Electrochemical Reduction Behaviour of α-Methylbenzylchloride

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Cyclic voltammetry at hanging mercury drop electrode (HMDE) and differential pulse polarography at dropping mercury electrode (DME) are used to two-electron cleavage of carbon-halogen bond in α-methylbenzylchloride in the presence of tetramethylammonium hexafluorophosphate (TMAHP), tetraethylammonium bromide (TEAB), tetrapropylammonium perchlorate (TPAP), and tetra-n-butylammonium iodide (TBAl) as the supporting electrolytes. The reduction potentials of α-methylbenzylchloride are found to be in the range -2.14 to -2.65V vs Ag/AgCl and are shown to be sensitive to the nature of the cation of the supporting electrolyte. As the size of the tetraalkylammonium cation of the supporting electrolyte increases the voltammetric/polarographic peak moves towards more negative potentials. The analytical procedure is developed by differential pulse polarography for the determination of α-methylbenzylchloride during the electrolysisis of 2-arylpropionic acids.

Introduction

Halogen compounds occupy a central position in organic chemistry and therefore electrochemistry of carbon-halogen bond is a subject of considerable importance. The ease of reduction is affected by the size of the cation of the tetraalkylammonium ions, which are used as the supporting electrolytes. For example, isobutylbromide is reduced at the DME at -2.14V in tetramethylammonium hexafluorophosphate. The same species is reduced at -2.65V in tetrabutylammonium perchlorate. In some instances the shift in potential to more negative values with increase in size of the tetraalkylammonium cation is so substantial that reduction cannot be affected before the onset of solvent decomposition. The phenomenon is due in part to a decrease in the rate constant for electron transfer as the electrolyte cation increases in size.

Stockelberg and Straecke have reported the first systematic investigation in carbon-halogen reductions. Several workers have extensively studied the carbon-halogen bond cleavage under different conditions. The majority of the organic monohalides are reduced at DME and HMDE in a single irreversible step corresponding to an overall two-electron transfer the product being a hydrocarbon. Reddy et al. have reported that phenacyl halides and other organic halides get reduced with two-electron addition in a single step reduction, forming the corresponding hydrocarbon. The polarographic/voltammetric behaviour of arylalkylhalides is shown to depend upon the experimental conditions employed and the nature of the supporting electrolyte.

Cyclic voltammetry and differential pulse polarography are employed in the present study for the electrochemical reduction behaviour of C-Cl bond in α-methylbenzyl chlorides by taking 1-chloro-1-phenylethane as model compound. As most of the non-steroidal anti-inflammatory agents are arylpropionic acids, they can be synthesized from α-methylbenzyl chlorides through electrocatalysis. The analytical procedure has been developed for the determination of α-methylbenzyl chlorides, present in the electrolyte solution during electrolysisis of 2-arylpropionic acids by differential pulse polarography. The use of analysis by this technique is, after the completion of electrolysis, if the halide still present in the aromatic side chain can be removed by passing CO₂ for longer duration.

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Materials and Methods

Cyclic voltammograms and differential pulse polarograms were obtained with Metrohm Unit 757VA Compturac. Metrohm Herisau, Switzerland, supplied the Teflon coated electrolyte cell used in the investigation. The cell consisted of three electrodes: (i) The working electrode whose potential was controlled at desired value, (ii) The reference electrode with reference to which the potential of working electrode was measured, and (iii) The counter or auxiliary electrode, which completed the electrolytic circuit. Nearly 10-15 mL of the electrolytic solution was sufficient to make the electrodes dip in the solution. The cell was designed in such a way that it had the provision for inserting working electrode, reference electrode, an auxiliary electrode, and an inlet and outlet for passing nitrogen gas. The dropping mercury electrode (DME) was used as the working electrode for DPP and the hanging mercury drop electrode (HMDE) for CV with an area of 0.15 mm, respectively. Double distilled mercury was used for the working electrode. Ag/AgCl as reference electrode and Pt electrode as an auxiliary electrode in both the techniques.

Compound 1-chloro-1-phenylethane was prepared, as reported by Moye. Tetramethylammonium hexafluorophosphate (TMAHP), tetrathylammonium bromide (TEAB), tetra-n-propylammonium perchlorate (TPAP) and tetrabutylammonium iodide (TBAI) used as supporting electrolytes were of AR grade. Double distilled dimethylformamide (DMF) was used as solvent from Aldrich chemicals.

Experimental Procedure

The test solution was prepared by dissolving required quantity of the substance under investigation with the solvent making up with the supporting electrolyte to get the desired concentration. Nearly 10-15 mL of the solution was taken into the electrolyte cell and deoxygenated by passing nitrogen gas for about 15 min. A test run with blank was taken to confirm that there was no reducible species in the supporting electrolyte.

Results and Discussion

The electrochemical reduction behaviour of 1-chloro-1-phenylethane by cyclic voltammetry and differential pulse polarography were studied in quaternary ammonium salts as supporting electrolytes. The compound 1-chloro-1-phenylethane was found to give a well-defined peak reducing in a single step, which may be attributed to the reduction of C-Cl bond in a two-electron process forming ethylbenzene. Typical cyclic voltammogram and differential pulse polarogram of 1-chloro-1-phenylethane are shown in Figure 1 and 2.

The data reveals that the potential moves to more negative value with increase in size of the electrolyte cation: Me₃N⁺, Et₃N⁺, Pr₃N⁺ and Bu₃N⁺. It is thus seen that polarographic/voltammetric potentials are sensitive to the nature of the supporting electrolyte. This, along with the observed large shift...
of reduction potential range for the reduction of C-Cl, the tetraalkylammonium ions, usually tetrabutylammonium ions are capable for studying reduction as negative as $-2.80\text{V}$ vs Ag/AgCl. In such media the interfacial tension of mercury approaches zero, as the potential becomes negative.

The kinetic data obtained for 1-chloro-1-phenylethane by above techniques is summarised in Table 1 and 2. The variation of peak potential with sweep rate and the absence of anodic peak on the reverse scan in cyclic voltammogram confirmed the reduction process to be irreversible. The forward rate constant values are found to decrease with size of the electrolyte cation due to the shift in reduction potentials to more negative values. This is the better method to present the data as relative rates of electron transfer to a given halide in the presence of different electrolytes, i.e., estimation of diffusion coefficients and measure of forward rate constants for the $\alpha$-methylbenzylichlorides in the presence of tetraalkylammonium ions. The rates do clearly depend upon the nature of the electrolyte substantially.

The mechanism proposed for the reduction of $\alpha$-methylbenzylichloride for the formation ethylbenzene is shown in Scheme 1. This suggests that the initial step in the electrolysis of $\alpha$-methylbenzylichloride is one-electron cleavage of carbon-halogen bond to give a radical. This radical exists only transiently, as evidenced by the absence of any dimeric products, and immediately accepts a second electron to yield the carbanion, because of the very negative potential employed for the electrolysis; this pair of one-electron transfer has the appearance of being a one-step, two-electron process. Once the carbanion is generated, this can be protonated by solvent-supporting electrolyte to give the ethylbenzene.

Differential pulse polarography is used in both calibration and standard addition methods for the determination of $\alpha$-methylbenzylichloride. Using calibration method the lower detection limit is found to be $1.25\times10^{-5}\text{M}$. Standard addition method is also utilised for the determination of $\alpha$-methylbenzylichloride. The optimum experimental conditions for the determination of $\alpha$-methylbenzylichloride is found to be drop time of $1\text{s}$ and pulse amplitude of $50\text{mV}$.

![Scheme 1 — Mechanism proposed for reduction of $\alpha$-methylbenzylichloride](image)

<table>
<thead>
<tr>
<th>Supporting electrolyte</th>
<th>$-E_p$ V</th>
<th>$I_p$ µA</th>
<th>$DX10^6$ cm$^2$/s</th>
<th>$k_{red}$ cm/s</th>
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<tr>
<td>TMAHP</td>
<td>2.16</td>
<td>6.34</td>
<td>8.72</td>
<td>7.20X10$^4$</td>
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<tr>
<td>TEAB</td>
<td>2.26</td>
<td>5.02</td>
<td>7.46</td>
<td>8.46X10$^4$</td>
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<tr>
<td>TPAP</td>
<td>2.34</td>
<td>4.15</td>
<td>5.36</td>
<td>8.42X10$^4$</td>
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<tr>
<td>TBAI</td>
<td>2.47</td>
<td>3.56</td>
<td>4.43</td>
<td>6.92X10$^4$</td>
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<th>Supporting electrolyte</th>
<th>$-E_p$ V</th>
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<th>$DX10^6$ cm$^2$/s</th>
<th>$k_{red}$ cm/s</th>
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<tr>
<td>TMAHP</td>
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<td>5.15</td>
<td>9.01</td>
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<tr>
<td>TEAB</td>
<td>2.28</td>
<td>4.67</td>
<td>8.72</td>
<td>3.74X10$^4$</td>
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<tr>
<td>TPAP</td>
<td>2.50</td>
<td>4.16</td>
<td>5.36</td>
<td>5.22X10$^4$</td>
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<tr>
<td>TBAI</td>
<td>2.56</td>
<td>3.56</td>
<td>3.70</td>
<td>1.73X10$^4$</td>
</tr>
</tbody>
</table>

Table 1 — Typical cyclic voltammetric data of 1-chloro-1-phenylethane

Table 2 — Typical differential pulse polarographic data of 1-chloro-1-phenylethane

Concentration: 0.5mM  
Scan rate: 50mV/s  
Drop time: 1s  
Pulse amplitude: 50mV

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Analysis

Electrolysis was carried out in the cell, using concentrated solutions by bubbling CO\textsubscript{2} gas for the synthesis of 2-arylpropionic acids from α-methylbenzyl chloride. When carrying out systematic electrolysis, a convenient procedure has been developed for analysing the solutions at the end or during the electrolysis for α-methylbenzyl chloride, present in the solution, without isolating the products and reagents. This analysis has been developed by DPP for the determination of α-methylbenzylchlorides still present there and electoreducible in the solution during electrosynthesis of 2-arylpropionic acid class of non-steroidal anti-inflammatory agents. This is applied successfully for the synthesis of 2-phenylpropionic acid from 1-chloro-1-phenylethane and supporting electrolyte by passing CO\textsubscript{2} through the electrolyte solution. A reduction peak, observed at -2.48V in DPP for the reduction of ‘C–C’ bond, present in 1-chloro-1-phenylethane. Again the electrolysis was carried out until the desired product was obtained. The same procedure can also be applied for the determination of α-methylbenzylchlorides in the electrosynthesis of 2-arylpropionic acid class of non-steroidal anti-inflammatory agents, such as ibuprofen, naproxen, indoprofen, fenoprofen, biphren, and cicloprofen.

Conclusions

The electrochemical reduction of 1-chloro-1-phenylethane is shown to be sensitive to the nature of the supporting electrolyte. The effect of the increasing size of the electrolyte cation for the reduction potentials of 1-chloro-1-phenylethane are substantial only at high threshold of structural complexity; this phenomenon may be of analytical and synthetic value because dependence of reduction potentials of 1-chloro-1-phenylethane on various supporting electrolytes offer a way to improve the resolution of polarographic/voltammetric peaks/waves.

Acknowledgement

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References

17. Inokuchi T & Kusumoto M, Selective dehalogenation of 6,6-dibromopinceillanes by indirect electroreduction with


