Electrochemical Behavior of 4-(5’,6’,7’, 8’-Tetrahydro-naphthalene)-1-tetralone in Aprotic Media

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Abstract: The electrochemical reduction of 4-(5’,6’,7’, 8’-tetrahydro-naphthalene)-1-tetralone was investigated in aprotic solvent dimethylsulphoxide at glassy carbon electrode (GCE) using the technique of cyclic voltammetry at room temperature. The reduction of tetralone carried out in acidic medium which is irreversible and involves transfer of two electrons. The intensity of cathodic peak current increases with increasing scan rate consistent with Randles-Sevcik equation. A linear behavior of peak current versus square root of scan rate indicates that the electrochemical reduction processes are diffusion controlled.

Keywords: Tetralone, Cyclic voltammetry (Glassy carbon electrode), Reduction, Irreversible

Introduction

In recent years, the chemistry of tetralones has received a lot of attention due to their wide application for analytical and synthetic purposes. The synthetic versatility of tetralones has stemmed from the interest in the biological and pharmacological properties of its derivatives. Although the presence of a carbonyl group makes it an attractive target to synthetic organic chemists, but little is known about its electrochemical behavior. The electrochemical behavior associated with electron transfer equilibrium and kinetics provides information on molecular structure and the environment of the basic process.

An electrochemical reaction mechanism is the step by step sequence of elementary steps, involving at least one outer sphere electron transfer, by which an overall chemical change occurs. Electron transfer is one of the important processes in organic chemistry and many organic are driven by electron transfer processes. Among several methods for electron driven reactions, the electrochemical methods serve as a straightforward and powerful method. Electrochemical technique is a novel alternative method in organic synthesis, where one can synthesize the desired compound by oxidation or reduction of the substrate. Electrochemical reactions are most often studied with standard three electrode techniques such as cyclic voltammetry, polarography, etc. Cyclic voltammetry, is finding extensively
use to provide information regarding potential corresponding to reduction, oxidation and formation of intermediates and also about the reversible nature of electrode transfer processes. Cyclic voltammograms provides valuable information regarding electrode processes\textsuperscript{9-10}. A number of industrial processes have now replaced routine methods of their synthesis by the electrochemical methods. Since, electro-organic synthesis is much more economical, eco-friendly, avoid massive chemical effluents. Such type of reactions is easy to control automatically as well as the reactions conditions are generally mild and effects of potential, pH, buffer, solvent and structural modifications of substrate can also be studied.

The electrochemical reduction is one of the greener approaches because it is pollution free as electrons may be regarded as one of the reagents and it reduces the use of at least one hazardous chemical reagent. Other advantages of this technique are specificity, selectivity and cost effectiveness\textsuperscript{11-12}. In the field of electrochemistry, high selectivity has also been achieved via electro organic syntheses. To investigate kinetics and mechanisms of the reactions electrochemical techniques are also very powerful and useful and electroorganic synthesis provides alternative synthetic route\textsuperscript{13-16}. The mechanism of reduction or oxidation of carbonyl compounds in aqueous media has been studied\textsuperscript{17-22}. Encouraged by these facts and lack of availability of report on the electrochemical behavior of tetralone compounds, as a part of the study aimed initially 4-(5',6',7',8'-tetrahydro-naphthalene)-1-tetralone was prepared according to the reported method\textsuperscript{23} (Scheme 1) and secondly their electrochemical behavior on glassy carbon electrode was examined.

![Scheme 1](image)

**Scheme 1.** Reagents and conditions: (a) Aluminium chloride, 100\(^\circ\)-110 \(^\circ\)C, 30 min (b) Ethyl acetate, Isopropyl alcohol 0\(^\circ\)-5 \(^\circ\)C

**Experimental**

All the reagents used were of analytical grade. 4-(5',6',7',8'-tetrahydro-naphthalene)-1-tetralone was prepared according to reported method\textsuperscript{23}. Stock solution of tetralone was prepared at a concentration of 1\(\times\)10\(^{-3}\) mol L\(^{-1}\) in DMSO. More diluted solutions were prepared from this solution in DMSO just prior to analysis. Britton -Robinson (BR) universal buffer of pH 3 were prepared and used and as a supporting electrolyte.

**Apparatus**

The voltammetric measurements were carried out on an electrochemical analyzer (CH instruments, USA, Model CHI 1230) equipped with a 10 mL single compartment three electrode glass cell. Glassy carbon electrode was used as the working electrode, a platinum wire as counter electrode and Ag/ AgCl electrode as reference electrode. All solutions used in the voltammetric system were deaerated with nitrogen for at least 15 min before executing the voltammetric experiments. All experiments were carried out at room temperature of 25±1 \(^\circ\)C. The GCE was polished using 0.3 micron aluminum oxide before each experiment.

**Results and Discussion**

The reduction of 4-(5',6',7',8'-tetrahydro-naphthalene)-1-tetralone at a GCE was studied by cyclic voltammetry in BR buffer of pH 3.0. The cyclic voltammogram obtained for
$1 \times 10^{-3}$ mol L$^{-1}$ tetralone solution (Figure 1) shows one well defined reduction peak at -0.67V. No peak was observed on the reverse scan, indicating the irreversibility of electrode processes and involves transfer of two electrons as explained in proposed mechanism of electrochemical reduction (Scheme 2). Reduction was carried out in acidic medium and electrons come from water which decomposes to yield hydrogen and hydroxyl ion.

The study of effect of scan rate was made in order to postulate the mechanism and the feasibility of electrochemical reactions involved at GCE. The relationship between the peak current ($i_{pc}$) and the voltage scan rate ($\nu$) was examined using the solution of concentration $1 \times 10^{-6}$ mol L$^{-1}$ and recording cyclic voltammograms at different scan rates of 50, 75, 100, 125 and 150 mVs$^{-1}$ (Figure 2). The relationship between the cathodic peak current $i_p$ (µA), the diffusion coefficient of the electro active species, $D_o$ (cm$^2$ s$^{-1}$) and the scan rate, $\nu$ (mVs$^{-1}$), is described by the modified Randles-Sevcik equation$^{24}$ (Eq. 1),

$$i_{pc} = (2.99 \times 10^{-5}) n^{1/2} A C_o^{1/2} D_o^{1/2} \nu^{1/2}$$  \hspace{1cm} (1)

Where $n$ is the number of electrons exchanged in reduction, $\alpha$ is the transfer coefficient, $A$ is the apparent surface area of the electrode (cm$^2$) and $C_o$ is the concentration of the electro active species (mol dm$^{-3}$). The transfer coefficient for an irreversible process can be calculated from following equation$^{25}$ (Eq. 2),

$$[E_{pc} - E_{pc/2}] = 47.7/ \alpha$$  \hspace{1cm} (2)

Where $E_{pc/2}$ is the potential at which the current equals one half of the peak current. The height of the peak decreased with respective scans, its potential being not shifted. The relationship between the peak potential ($E_{pc}$) and the scan rate ($\nu$) is expressed as (Eq.3),
\[ E_{pc} = (2.303RT \alpha n F) \log (RT/\alpha n F) - (2.303RT \alpha n F) \log v \] (3)

In the present work, the plot of \( E_{pc} \) vs. \( \log v \) was linear having a correlation coefficient of 0.998 (Figure 3) in pH 3.0 and can be expressed as (Eq. 4),

\[ (E_{pc}) = 0.194\log v + 0.270(V), \] (4)

According to the Randles-Sevcik equation in a linear diffusion controlled process (\( i_{pc} \) verses \( v^{1/2} \)), for the adsorptive process (log \( i_{pc} \) verses \( v^{1/2} \)) and (\( i_{pc} \) verses \( v \)). The peak current (\( i_{pc} \)) increases linearly with the increasing scan rate (\( v \)). A linear relationship was observed between the reduction peak current versus the square root of the scan rate (Figure 4, 5 & 6) with the significant correlation coefficient of 0.99 indicating thereby that the electrode process is diffusion-controlled between the scan rate of 50 and 150 mVs\(^{-1}\) which is expressed as (Eq. 5),

\[ i_{pc} (\mu A) = 0.212 \cdot v^{1/2} \cdot (mVs^{-1}) - 1.057 \] (5)

**Figure 3.** Plot of \( E_{pc} \) (v) v/s \( \log v \) for the cyclic voltammogram of \( 1 \times 10^6 \) mol L\(^{-1}\) 4-(5',6',7',8'-tetrahydro-naphthalene)-1-tetralone

**Figure 4.** Plot of \( i_{pc} \) v/s \( v^{1/2} \) for the cyclic voltammogram of \( 1 \times 10^6 \) mol L\(^{-1}\) 4-(5',6',7',8'-tetrahydro-naphthalene)-1-tetralone

**Figure 5.** Plot of log \( i_{pc} \) v/s \( v^{1/2} \) for the cyclic voltammogram of \( 1 \times 10^6 \) mol L\(^{-1}\) 4-(5',6',7',8'-tetrahydro-naphthalene)-1-tetralone

**Figure 6.** Plot of \( i_{pc} \) v/s \( v \) for the cyclic voltammogram of \( 1 \times 10^6 \) mol L\(^{-1}\) 4-(5',6',7',8'-tetrahydro-naphthalene)-1-tetralone

The value of \( \alpha \) as calculated from the slope of the plot between \( E_{pc} \) vs. \( \log v \) is 0.387. In most of the irreversible cases \( \alpha \) lies in the range of 0.30 to 0.70. On the basis of above studies it is observed that the reduction of 4-(5',6',7',8'-tetrahydro-naphthalene)-1-tetralone occurs in the acidic medium and it is irreversible and almost constant an values clearly indicates that the reaction is diffusion controlled.
Table 1. Effect of scan rate on cyclic voltammetric parameters

<table>
<thead>
<tr>
<th>Scan rate (ν), mV/sec</th>
<th>( i_{pc} ), µA</th>
<th>log SR, mV/sec</th>
<th>( E_{pc} ), V</th>
<th>( E_{pc2} ), V</th>
<th>( ν^{1/2} ), mV/sec</th>
<th>( α )</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>2.597</td>
<td>1.689</td>
<td>-0.601</td>
<td>-0.476</td>
<td>7.071</td>
<td>0.381</td>
</tr>
<tr>
<td>75</td>
<td>2.845</td>
<td>1.875</td>
<td>-0.635</td>
<td>-0.510</td>
<td>8.66</td>
<td>0.381</td>
</tr>
<tr>
<td>100</td>
<td>3.149</td>
<td>2.0</td>
<td>-0.659</td>
<td>-0.534</td>
<td>10.00</td>
<td>0.381</td>
</tr>
<tr>
<td>125</td>
<td>3.469</td>
<td>2.096</td>
<td>-0.676</td>
<td>-0.553</td>
<td>11.18</td>
<td>0.387</td>
</tr>
<tr>
<td>150</td>
<td>3.657</td>
<td>2.176</td>
<td>-0.695</td>
<td>-0.572</td>
<td>12.24</td>
<td>0.387</td>
</tr>
</tbody>
</table>

Conclusion
The investigations have demonstrated that examined 4-(5',6',7',8'-tetrahydro-naphthalene)-1-tetralone gave a well defined single irreversible peak at glassy carbon electrode in DMSO. The electrochemical reduction of carbonyl group occurs through acceptance of two electrons in acidic media to give hydroxyl group. The electrochemical procedure with the use of electrons as reducing agents are more effective, safe, economical, environmental friendly and having no toxic effects.

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References