Voltammetry of 1-(m-chlorophenyl)-3-phenyl-1,2-epoxypropan-3-one

G Srinivasulu Reddy & S Jayarama Reddy
Department of Chemistry, Sri Venkateswara University,
Tirupati 517502
Received 15 April 1991; revised 8 October 1991; accepted 6 February 1992

Electrochemical reduction of 1-(m-chlorophenyl)-3-phenyl-1,2-epoxypropan-3-one has been carried out in the pH range 2.0 to 12.0 in 25% aqueous DMF by differential pulse polarography, AC polarography, DC polarography and cyclic voltammetry. The electrochemical reduction mechanism given is consistent with the data obtained. The kinetic parameters, such as transfer coefficient, diffusion coefficient and heterogeneous forward rate constant value have been evaluated and reported.

In an earlier investigation on the electroreduction of simple epoxychalcone it was shown that the epoxy group is reduced at d.m.e. In the present investigation, DC polarography, cyclic voltammetry, AC polarography, differential pulse polarography and millicoulometry are employed to study the reduction of the title compound in 25% aqueous DMF as solvent.

Experimental

1-(m-chlorophenyl)-3-phenyl-1,2-epoxypropan-3-one (Aldrich Chemicals, U.S.A.) was used as solvent and its solution was prepared by dissolving it in DMF and the required concentration of the solvent made up with the supporting electrolyte in triply distilled water. The universal buffers used were prepared from 0.2 M boric acid, 0.05 M citric acid and 0.1 M triiodium orthophosphate. The test solution was made oxygen-free before taking the voltammograms. All experiments were carried out at 27 ± 1°C.

‘Metrohm unit’ model E 506 polarecord coupled with E 612 VA Scanner, E 608 VA Controller and model X-Y/t Digraphic recorder were used for cyclic voltammetry, differential pulse polarography and AC polarography techniques. DC polarograms were recorded on a PARC unit, model-364 coupled with Kipp and Zonen recorder. Techno potentiostat coupled with digital multimeter were used for controlled potential electrolysis measurements. Mercury pool was used as working electrode, platinum as the auxiliary electrode, and saturated calomel electrode (SCE) as the reference electrode. The solution was stirred by means of a magnetic stirrer. The d.m.e. at a flow rate 2.4805 mgs⁻¹ was used as working electrode and SCE/Ag/AgCl(s), Cl⁻ as the reference electrodes in DC polarography. However in the case of cyclic voltammetry, hanging mercury drop electrode (hmde) was used as the working electrode. Platinum served as the auxiliary electrode for all techniques.

Results and discussion

1-(m-chlorophenyl)-3-phenyl-1,2-epoxypropan-3-one exhibits a single well-defined cathodic wave/peak in the pH range of 2.0 to 6.0. Whereas in the pH range of 8.0 to 12.0, besides this cathodic peak/wave an additional second wave/peak is observed. The cathodic peak observed in the entire pH range of 2.0 to 12.0 may arise as a result of reduction of epoxy group, whereas peak observed in the pH range of 8.0 to 12.0 may be the reduction of keto group to the hydroxy group. Typical cyclic voltammogram is shown in Fig. 1.

The number of electrons involved in the reduction process has been calculated from the results obtained with millicoulometry. At all pHs, the number of electrons with reduction process are found to be two. Controlled potential electrolysis has been carried out in 25% DMF (pH 10.0) solution at −1.52 V (vs. SCE) and the isolated product has been identified as the corresponding hydroxy compound by IR spectral data (KBr, 3280, 2975 cm⁻¹). In this method 55% yield of 1-(m-chlorophenyl)-3-phenyl-1,3-di-hydroxy-propane is obtained.
The plots of $i_\text{a}$ versus $h^{1/2}$, $i_\text{p}$ versus $v^{1/2}$ and $i_\text{m}$ versus $t^{2/3}$ are all linear passing through the origin in each of the supporting electrolytes employed indicating adsorption-free and diffusion-controlled nature of the electrode process. The decrease in the base current is not observed before or after the AC peaks, indicating that the electrode process is free from adsorption complications. Variation of current function $i_\text{p}/CV^{1/2}$ with scan rate ($v$) in cyclic voltammetry is found to be almost negligible indicating the electrode process to be free from any kinetic complications.

The reduction process for the two waves/peaks is irreversible in all the techniques employed as evidenced from the disobedience of Tome's criterion, log-plot analysis and dependence of half-wave potential on the concentration of the electroactive species, in DC polarography and the absence of anodic peak in the reverse scan and the variation of peak potential with scan rate in cyclic voltammetry. The marginal variation of peak potential ($E_\text{m}$) with concentration and non-linearity in the plot of $i_\text{m}$ versus $1 - 1/\alpha + 1/\alpha$ in differential pulse polarography also confirm the irreversible nature of the electrode process.

The values obtained for the transfer coefficient, diffusion coefficient and heterogeneous forward rate constants in various supporting electrolytes in different techniques are given in Table 1. The diffusion coefficient values evaluated from all the techniques are in good agreement. The decrease in diffusion coefficient with increase in pH may be attributed to the decrease in the availability of protons with increase in pH of the supporting electrolyte. The DC polarographic diffusion coefficient values are considered as more reliable, since it is a slow technique and the renewal of the surface of mercury drops at d.m.e. also adds to the credibility of the values. The number of protons involved in the rate determining step as evaluated from $E_{1/2}$ versus pH plot is found to be two in both the cases. The heterogeneous forward rate constants are found to decrease with increase in pH and percentage at DMF in aq. DMF as solvent indicates that the electrode reaction tends to become more and more irreversible. The rate constants obtained in AC polarography are found to be high as compared to other techniques since the rate constants are evaluated at standard potentials in AC polarography.

**Electrode mechanism**

In the entire pH range of 2.0 to 12.0, the reduction process may be represented by Eq. (1)

\[
\begin{align*}
\text{m-ClPh-CH-C-} & \xrightarrow{2e^-+2H^+} \text{m-ClPh-CH} \cdot \text{-CO-Ph} \\
\text{OH} & \quad \text{pH 2.0 to 6.0} \\
\text{OH} & \quad \text{pH 8.0 to 12.0} \\
\end{align*}
\]

**Analysis**

In the present investigation, the peak obtained at pH 4.0 (potential = -0.79 V) in differential pulse polarography is well resolved and can be utilized for the estimation of title compound. Using the calibration method, the peak height is found to be linear in the concentration range of 2.5 x 10^{-4} M to 4.5 x 10^{-6} M. The lower detection limit is found to be 4.3 x 10^{-6} M.

<table>
<thead>
<tr>
<th>pH</th>
<th>DC Polargraphy (Drop time = 3 sec)</th>
<th>Cyclic voltammetry (Scan rate = 40 mV s^{-1})</th>
<th>AC Polargraphy (Drop time = 3 sec)</th>
<th>Diff. pulse polargraphy (Drop time = 2 sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$-E_{1/2}$ V</td>
<td>$D \times 10^6$ cm^{2} s^{-1}</td>
<td>$K_{\text{gh}}^0$ cm s^{-1}</td>
<td>$-E_{\text{p}}$ V</td>
</tr>
<tr>
<td>2.0</td>
<td>0.70</td>
<td>3.42</td>
<td>2.97 x 10^{-9}</td>
<td>0.71</td>
</tr>
<tr>
<td>4.0</td>
<td>0.78</td>
<td>3.27</td>
<td>7.49 x 10^{-10}</td>
<td>0.78</td>
</tr>
<tr>
<td>6.0</td>
<td>0.87</td>
<td>3.16</td>
<td>1.92 x 10^{-10}</td>
<td>0.89</td>
</tr>
<tr>
<td>8.0</td>
<td>a) 1.00</td>
<td>3.08</td>
<td>6.49 x 10^{-11}</td>
<td>a) 1.01</td>
</tr>
<tr>
<td></td>
<td>b) 1.36</td>
<td>3.01</td>
<td>8.43 x 10^{-13}</td>
<td>b) 1.35</td>
</tr>
<tr>
<td>10.0</td>
<td>a) 1.13</td>
<td>2.87</td>
<td>4.72 x 10^{-12}</td>
<td>a) 1.13</td>
</tr>
<tr>
<td></td>
<td>b) 1.44</td>
<td>2.65</td>
<td>1.92 x 10^{-15}</td>
<td>b) 1.45</td>
</tr>
<tr>
<td>12.0</td>
<td>a) 1.26</td>
<td>2.42</td>
<td>8.43 x 10^{-14}</td>
<td>a) 1.27</td>
</tr>
<tr>
<td></td>
<td>b) 1.58</td>
<td>2.52</td>
<td>4.73 x 10^{-17}</td>
<td>b) 1.59</td>
</tr>
</tbody>
</table>

a) First wave/peak; (b) Second wave/peak.
Acknowledgement

The authors are thankful to the DNES, New Delhi, for providing financial assistance.

References