Electrochemical reduction of 2-acetyl benzofuran and its derivatives at glassy carbon electrode

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Electrochemical reduction of 2-acetylbenzo[b]furan and its derivatives namely 2-acetylbromboenzo[b]furan, 2-acetyl bromo-5-bromobenzo[b]furan and 2-acetyl naphtha[2,1-b] furan has been carried out in four different aqueous solvents namely DMSO, DMF, acetonitrile, ethanol using Britton Robinson buffer as supporting electrolyte at glassy carbon electrode employing cyclic voltametric technique. Single irreversible wave was observed due to the reduction of >C=O moiety to secondary alcohol derivatives of benzofuran. Formation of pinacol due to dimerization of the intermediate radical was ruled out on steric consideration. The other data viz. the effect of sweep rate, concentration of the electroactive species, effect of temperature, effect of surfactant, effect of dielectric constant on cathodic peak potential ($E_{pc}$), and cathodic peak current ($i_{pc}$) has been found out. Diffusion coefficient ($D_0$) and heterogeneous rate constant ($k_0$) have been evaluated. The electrode process was shown to be diffusion controlled and irreversible. The electrolytic products are characterised/identified by controlled potential electrolysis. The results of the electroreduction are compared with that of the chemical reduction method.

Keywords: Voltammetry, 2-Acetyl benzo [-b] furan, Reduction, Glassy carbon electrode

IPC Code (s): C25B3/04, G01N

Benzo[b]furans are an important class of organic compounds, which are known to be present in many natural products and possess physiological activity. They find applications in agrochemicals, pharmaceuticals and cosmetics. Benzo[b]furans are building blocks of optical brighteners.

Synthetic 2-acetylbenzo[b]furan and its derivatives are found to possess wide range of biological activities such as antiviral, antimicrobial, anti-inflammatory and analgesic. Reduction of 2-acetylbenzo[b]furan by sodiumborohydride yields secondary alcohol derivative of benzofuran. In an effort to understand the mechanism of electro reduction/oxidation of various molecules, results of the investigations on the electrochemical reduction of 2-acetyl benzo[b]furan and its derivatives in four different aqueous solvents namely ethyl alcohol, dimethyl formamide (DMF), acetonitrile and dimethyl sulphoxide (DMSO), at different pH at glassy carbon electrode are presented here.

Experimental Procedure

All the reagents were of analytical grade. 2-Acetylbenzo[b]furan and its derivatives (i) 2-acetyl bromobenzo[b]furan (ii) 2-acetyl bromo-5-bromobenzo[b]furan and (iii) 2-acetyl naphtho furan were prepared as reported in literature. 2-Acetylbenzo[b]furan was prepared by the reaction of salicylaldehyde with chloroacetone in potassium carbonate. 2-Acetyl naphtho furan was prepared by the reaction of salicylaldehyde with chloroacetone in potassium carbonate. 2-Acetyl bromobenzo[b]furan was prepared by the reaction of 2-acetyl benzo[b]furan with bromine in acetic acid, chloroacetone with 6-bromosalicylaldehyde. 2-acetyl naphtho furan was prepared by the reaction of salicylaldehyde with 2-hydroxy-1-naphthaldehyde in potassium carbonate, acetone and chloroacetone. The products were recrystallised from ethanol. The purity of compounds were tested by thin layer chromatography and its melting point.

Method

Cyclicvoltammetric measurements of the above said compounds in different partially aqueous media using DMF, DMSO, acetonitrile, ethanol were carried out using Britton Robinsson buffer as supporting electrolyte in a cell at 298 K. All samples were purged well with nitrogen to remove any dissolved oxygen before voltammetric measurements were recorded.
All experiments were carried out at laboratory temperature (298 ± 1) K.

A stream of nitrogen gas was passed over the thermostated reaction mixture. The three electrodes saturated calomel electrode (reference), platinum electrode (auxiliary), glassy carbon electrode (working) were connected to a computer controlled potentiostat and required scan rate, current sensitivity, initial potential and final potential were provided and the resulting current was measured as a function of applied potential.

**Results and Discussion**

Cyclic voltammetric reduction of 2-acetylbenzo[b]furan and its derivatives (A), (B), (C) and (D) in partially aqueous DMF, DMSO, ethanol, acetonitrile using Britton Robinson buffer as supporting electrolyte was carried out at glassy carbon electrode. The cyclic voltammogram of above benzofurans are shown in Fig. 1.

**Electrochemical behaviour of benzofurans**

Single irreversible wave was observed due to the reduction of >C=O moiety to secondary alcohol derivative of benzofuran in all the cases.

**Effect of concentration**

The effect of 2-acetylbenzo[b]furan concentration was studied in DMSO-water (10:90, v/v) medium containing Britton-Robinson buffer as supporting electrolyte. As the concentration of 2-acetylbenzo[b]furan was varied from 0.2 to 1 mM, the cathodic peak current $i_{pc}$ obtained were found to increase with increase in concentration. The plot of $i_{pc}$ versus 2-acetylbenzo[b]furan concentration shows linearity further indicating electrode process was diffusion controlled\(^{29,30}\) (Fig. 2). It was also observed that the peak potential $E_{pc}$ and half peak potential $E_{p/2}$ were shifted towards more negative value (Table 1).

**Effect of scan rate**

The effect of scan rate on the peak potential and peak current of 2-acetyl benzofuran was studied in DMSO: water solvent system at different pH (5.18, 7.9, 9.15 and 10.09) using Britton Robinson buffer. In all cases the cathodic peak current was proportional to the square root of the scan rate confirming to the diffusion controlled nature of the process\(^{31}\) (Fig. 3). The peak potential was shifted towards the more negative values with an increase in the scan rate indicating that electrochemical process was irreversible (Table 2). The cathodic charge transfer

![Fig. 1—Cyclic voltammogram of 1 mM (A) 2-acetyl benzofuran, (B) 2-acetyl α bromo benzo[b]furan, (C) 2-acetylbromo-5-bromobenzo[b]furan and (D) 2-acetyl naphthofuran at glassy carbon electrode in DMF solvent and Britton Robinson Buffer at temperature 295 K, scan rate 50 mVs\(^{-1}\).](image1)

![Fig. 2—Effect of concentration on the reduction of 2 mM 2-acetyl benzo [-b] furan at GCE. Supporting electrolyte: Britton-Robinson buffer, scan rate 50 mVs\(^{-1}\), media DMSO: water (10:90).](image2)

<table>
<thead>
<tr>
<th>Britton-Robinson buffer</th>
<th>Scan rate: 50 mV/s</th>
<th>$pH = 5.14$</th>
<th>Solvent: DMSO : Water (10:90)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Actyl benzofuran (mM)</td>
<td>$E_{pc}$, mV</td>
<td>$i_{pc}$, μA</td>
<td>$E_{pc/2}$, mV</td>
</tr>
<tr>
<td>0.2</td>
<td>1212</td>
<td>54</td>
<td>1127</td>
</tr>
<tr>
<td>0.4</td>
<td>1256</td>
<td>92</td>
<td>1146</td>
</tr>
<tr>
<td>0.6</td>
<td>1285</td>
<td>95.5</td>
<td>1149</td>
</tr>
<tr>
<td>0.8</td>
<td>1301</td>
<td>104.9</td>
<td>1152</td>
</tr>
<tr>
<td>1.0</td>
<td>1326</td>
<td>115.6</td>
<td>1160</td>
</tr>
</tbody>
</table>
coefficients $\alpha_n$ were evaluated by measuring the $E_p\text{-}E_{p/2}$ using the expression \(^{31}\),

\[
E_p - E_{p/2} = 47.7 \text{ mV}/\alpha_n \quad \ldots (1)
\]

where $n$ is the number of electrons, $\alpha$ is the charge transfer coefficient. The values of $\alpha_n$ were found to be $0.50 \pm 0.05$.

**Effect of $pH$**

The reduction was found to be easier at lower $pH$ than at higher $pH$ (Table 2), and for $pH > 11$ there was no reduction peak due to involvement of protons in acidic media \(^{24,25}\).

**Effect of solvent**

Cyclic voltammetric behaviour of 2-acetylbenzofuran was studied in aqueous ethanol, aqueous acetonitrile, aqueous DMF and aqueous DMSO. It was observed that the reduction potential values shifted towards more negative values \(^{30}\). The magnitude of the shift depends on the nature of the solvent. The order of the shift observed in the present study is C$_2$H$_5$OH > CH$_3$CN > DMF > DMSO (Table 3). This follows the reverse trend of the increase in the dielectric constant of these solvents. The values of dielectric constant for C$_2$H$_5$OH, CH$_3$CN, DMF and DMSO being 24.6, 37.0, 36.7 and 46.7, respectively. This suggests that the reduction becomes more difficult in solution of low dielectric constant.

**Effect of substituent**

For substituted 2-acetylbenzo[b]furan the reduction potential depends on the electronic effects of the substituents. In presence of electron withdrawing group (-Br) the reduction occurs at lower potential. 2-Acetyl benzo[b]furan gets reduced at $-1493 \text{ mV}$ and $138.5 \mu\text{A}$ while 2-acetyl bromobenzo [-b] furan, 2-acetylbromo-5-bromobenzo[b]furan and 2-acetylnaphtha [2, 1-b] furan are reduced at $-1419 \text{ mV}$ and $37.6 \mu\text{A}$, $-1450 \text{ mV}$ and $92.4 \mu\text{A}$, and $-1464 \text{ mV}$ and $130.6 \mu\text{A}$ respectively.

**Effect of cationic surfactant**

Effect of cationic surfactant cetyl trimethyl ammonium bromide on the reduction behaviour of 2-acetyl benzo [-b] furan was studied in ethanol-water media (10:90, $v/v$) using Britton Robinson buffer as supporting electrolyte.

Addition of surfactant from 0.2 to 3.0 mL to the reaction mixture causes a decrease in the cathodic peak current and a shift of $E_{pc}$ towards more negative potential \(^{32}\) (Table 4). Surfactants even in trace quantities can exert a strong effect on the electrode process. Adsorption of such substances at the electrode may inhibit the electrolytic process, cause shift in the wave to more negative potential \(^{32}\).

**Effect of temperature**

The effect of temperature on the reduction of 2-acetylbenzo[b]furan has been studied in DMSO-water (10:90, $v/v$) media and Britton Robinson buffer as supporting electrolyte. The peak potential values shift towards more negative value with increase in temperature indicating that reduction becomes easier at higher temperature.

<table>
<thead>
<tr>
<th>pH</th>
<th>$E_{pc}$ (mV)</th>
<th>$i_{pc}$ (μA)</th>
<th>$E_{pc}$ (mV)</th>
<th>$i_{pc}$ (μA)</th>
<th>$E_{pc}$ (mV)</th>
<th>$i_{pc}$ (μA)</th>
<th>$E_{pc}$ (mV)</th>
<th>$i_{pc}$ (μA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.18</td>
<td>1248</td>
<td>35.9</td>
<td>1392</td>
<td>50.5</td>
<td>1429</td>
<td>68.6</td>
<td>1432</td>
<td>69</td>
</tr>
<tr>
<td>7.9</td>
<td>1252</td>
<td>61.3</td>
<td>1414</td>
<td>92.6</td>
<td>1445</td>
<td>70.5</td>
<td>1452</td>
<td>73.8</td>
</tr>
<tr>
<td>9.15</td>
<td>1312</td>
<td>116.2</td>
<td>1463</td>
<td>150.6</td>
<td>1487</td>
<td>148</td>
<td>1501</td>
<td>160.8</td>
</tr>
<tr>
<td>10.9</td>
<td>1359</td>
<td>159</td>
<td>1494</td>
<td>206.1</td>
<td>1515</td>
<td>157</td>
<td>1528</td>
<td>227.5</td>
</tr>
</tbody>
</table>

Table 2 — Cyclic voltammetry data of 2-acetyl benzofuran 1 mM at different $pH$ values in Britton Robinson buffer
Table 3—Effect of solvents on the cyclic voltammetric parameters of 0.5 mM 2-acetyl benzofuran at GCE

<table>
<thead>
<tr>
<th>Solvents (10%)</th>
<th>$E_{pc}$, mV</th>
<th>$i_{pc}$, $\mu$A</th>
<th>$D_0 \times 10^2$ cm$^2$/s</th>
<th>$k_0 \times 10^2$ cm/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMSO</td>
<td>1484</td>
<td>129.2</td>
<td>3.675</td>
<td>8.547</td>
</tr>
<tr>
<td>DMF</td>
<td>1488</td>
<td>138</td>
<td>3.798</td>
<td>9.130</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>1491</td>
<td>142.8</td>
<td>4.124</td>
<td>9.447</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1534</td>
<td>177</td>
<td>4.676</td>
<td>11.710</td>
</tr>
</tbody>
</table>

Table 4 — Cyclic voltammetric data for the reduction of 2-acetylbenzofuran 0.2 mM in presence of cetyltrimethyl ammonium bromide at glassy carbon electrode.

<table>
<thead>
<tr>
<th>Amount of surfactant in mL (0.1%)</th>
<th>$E_{pc}$, mV</th>
<th>$i_{pc}$, $\mu$A</th>
<th>$D_0 \times 10^6$ cm$^2$/s$^{-1}$</th>
<th>$k_0 \times 10^2$ cm/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>1423</td>
<td>101.1</td>
<td>5.5704</td>
<td>1.6703</td>
</tr>
<tr>
<td>0.4</td>
<td>1432</td>
<td>96.3</td>
<td>5.3548</td>
<td>1.5926</td>
</tr>
<tr>
<td>0.8</td>
<td>1437</td>
<td>86.1</td>
<td>5.3302</td>
<td>1.4239</td>
</tr>
<tr>
<td>1.4</td>
<td>1443</td>
<td>82.2</td>
<td>5.2981</td>
<td>1.3594</td>
</tr>
<tr>
<td>2.0</td>
<td>1445</td>
<td>79.8</td>
<td>5.2306</td>
<td>1.3197</td>
</tr>
<tr>
<td>3.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 5 — Cyclic voltammetric data on reduction of 2-acetyl benzofuran at different temperature at GCE.

<table>
<thead>
<tr>
<th>Temp, K</th>
<th>$E_{pc}$, mV</th>
<th>$i_{pc}$, $\mu$A</th>
<th>$D_0 \times 10^6$ cm$^2$/s$^{-1}$</th>
<th>$k_0 \times 10^2$ cm/s</th>
<th>$\Delta G$ kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>1484</td>
<td>156.3</td>
<td>2.66</td>
<td>5.216</td>
<td>67.733</td>
</tr>
<tr>
<td>308</td>
<td>1489</td>
<td>199.4</td>
<td>3.250</td>
<td>6.595</td>
<td>69.879</td>
</tr>
<tr>
<td>313</td>
<td>1493</td>
<td>208.6</td>
<td>3.280</td>
<td>6.899</td>
<td>71.282</td>
</tr>
<tr>
<td>324</td>
<td>1499</td>
<td>257.2</td>
<td>3.777</td>
<td>8.507</td>
<td>73.880</td>
</tr>
</tbody>
</table>

difficult at higher temperature. When the temperature is increased from 298 K to 324 K, the reduction potential changes from −1484 to −1499 mV. The apparent diffusion coefficient values for reduction of 2-acetylbenzo[b]furan increase markedly with increase of temperature further indicating that the reaction is favoured at low temperature. Using the thermodynamic equations, the kinetic and thermodynamic parameters such as $D_0$ and $k_0$ calculated (Table 5). Figure 4 shows linearity with temperature and at higher temperature favours reduction processes.

Controlled potential electrolysis (CPE)

The CPE of 2-acetylbenzo[b]furan was carried out in an H type electrochemical cell at −1.2 V versus SCE. The reduction products were characterised by monitoring UV-visible spectra (190 to 400 nm). The absence of absorption band above 260 nm showed the absence of >C=O group. Further examination of the IR spectra of the isolated reduction product suggests the absence of peak corresponding to stretching frequency of >C=O group at 1670 cm$^{-1}$ and presence of broad IR absorption band at 3200 - 3400 cm$^{-1}$ for -OH group (Fig. 5). Further $^1$HNMR showed new peaks appeared at δ1.45 as doublet corresponds to three protons of –CH$_3$ group. Another quartet appeared at 4.9 attributed to the –CH proton, -OH proton comes to resonance at 5.5 as singlet. Five aromatic protons appeared between 7-8 (Fig. 6). From this spectral evidence it is clear that, compound underwent electrochemical reduction to give 1-(benzofuran-2-yl)-ethanol. On the basis of above results the whole process may be understood as two
electrons transfer reduction leading to the formation of secondary alcohol product. Since the reaction is carried out in acidic and basic conditions, pinacol-pinacolone (II) rearrangement is favoured. Due to steric interactions the reaction stops at alcohol stage itself and pinacolization is not favoured. Therefore, the pinacol is not formed as the reduction product.

The results of electro reduction are compared with the data on chemical reduction of these compounds by sodiumborohydride\textsuperscript{34}. Though the reduction products are the same in both the cases there are certain distinct advantages in electrochemical process over the chemical process like specificity, selectivity, ecofriendliness, cost effectiveness etc. Scheme I illustrates the electrochemical process.

**Determination of the number of electrons**

For totally irreversible systems, the peak current \( i_{pc} \) is given by the following equation\textsuperscript{31},

\[
i_{pc} = (2.99 \times 10^5) n (\alpha_{na})^{1/2} A C_o D_o^{1/2} \nu^{1/2}
\]

where \( A \) = area of the electrode 0.069 cm\(^2\); \( D_o \) is diffusion coefficient; \( \nu \) is sweep rate and \( \alpha_{na} \) is charge transfer coefficient.

The values of \( n \) calculated using the above equation is found to be nearly equal to two.

**Conclusion**

The following inferences can be drawn from the studies

(i) Reduction of 2-acetylbenzo[b]furan involves the transfer of two electrons resulting in the formation of its secondary alcohol derivative.
Pinacolisation is ruled out due to steric consideration.

The cathodic peak potentials for 2-acetylbenzofuran and its derivatives are shifted to more negative values with increase in concentration of electroactive species.

Electron withdrawing group accelerates reduction process.

The cathodic peak current was found to increase linearly with square root of sweep rate and also with concentration of electroactive species, suggesting that the overall electrode process is diffusion controlled irreversible process.

At higher concentration of the surfactant (within critical micelle concentration) no reduction peak was observed.

When compared with the data on chemical reduction of these compounds by sodiumborohydride. The reduction products are found to be the same in both the cases.

References