has been ascribed to the electron reduction. The generation of radical species has been established in the study of electroreductions of 4-methyl and 4-methoxy benzene diazo compound and Aryl hydrazines by isolating organomercuric compounds when a pool of mercury has been provided in the system. Further the polarographic reduction of arenyldiazonium ions reveals that the product elucidations implicate the corresponding radicals as intermediates. Deactivation of the metallic surfaces at the cathode by covering the radicals has been encountered in every ease of voltammetric measurement at Platinum, gold and mercury electrodes.

An identical situation has been observed in the present study, when Platinum electrode is employed in the protic medium. Depletion in the current flow and formation of resinous material on the Platinum electrode surface were observed during the electrolytic work. Further, formation of opalescent crystalline material during electrolysis, when methyl methacrylate is added, confirms the possibility of radical identity in the electrolytic solution.
Alternately, the anionic species II might have undergone protonation to yield imine which would have yielded the 1° amine through immonium ion III and its carbonium ion as illustrated in Scheme 3. In addition, unlike at the Graphite electrode, the Platinum electrode material might have favored another 1-electron reduction of the carbocation, in the diffusion layer and the resulting radical might have dimerized to form N:N'- Diphenyl ethylenediamine [Scheme 6]. The diamine has been isolated in the present study, in very poor yield. (Table 4.15)

With hydrazones, phenylhydrazones and semicarbazones, their electrochemical behaviors at Platinum surface are observed similar to at Graphite surface. Liberation of ammonia, aniline or urea has been observed at Platinum surface too, suggesting similar mechanistic routes through the crucial formation of the iminium ion I [Scheme 4]. 1° amine in major yield, the
Hydrazoderivative in proportionate yields and Diamines in poor yields have been isolated after electrolyses on Platinum cathodes.

**TABLE 4.15: PRODUCT DISTRIBUTION AT PLATINUM ELECTRODE**

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Substrate</th>
<th>Working potential V [vs SCE]</th>
<th>Net conversion (%)</th>
<th>Product Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Amine</td>
<td>Hydrazo</td>
</tr>
<tr>
<td>1</td>
<td>Oxime</td>
<td>-1.5</td>
<td>32</td>
<td>45</td>
</tr>
<tr>
<td>2</td>
<td>Hydrazone</td>
<td>-1.5</td>
<td>26</td>
<td>45</td>
</tr>
<tr>
<td>3</td>
<td>Phenylhydrazone</td>
<td>-1.4</td>
<td>25</td>
<td>40</td>
</tr>
<tr>
<td>4</td>
<td>Semicarbazone</td>
<td>-1.5</td>
<td>30</td>
<td>45</td>
</tr>
</tbody>
</table>

The preference for 1-electron reduction leading to a radical intermediate at Platinum surface in acetic acid medium has been reported by earlier workers. It has been conceived from the various electrochemical studies, that while Graphite electrode favors the formation of radical ions, Platinum surfaces accomplishes radical species as intermediates.

**C. At Nickel Electrode**

The electrochemical behavior of these Carbonyl derivatives at Nickel Cathode has been observed to resemble that of the Graphite surface. In the present work, it has been noticed that Nickel surface though resembles in its behavior under the experimental electrochemical conditions, to Graphite, the conversion seems to be exclusive and specific towards the formation of \(^1\)
amine. It is to be mentioned here that much more work with Nickel and Nickel alloy material needs to be undertaken. To overcome the constraints of working within the small range of over potential at Nickel surface, further studies under diffusion limited electrode process and with rotatory electrode conditions need to be attempted.

4.5 FACTORS INFLUENCING THE CATHODIC PROCESS

The basic concept of elucidating the influential factor for product-selective electro synthesis has not yet been established effectively\textsuperscript{293-298}, although various factors have been discussed in reference\textsuperscript{36}. Keen demand arising from the manufacturing processes to solve environmental pollution problems pay much attention to synthetic methods which are operative as non-polluting processes. In this sense, modern electrosynthetic methods are facing a good opportunity to provide the solution of the environmental problems due to their high product selectivity under mild and easy reaction conditions as well as to save total amounts of materials being used for synthetic operations.

As has been authoritatively established in the numerous organic reactions under electrochemical environment, the electrode processes, both anodic and cathodic, are influenced by a variety of experimental parameters. It has been demonstrated that electrolytic processes characteristically controlled and affected by many variables, some of which are mechanical, electrical and chemical as well as combinations thereof. The effect and relative importance of these depend on the particular situation at hand and it is only by
understanding and considering their possible effects that electrolytic reactions can be controlled and optimized effectively.

In the last decade, a wide range of electroreduction reactions have been developed intensively so that organic compounds are readily functionalized by selecting suitable conditions. Today, different compounds can be synthesized selectively from the same starting compound by choosing the proper electroreduction conditions. These facts recall attention to the phenomena in which the fate of reactive species formed in electrolysis media can be controlled by choosing different chemical potential surface (CPS) under changing influential factors in electrolysis media. For example, the substrate which undergoes electron transfer under electrolysis conditions show different reduction potentials depending on not only the intrinsic nature of its functional groups but also on the interaction with the surroundings so that one may expect to have a variety of potential diagrams as CPS whose largest peak probably plays an important role for the determination of the reaction fate. Thus, the selective synthesis of different compounds arising from the same compound can be realized by choosing the proper CPS from the CPS diagrams which would be affected by numerous parameters, e.g., effects of solvents, electrolytes, additives, electrode materials, pH values, etc. The characteristic features of the electroreduction reactions involving activated olefins hydrodimerization, reductive addition of halides to Carbonyl compounds, Metal – Complex synthesis, Metal – Complex catalyzed reactions, electrosynthesis of hypervalent compounds, intermolecular Carbon – Carbon bond formations, electroreductive cyclization, stereocontrol of
Electroreductive coupling reactions, radical induced reactions by indirect electro reductions, electrogenerated base – assisted reactions, and reaction of electrogenerated nucleophiles are demonstrated. A new challenge for workers in the field is asymmetric induction in electrolysis systems. The important results obtained over the past decade have been reviewed in several monographs.306-309

In the present study, the influences of crucial parameters—nature of substrate, electrode material, cell modification, solvent, pH of the medium and temperature have been observed, with an intention of arriving at the optimum condition by which process efficiency and product selectivity could be achieved.

4.5.1 Nature of Substrate

The substrates employed in the work may be visualized to have two basic components - the aromatic moiety and the functional derivative–fragment. Variations in these two components are observed to bring about changes in the quantum yields of the products formed and the analytical parameter, namely the working potential at which the electrolyses could be brought about.

a. Variation in Aromatic Moiety

The basic aromatic Carbonyl compounds chosen for the present study are Benzaldehyde, salicylaldehyde, Cinnamaldehyde, Acetophenone and Benzophenone. The selective and characteristic derivatives of these Carbonyl compounds have been subjected to the cathodic treatment mainly at Graphite and Platinum electrodes in protic medium. Irrespective of the electrode
material employed, the initial step is being contemplated as the formation of iminium ion I in a chemical step (Scheme.1) and subsequent electron transfer from the cathode to the iminium ion I, in an E process (Scheme:2 & 5). The E process is visualized as a 1-electron process at Platinum and 2-electron addition at Graphite electrode. Obviously, the formation and stability of the iminium ion I and their inclinations towards the favor of electron addition may ultimately bring about the changes in the working potential and the quantum yields of products, although the nature of products observed are similar in character.

<table>
<thead>
<tr>
<th>No.</th>
<th>Aromatic moiety</th>
<th>Net Conversion %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Oximes</td>
</tr>
<tr>
<td>1.</td>
<td>Benzaldehyde</td>
<td>37</td>
</tr>
<tr>
<td>2.</td>
<td>Salicylaldehyde</td>
<td>84</td>
</tr>
<tr>
<td>3.</td>
<td>Cinnamaldehyde</td>
<td>52</td>
</tr>
<tr>
<td>4.</td>
<td>Acetophenone</td>
<td>48</td>
</tr>
<tr>
<td>5.</td>
<td>Benzophenone</td>
<td>64</td>
</tr>
</tbody>
</table>

The ease of forming the Iminium ions I and their stability are moderately influenced by the nature of aromatic moiety. The following are the different Iminium ions with different aromatic moieties.
Invariably, these iminium ions are formed after protonation and subsequent removal of water in the case of Oxime, ammonia from hydrazones, Aniline from phenylhydrazones and Urea from semicarbazones. [Scheme 4]. The ease of formation of iminium ion I will play a crucial role in the observed percentage of net conversion. Thus, on the basis of percentage of net conversion, the Carbonyl derivatives are found to undergo electrochemical conversion in the following descending order.

Derivatives of

Salicylaldehyde > Benzophenone > Cinnamaldehyde >

Acetophenone > Benzaldehyde.

The observed order finds its correlation to the comparative ease of formation and subsequent stability of the corresponding iminium ion I. The ease with which protonation followed by removal of water, ammonia, aniline or urea occurs, may well be controlled by the aromatic ring moiety and its
assembly. Greater the electron release towards the leaving group, easier for the leaving group to leave.

Benzaldehyde and Benzophenone derivatives may not aid much in the removal of the leaving group, due to the presence of aromatic ring which acts adversely as electron sink. On the contrary, it is the effective +M influence of –OH at the ortho position which relays the electrons vigorously towards the leaving group while the conjugated double bond in Cinnamaldehyde and the +I influence of adjoining –CH$_3$ in Acetophenone bring about this influence in that order. Therefore, on the basis of the assistance extended by way of electron release towards the removal of the leaving group, the order must be descending as

Derivatives of

Salicylaldehyde > Cinnamaldehyde > Acetophenone

Benzaldehyde > Benzophenone

However, whatever be the assistance acquired for the removal of the leaving group, protonation and loss of water and others, may take place in the protic medium, it is the stability of the iminium ion I, that is formed subsequently seems crucial in favoring the forward reaction to take place.

The comparative stability of the respective Iminium ion is decisively controlled by the resonance stabilization, as far as the molecular structure is concerned. In the light of the fact that all other stabilizing factors like polarity of the solvent and so on remain the same for all substrates, it must be the resonance effect that is operative in all these structures, that ultimately favor the stability of the ion I.
Iminium ion of Benzaldehyde Ia can be stabilized by (4+1) resonance structure while that of salicyldehyde, in addition to these (4+1) resonance structures, may be stabilized to a considerable extent by the mesomeric release of electrons by the ortho –OH group. The stabilization by mesomeric influence has great and effective enhanced effect. The field effect comprising of resonance stabilization and mesomeric influence found in the iminium ion of Salicylaldehyde enables this ion Ib to be comparatively stabler amongst all
others under consideration. The ion corresponding to Cinnamaldehyde, $I_c$ empowers stability greater than $I_a$ and lesser than $I_b$, due to its extended conjugation. The hyperconjugative influence, operative in the ion from Acetophenone, $I_d$, facilitates its stability considerably, if not to the extent by resonance effect. Hence the ion $I_d$, may be considered stabler than $I_a$ but lesser stable than $I_b$ and $I_c$. The iminium ion, $I_e$ obtained from Benzophenone, because of its stabilization by (7+1) canonical structures, is obviously stabler than $I_a$, $I_c$ and $I_d$ but found lesser stable than $I_b$.

The above considered polar influences substantiate the observed percentage net conversion data. Hence it is the chemical factor pertaining to the stability of the ionic intermediate that attributes to the overall net conversion observed during the study.

It is strangely observed, in this study, that the ease with which the electrode process is executable does not have relevance to the quantitative aspects of the electrochemical process. Normally the range of working potentials found correlation with the quantitative yield of products in electrochemical processes. In this study, the order of working potentials for these substrates is found to be almost reversed to the order of net conversions.

The polarization curves and the cyclic voltammograms of these systems indicate the following decreasing order.

Derivatives of

Benzophenone > Benzaldehyde > Acetophenone >

Cinnamaldehyde > Salicylaldehyde
This order may well be justified by the fact that the potential to be maintained must be decided by the nature of species at which the electron transfer is to occur. It is again the iminium ion I in which the electrochemical step gets initiated.

The ease of electrochemical reduction depends on the enhancement of the positively charged reaction centre by the supplementary forces exerted by the neighbouring groups. Electrons are to be added to the Nitrogen centre at which both supportive and adverse effect exist due to its environment. If the neighbouring groups exert their influences to the effect that the charge density on Nitrogen gets enhanced, it makes the addition of electrons to that reaction centre, easier and hence the potential needed for the execution of electron transfer becomes lower. In other words, groups which drain the electron density away from the reaction centre, lowers the working potential and groups which release the electrons towards the reaction centre may tend to increase the working potential.
In all these systems under study, the phenyl group exerts its electron withdrawing influence. This effect is commonly observed in all the systems. But in the iminium ions of Salicylaldehyde and Cinnamaldehyde, adverse effects to discourage the addition of electrons exist. Effective mesomeric release of electrons, due to +M effect of ortho –OH group in Ib and the conjagative π electron relay, in Ic towards the activity centre, make electron transfer, somewhat difficult. As a result, the cathodic processes in these systems have been observed to occur at slightly higher potentials. Viz., - 1.0V (vs SCE) in the case of Cinnamaldoxime and – 0.8V (vs SCE) for Salicylaldoxime.

Hence, it is to be assumed that the net conversion is controlled by the chemical step and the working potential is controlled by the electrochemical step. Further, these observations on the net conversions and working potentials indirectly support the proposed mechanisms.

The formation of 20 amines is characteristically observed in negligible yields, when oximes of Acetophenone and Benzophenone are cathodically treated at both Graphite and Platinum, only in acidic solutions. This must obviously due to the chemical behaviour of these compounds in acidic solutions. It is known for such ketoximes which prefer to undergo Beckmann rearrangement in acid solutions. In protic presence, these ketoximes must have rearranged to their corresponding N-alkyl or N-aryl substituted amides. Such amides must have involved in electron transfer at the working potential maintained for the runs. Cathodic reduction at carbonyl function must have resulted in the formation of appropriate 20 amines.
To substantiate such a proposition, it has been described by earlier researchers that at lesser negative potentials, amides are reported to have yielded a wide range of products, inclusive of $2^0$ amines under similar electrochemical conditions.

b. Variation in Functional Derivative – Fragment

Variations in the functional derivative – fragment, viz., oximes, hydrazones, phenylhydrazones and semicarbazones, are observed to have not much impact on the working potential required for the occurrence of cathodic process. However, slight variations in the net conversion values prompt the impact of these groups on the initial chemical step in which the equilibrium shifts towards the formation of iminium ion in the protic medium. It is very much to be understood, that as it is the same iminium ion $I$ that is involved in electron transfer there are no significant variations in the working potential required for the electrode process.
The fluctuations in the net conversion values can however be attributed to the ease of forming the iminium ion. The decreasing order by which these values differ is observed as

Oximes > Semicarbazones > Hydrazone > Phenylhydrazone

The variation in the net percentage conversion values due to disparity in the functional derivative – fragments are found to be corresponding to that for differences in the aromatic moiety (Table 4.14 & 4.15).

The observed order may be justified on the basis of the inclinations of the carbonyl derivatives to get protonated followed by the removal of the molecular fragment. It is observed ultimately to depend on the extent of activity coefficient of the electrophilic centre in these derivatives to accept a proton, initially. Protonation is assumed to take place at the oxygen in oximes, nitrogens in hydrazones and phenylhydrazones and carbonyl oxygen in semicarbazones. Protonation and subsequent fission of the adjacent bond are to be collectively considered. Protonation at the oxygen in oximes and semicarbazones are preferentially less favored than at Nitrogen in hydrazones and phenylhydrazones, due to the availability of lone pair of electrons on them. But after protonation, fission of the adjacent bond may be facilitated by the electronegative characters of these centers. Oxygen, due to its higher electronegative character may not bear a positive charge on it, in comparison to Nitrogen. As a result, the bond fission may be greatly favoured heterolytically in N-0 bond rather than homolytically in N-N bond with a positive centre on the more electronegative atom (Oxygen / Nitrogen). Hence, the formation of iminium ion is highly favored in derivatives where in protonation
occurs at oxygen. In other words, oximes and semicarbazones form iminium ions more readily. Moreover, the heterolytic bond cleavage preferentially occurs in heteropolar bonds (N-O) than in homopolar bonds (N-N). On this basis, it can be derived that the equilibrium shift towards iminium ion is greatly felt in oximes than in semicarbazones. Consequently, the net conversion value is found to be greater in oximes than from semicarbazones.

Between hydrazone and phenyl hydrazone, the availability of lone pair for protonation gets decreased due to the phenyl group in phenylhydrazone. Correspondingly, the iminium ion formation and hence the net conversion value is greater in hydrazones than in phenylhydrazones.

4.5.2 Nature of Electrode Material

It has been established from a number of electrochemical works and from the study of surface phenomena, the surface characteristics of the electrode materials exert crucial impacts in assuming the electrochemical routes. With regards to Graphite electrode, its porous surface plays a pivotal role in the reaction pathway. It has been conceived in a number of anodic and cathodic processes, that most of the aromatic substrates are strongly adsorbed on Carbon electrode to a far greater extent than on Platinum surface\textsuperscript{36, 268,269}. Electron transfer from the electrode to the substrate therefore occurs on Carbon different from that on Platinum. Hence the aromatic substrate in the electrical double layer is involved additionally in adsorption. The surface activity of Carbon subsequently chemisorbs these radical ions. As the bondage due to chemisorption is stronger than the electromotive force realized at the
applied potential, the radical ion may not let out to the diffusion layer. Consequently dimerization of such radical ions may not happen\textsuperscript{310,311}.

The arguments extended to the electrochemical behavior of the aromatic systems at Graphite can very well be carried over to that at Platinum. However, there seems to be a major deviation in the aspects of the electroanalytical parameters and the nature of the products formed. Though the trend for the working potentials required for the various substitutions at Graphite is observed to be the same at Platinum too, their values are found to be at higher stride. As described in the mechanisms proposed at Graphite and Platinum electrodes, in addition to the products observed on Graphite, dimerization seems to be on the card at Platinum in acid medium.

The formation of the additional products and the variation in the product yields on Platinum, in comparison to Graphite are likely to have dependency on the diversified surface activities of these electrodes. In other words, the phenomenon of adsorption controlled reactivity on the part of Graphite and the diffusion controlled characteristic of the Platinum surface seem to be the core factor for the behavioral pattern of these electrodes.

Though the same set of products as at Graphite is observed in Platinum also, the yields of the products are found to be varying. In almost all cases, the net conversion at Platinum is comparatively lower in comparison to that at Graphite. The probable reasons for this characteristic observation may be to multidimensional nature. This may be

i. coating of polymeric films on the surface of the electrode which has resulted in frequent drops in current flow. This must have led to
inadequate quantum of current as per Faraday's laws that would have been realized, during the electrolyses. Even in the cases of the formation of conducting polymeric films, the ohmic resistance developed would have facilitated the passage of only lesser quantum of current and ii. The reversible nature of the electrochemical reactions at the Platinum must have established a dynamic equilibrium in the electrolytic cell.

Some of the cyclic voltammetric findings also support this point of view. Unlike at Graphite, where chemisorbed species is involved in the electrode phenomenon, at Platinum, as the electron transfer occurs on the species in the diffusion layer, the second electron reduction obviously can be brought about only at a higher potential. As a result, at the potential maintained for the reaction, the radical ion formed, that too with not much ease, may prefer to dimerize in preference to opting for the second electron reduction.

4.5.3 Cell Modification

In the Present study, the main electrochemical work has been performed with Divided H-cell, in order to avoid the possibility of some proportion of the substrates and the products formed, getting involved in the anodic process. However, to study the implications of an alternative cell, electrolysis of Benzaldoxime has been performed in a Beaker type undivided cell at Graphite electrode in the aqueous protic solvent.

While the electrolysis performed in undivided cell, yielded 1° amine as the major product in good yield at Graphite electrode, the process carried out in the open type undivided cell, can bring about lesser yield of 1° amine as the major product. Expectedly, the exposure of the substrate to both the anodic
and cathodic processes, the substrate would have also undergone oxidative transformation at the maintained potential. More so the products might have subjected to anodic oxidation.

In the present study, when Benzaldoxime is subjected to electrolysis in the undivided cell, Benzonitrile has been observed in the cell content along with other regular products already reported in the earlier discussion. The formation of nitriles from aldoxime under electrochemical condition might have involved a pair of oxidation and reduction process in the undivided cell in which the whole content of electrolytic cell is exposed to both anode and cathode. With acetic acid and sodium acetate in the medium, it may be assumed that initially acetate ion might have undergone 2-electron oxidation at the anode to form an electrochemically generated methyl cation. This highly energized cation might have reduced the aldoxime to its Nitrile oxide and subsequently to Nitrile in the acid medium [Scheme 7].
The possibility of such a proposition finds its support from the earlier works on Benzaldoxime in undivided cell in methanolic solutions containing Sodium Chloride as electrolyte at Platinum electrode \(^{312}\). Investigations carried out on the controlled potential electrolysis of 2, 4, 6 – Trimethyl benzonitrile – N-oxide in a wide range of pH values, giving nitriles in good yield also support such possibility \(^{313}\). Montoya and other workers on their investigations on the electroreduction of N-oxides of Nicotinamide and pyridine monocarboxylic acids, ie., Picolinic, Nicotinic and iso Nicotinic acids, in acid and neutral media, expressed very similar approach \(^{314-316}\). The effect of solvent on such electrochemical studies of Picolinic acid derivative has also been detailed \(^{317}\).

The work on the cathodic reduction of Nitrone of Pyrrolidine, especially in acid medium, explains the conversion of \(\text{>N}^\oplus \text{O}^\ominus\) bonds to \(\text{>NH}\) at the potential range of 0.95V vs SCE \(^{318}\).

Further, behaviour of carboxylate ions under electrochemical environment has been exhaustively explored by a number of electroorganic chemists. The familiar Kolbe’s – electrolysis proposed a 1-electron oxidation in which decarboxylation of carboxylate anion leads to an alkyl radical. But considerable works on this electrolysis has been subsequently reported. From the comprehensive reports on the anodic behavior of Carboxylate anion it is understood that it can undergo either 1-electron or 2-electron oxidation to give either radical or cation depending on the solvent, pH and electrode material. It has been established by a number of electroorganic methods that dimerization after the formation of radical occurs at Platinum, while substitution, elimination
and rearrangement after the formation of the corresponding cation occur at Graphite electrode \(^{319-325}\).

In this study at the maintained working potential the carboxylate anion might have undergone a 2-electron oxidative process at the Graphite electrode and the alkylcation consequently formed might have involved in the reduction of oxime to ultimately yield the nitrile. Formation of nitrile in poor yield may be due to the fact that adsorption controlled electrolysis occurs at Graphite. As a result of this attribute at Graphite, the substrate would have undergone reduction preferentially in the electrical double layer rather than it is available in the diffused layer for the paired electrolysis might have got initiated.

### 4.5.4 Nature of solvent

The major work in the present study has been performed in aqueous medium. However, in order to bring in the organic substrate in solution, use of non-aqueous solvent becomes necessary. 20% Glacial acetic acid solutions are employed in most of the experimental runs.

It has been observed that acetic acid-water ratio has an impact on the extent of product distribution in general, and particularly on the percentage of yields of major products-amines and dimerized products. In combination with the electrode material, the polarity of the medium seems to have a pronounced effect on product distribution.

On Graphite, \(1^\circ\)amines are observed as the reduction product. When the proportion of acetic acid component is increased in the medium, polarity decreases. There observed a corresponding decrease in the percentage yield
of \(1^\circ\)amine. (Table 4.16). On the other hand when electrolysis is performed at Platinum cathode, along with \(1^\circ\)amine hydrazo derivatives are formed in considerable yields. As polarity of the medium is decreased by increasing the proportion of acetic acid in solvent mixture, there observed a decreasing trend in the formation of \(1^\circ\) amines while an increase in the yield of dimerized Diazo compound. (Table-4.16).

**Table 4.16 Effect of Solvent Polarity**

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Acetic Acid (%)</th>
<th>Product yield</th>
<th>@ Graphite</th>
<th>@ Platinum</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>@ Graphite (1^\circ) amine (%)</td>
<td>@ Platinum (1^\circ) amine(%)</td>
<td>Azo compound (%)</td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>20</td>
<td>90</td>
<td>45</td>
<td>35</td>
</tr>
<tr>
<td>2.</td>
<td>40</td>
<td>75</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>3.</td>
<td>50</td>
<td>60</td>
<td>30</td>
<td>50</td>
</tr>
<tr>
<td>4.</td>
<td>60</td>
<td>45</td>
<td>15</td>
<td>65</td>
</tr>
<tr>
<td>5.</td>
<td>80</td>
<td>25</td>
<td>10</td>
<td>70</td>
</tr>
</tbody>
</table>

The decrease in the percentage yield of \(1^\circ\) amines at Graphite electrode can very well be justified on the consideration of the nature of intermediate visualized during the conversion. Formation of ionic intermediates – iminium ion \(\text{I}^+\), immonium ion \(\text{III}^+\), Carbanion \(\text{IV}^-\) etc., and their stabilities thereof are the
characteristic features during the formation of 1° amines, as conceived in the proposed mechanism [ Schemes 1, 2 and 3 ]. The stabilities of these charged species are obviously increased with the increase in the polarity of the medium. Thus, the yield of 1° amine at Graphite is found to decline with decrease in the polarity of the solvent due to increase in the proportion of Glacial acetic acid. [ Table 4.16 ].

The reverse order occurs in the trend of forming the products of the cathodic reduction at Platinum electrode. The proposed route of the reaction path at Platinum is characterized by the generation of radicals for the formation of azo compound [ Scheme 5 ] and ions during the formation of amines [ Scheme 1,2& 3]. The increase in the polarity is in any way, going to favor the stabilization of radical intermediate, while favorably aid in the ionic stabilization. Thus, increase in the percentage of acetic acid which amounts to a decrease in the polarity favor the formation of azo compound while adversely affecting the formation of 1° amines [Table 4.16]

4.5.5 Effect of pH

To study the effect of pH on the cathodic process, experimental runs have been performed with the wide range of pH – viz., acidic (pH=3 and 5), neutral (pH=7) and basic (pH=9, 12) conditions. Acetic acid – Sodium acetate, DMF-Ammonium acetate and KOH have been employed in aqueous solutions. Appropriate Buffers have been employed to maintain the required pH.

The Cathodic behaviors of the chosen systems in acid medium have been deliberated in the earlier discussion. There has been no characteristic
electrochemical reduction observed under neutral conditions. This has been evidenced by the absence of any noticeable peaks in the reverse sweep of cyclic voltammograms obtained for all these cases.

However, proactive responses have been observed when electrolysis was carried out in the alkaline range. Furthermore, the working potentials shift to higher reduction potential value and almost coincide with the decomposition potential value of water (0.8V vs SCE). The cathodic processes have been observed at almost the same working potential in alkaline medium irrespective of the variations in aromatic moiety or functional components. These observations prompt a situation at which an ECEC mechanism can be visualized. It is the water molecule in alkaline pH that undergoes initial electrolysis to generate $H^+$ ions which may enable protonation and subsequent electron transfers to yield amines, predominantly at Graphite and azo compound at Platinum (Scheme 1-5). The cyclic voltammograms obtained at pH=9 and 11 show multiple peaks in the reverse sweep, unlike a single peak at acidic pH values. This proposal is supplemented by the observation that these carbonyl derivatives do not found to undergo electrochemical reduction at neutral solutions, the obvious reason being the inability of electrolysis of water under neutral conditions.

4.5.6 Temperature

The studies on the electrolyses, performed with Benzophenonoxime on Platinum and Carbon reveal some deviations in the net conversion values
depending on the temperature maintained for the process. However temperature variations do not disturb the nature of products formed.

It is to be observed that temperate changes bring about not much variation in electrolytic processes carried out on Platinum while significant changes have been observed when the process is performed on Graphite. Changes in temperature of the experimental conditions do not influence absolutely the process at Platinum. The nature and quantum yields of the products formed have been found to be the same. On the other hand, if not in the nature of the products, there is a significant increase in the net conversion value at Graphite as the temperature gets increased. The cause may be attributed to the nature of the process that is taking place at these electrodes.

The diversified behaviors of these systems corresponding to changes in temperature supports the assumed view of Adsorption controlled process at Graphite and Diffusion controlled process at Platinum. The enhanced net conversion at Graphite in comparison to that at Platinum is attributed to the phenomenon of Adsorption at the porous surface of Graphite which enables the availability of chemisorbed substrate material for electron transfer at the surface of the electrode. As adsorption coefficients of electrolytes at the activated surfaces are known to be influenced favorably with increase of pressure and adversely with temperature, a decrease in net conversion value at Graphite is expected. On the contrary, a moderate increase in net conversion with increase in temperature to certain level has been observed.

Generally, Increase of temperature is known to decrease the extent of adsorption, if the absorption is of Vander Waals adsorption type. But in
electrochemical field, the organic substrate might have involved in adsorption on Graphite surface due to chemical forces. This type of chemisorption has been reported to get increased as the increase of temperature activates the solid surface for the electrolytes to get adsorbed. This ‘Activated chemisorption’ might be the reason for the observation of moderate increase in the net conversion value at room temperature and above to an optimum level. At low temperatures and at very high temperatures, the net conversion values are observed to be lower.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Temperature</th>
<th>Net Conversion @ Graphite</th>
<th>Net Conversion @ Platinum</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0 – 4°</td>
<td>56%</td>
<td>52%</td>
</tr>
<tr>
<td>2.</td>
<td>30°</td>
<td>65%</td>
<td>50%</td>
</tr>
<tr>
<td>3.</td>
<td>40°</td>
<td>72%</td>
<td>49%</td>
</tr>
<tr>
<td>4.</td>
<td>60 – 65°</td>
<td>50%</td>
<td>46%</td>
</tr>
</tbody>
</table>

Based on the above considerations it may very well be suggested that a prospective cathodic process on any of these systems under study can be effected on any of these two electrodes at the optimum temperature level which may be around the laboratory temperature.
4.6 ELECTROANALYTICAL INTERPRETATION

The technique of cyclic voltammetry is favourably exploited in this study with the only intention of substantiating the electrochemical aspects proposed for the cathodic reduction of nitrogenous derivatives of selective carbonyl compounds. Cyclic voltammograms have been obtained under different electrolytic conditions on glassy Carbon cathode with Platinum as counter electrode, mainly under the sweep rates of 50, 250 and 500 mV/sec. The potential values have been obtained with reference to Ag / Agcl electrode.

The signals derived from cyclic voltammograms have been utilized exclusively for justifying the interpretations proposed earlier in study. However, these data generated from the electroanalytical work may find its use for the physicochemical and electroanalytical discussions and for the evaluation of electron transfer kinetics in particular and electrodynamics in general, in correlation with similar such studies reported by earlier workers 328-333.

4.6.1 Substrate Variation studies

For the purpose of analyzing the impacts on electroanalytical behaviour due to the variations in the substrate molecule cyclic voltammetry has been performed at glassy Carbon cathode in aqueous Acetic acid solutions for pH=3 under the following two categories

Category 1: Variation in Aromatic moiety

- Benzaldoxime
- Salicylaldoxime
- Cinnamaldoxime
- Acetophenonoxime
- Benzophenonoxime
Category 2: Variation in Functional derivative fragment

Benzaldoxime  Benzaldehydehydrazone
Benzaldehydephenylhydrazone  Benzaldehydesemicarbazone

The cyclic voltammograms for the above sets have been obtained in the range of scan rates of 250-500 mV/sec [Fig.4.6.1 – 4.6.8].

It has been observed that there are specific deviations in the peak potential values depending on the nature of Aromatic moiety or Functional derivative-fragment in the substrate molecule.

With respect to aromatic moiety, the peak potential values formulate the following increasing order.

\[
\text{Benzophenonoxime} < \text{Benzaldoxime} < \text{Acetophenonoxime} \\
-1.6V \quad -1.4V \quad -1.0V \\
< \text{Cinnamaldoxime} < \text{Salicylaldoxime} \\
-0.9V \quad -0.75V
\]

Similarly on the basis of the functional derivative-fragment the peak potential values are found to be in the following increasing order.

\[
\text{Semicarbazone} < \text{Oxime} < \text{Phenylhydrazone} < \text{Hydrazone} \\
1.9V \quad -1.6V \quad -1.2V \quad -0.6V
\]

These observations have concurrent correlations with the mechanistic proposals discussed already for the electron transfer processes under investigation. Further the cyclic-voltammograms also support the electrochemical aspects of the cathodic process, credibly. It is understood that the peak height along the anodic scan and peak depth along the cathodic sweep are indicative of the extent of current flow higher or deeper the peak,
more the current flow. The peak current signifies the Faradaic current due to charge transfer and to change electrical double layer. Indirectly it is proportional to the duration of flow of current. According to the electro kinetic principles, the peak height or the peak depth has direct correlation with the rate of the reaction \(^{334, 335}\). Accordingly the peak height increases, the rate of the reaction is slow and the formation of reactive intermediate becomes difficult \(^{41, 336, 337}\). From the cyclic voltammograms obtained for the substrates with different aromatic moiety or functional derivative-fragment, the above electrokinetic principle very much explains the proposed mechanistic pathway for the cathodic process.

### 4.6.2 pH Variation Studies

The cyclic voltammograms have been obtained for carbonyl derivatives on glassy Carbon in acidic solutions of pH=3 and 5, neutral solution of pH=7 and basic solutions of pH=9 and 12 indicate the preference for cathodic process in acidic solutions. The electrochemical reduction of \(>\text{C=N}^-\) of nitrogenous derivative of carbonyl compounds does not seem to be possible under the maintained experimental conditions. However electroreduction of these compounds do occur in alkaline solutions not significantly but probably by different mechanistic route [Fig.4.6.9 – 4.6.13].

### 4.6.3 Scan rate variation studies

The cyclic voltammograms obtained at different scan rates indicate the reversible or irreversible character of the electrochemical process. In the
present study, the cyclic voltammograms obtained at different scan rates (50, 250 and 500 mv/s) for all the systems show further negative shift in the higher peak potential value as the scan rate is increased. This behavior is a typical characteristic of reversible electrochemical conversions. In addition, the plots between the peak current ($i_p$) and square root of the scan rate ($v^{1/2}$) produce straight lines passing through origin. This also suggests the reversible character for the electrochemical conversion. However, the systems associated with Cinnamaldehyde deviate from this behavior. The extensions of plots for these systems are not passing through the origin, indicating irreversible electron transfer process for these systems.

The electroanalytical parameters obtained from the cyclic voltammograms of selective systems are tabulated. The peak current values ($i_p$) are plotted against the square root of the scan rates ($v^{1/2}$). The slope values for the linear plots obtained for these range of systems are observed to be higher than 0.5. This observation conforms the fact that these electrochemical processes carried out on Graphite electrode are adsorption controlled phenomena. Such analytical interpretation accomplishes a vital support for the electrochemical behavior of substrates chosen in this study at Graphite.

Further, the diagnostics of cyclic voltammograms of systems under study correlate to the ECE mechanisms. As the scan rate gets increased, the $(i_p)/(v^{1/2})$ value also increases still it reaches a steady value at
higher scan rate. This characteristic observation is phenomenal for ECE reactions.

4.6.4 Multiple Scan studies

In the multiple scan technique, the potential sweep at a specific scan rate namely 500 mV / sec is repeatedly performed for 10 segments through the same solution, without disturbing the assembly of the experiment. This technique finds its use in ascertaining the probable formation of any polymer films on the surface of the working electrode.

For a system capable of forming polymer coats, the potential sweep is responsible for the first segment by way of initiating polymerization. As the electrode gets coated with the polymer of non-conducting nature, the subsequent sweeps cannot show any peak current.

In the present study, cyclic voltammograms with such multiple scans for benzophenonoxime, Acetophenone semicarbazone, Cinnamaldehyde hydrazone and Cinnamaldehyde phenylhydrazone in aqueous protic solutions are studied [Fig.4.6.18 – 4.6.22]. Multiple scan studies reveal that polymeric coatings seemed to occur in the cases of benzophenonoxime and Cinnamaldehyde hydrazone. No such film formation occurred in other cases. This conclusion has been drawn on the basis of the fluctuations in the peak current at the respective peak potentials have been observed during the forward sweep at the multiple scan rates.

For Cinnamaldehyde hydrazone in its multiple scan cyclic voltammogram, there is systematic drop in the peak current hub following to a
minimum value at the consecutive segments. This is indicative of formation of non-conducting polymeric film [Fig.4.6.20]. On the contrary, in the case of Benzophenonoxime, the sensing of peak potential with an appropriate peak current value appears during the first segment which disappears in the subsequent segments. This observation prompts the initial formation of a polymeric film which is conducting in nature. Because of this conducting polymeric film not much variation in the peak current at the peak potential is realized in the subsequent segments. [Fig. 4.6.19].

These conclusions are arrived at on interpreting electroanalytical data generated from various cyclic voltammograms performed in glassy Carbon. These data may further be analyzed on the basis of electroanalytical principles to draw more useful conclusions.