Electrochemical studies of 4-chloro-3-nitrobenzophenone

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The electrochemical behaviour of 4-chloro-3-nitrobenzophenone has been studied at dropping mercury electrode (d.m.e.) and hanging mercury drop electrode (HMDE) employing d.c. polarography, a.c. polarography, cyclic voltammetry, chronomeromery and chronopotentiometry in different supporting electrolytes in methanol-water and DMF-water mixtures. Millioulometry and controlled potential electrolysis have been used to estimate the number of electrons and to identify the reduction product respectively. Kinetic parameters such as transfer coefficient, diffusion coefficient and heterogeneous forward rate constant values have been evaluated. A reduction mechanism consistent with the data, has been proposed.

In an ongoing programme on the electrochemical reduction of substituted benzophenones so far only such substrates have been chosen which have only one electro reducible group, viz. the carbonyl functional group. Presently, the reduction behaviour of 4-chloro-3-nitro-benzophenone is studied in different acidic and basic supporting electrolytes in methanol-water and DMF-water mixtures. This substrate has two electro reducible functionalities, viz. carbonyl and nitro groups.

Materials and Methods

4-Chloro-3-nitrobenzophenone (Ega-Chemie, West Germany) was dissolved in minimum amount of solvent and made up with the supporting electrolyte to the desired concentration. Triton X-100 was used as maximum suppressor wherever necessary. All reagents used were of AR grade. Polarograms were recorded under N₂ atmosphere, using polarographic analyser model 364 supplied by Princeton Applied Research Corporation, USA. The d.m.e. used as working electrode had the following characteristics: m = 1.9392 mg sec⁻¹; t = 3 sec in phosphate buffer of pH 6.85. The HMDE used for voltammetric measurements had an area of 0.03294 cm². The theoretical details and the experimental procedure of these techniques were discussed elsewhere.

Results and Discussion

(a) Polarographic reduction

Two waves are observed for the reduction of 4-chloro-3-nitrobenzophenone in all the supporting electrolytes employed, except in 0.1 M HCl in which three waves are noticed. The first wave is attributed to the reduction of nitro group and the second wave to the reduction of carbonyl group. As \( i_t \) versus \( j_t \) plots pass through the origin, the reduction of nitro group is concluded to be diffusion-controlled and free from adsorption. From the Tomes' criterion, log-plot analysis and dependence of half-wave potential on the drop time, the reduction process of nitro group is noticed to be irreversible. The number of electrons involved in the reduction process of nitro group is found to be four. This is further supported by the millioulometric analysis. The half-wave potentials of the two groups increase linearly with pH upto pH = 6.85 and thereafter \( E_i \) values remain practically constant indicating the involvement of protons in the reduction process in acid solutions. Controlled potential electrolysis has been carried out at the limiting region of the first wave of the nitro group, to identify the product of reduction of nitro group. A divided cell was used for the electrolysis. UV spectrum of the electrolysis product after extraction with ether, exhibits \( \lambda_{max} \) at 320 nm indicating the presence of azo linkage in the electrolysis product. IR peak observed at 1620 cm⁻¹ for the above product supported the presence of azo group. Typical polarographic data for the nitro group are presented in Table 1.

(b) Cyclic voltammetric results

Two peaks are obtained for the reduction of 4-chloro-3-nitrobenzophenone in all the supporting electrolytes. An anodic peak in the reverse scan has been noticed in all the supporting electrolytes. By reversing the scan at the limiting region of the first peak, an anodic peak is obtained.
Table 1 — Typical polarographic data of reduction of 4-chloro-3-nitrobenzophenone
[Data related to nitro group reduction]

<table>
<thead>
<tr>
<th>Supporting electrolyte</th>
<th>( i_0 ) (( \mu A ))</th>
<th>(-E_i) (V vs SCE)</th>
<th>( \alpha_n )</th>
<th>( D \times 10^2 ) (cm² s⁻¹)</th>
<th>( K_{p/n} ) (cm s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetate buffer (pH 4.7)</td>
<td>16.00</td>
<td>0.45</td>
<td>1.08</td>
<td>9.15</td>
<td>1.99 ( \times 10^{-7} )</td>
</tr>
<tr>
<td>Phosphate buffer (pH 6.85)</td>
<td>15.50</td>
<td>0.64</td>
<td>0.66</td>
<td>8.59</td>
<td>4.08 ( \times 10^{-8} )</td>
</tr>
<tr>
<td>Carbonate buffer (pH 10.0)</td>
<td>14.70</td>
<td>0.71</td>
<td>1.49</td>
<td>7.73</td>
<td>1.65 ( \times 10^{-15} )</td>
</tr>
<tr>
<td>Phosphate buffer (pH 11.70)</td>
<td>14.63</td>
<td>0.70</td>
<td>2.27</td>
<td>7.65</td>
<td>1.95 ( \times 10^{-21} )</td>
</tr>
</tbody>
</table>

Table 2 — Typical kinetic parameters during cyclic voltammetry (CV), chronoamperometry (CA) and chronopotentiometry (CP) of 4-chloro-3-nitrobenzophenone
[Data related to nitro group reduction]

<table>
<thead>
<tr>
<th>Supporting electrolyte</th>
<th>( i_p ) (( \mu A ))</th>
<th>(-E_i) (V vs SCE)</th>
<th>( \alpha_n )</th>
<th>( D \times 10^6/\text{cm}^2\text{s}^{-1} )</th>
<th>( K_{p/n}^0/\text{(cm}^2\text{s}^{-1})^n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clarks &amp; Lubs buffer (pH 1.5)</td>
<td>10.20</td>
<td>-0.15</td>
<td>0.76</td>
<td>2.17</td>
<td>2.79</td>
</tr>
<tr>
<td>Acetate buffer (pH 4.7)</td>
<td>10.80</td>
<td>0.42</td>
<td>0.55</td>
<td>3.35</td>
<td>2.43</td>
</tr>
<tr>
<td>Phosphate buffer (pH 6.85)</td>
<td>11.60</td>
<td>0.46</td>
<td>0.76</td>
<td>2.82</td>
<td>3.08</td>
</tr>
<tr>
<td>Borate buffer (pH 9.2)</td>
<td>13.00</td>
<td>0.48</td>
<td>1.20</td>
<td>2.24</td>
<td>2.98</td>
</tr>
<tr>
<td>Carbonate buffer (pH 10.0)</td>
<td>13.20</td>
<td>0.52</td>
<td>1.45</td>
<td>1.90</td>
<td>3.08</td>
</tr>
<tr>
<td>Phosphate buffer (pH 11.70)</td>
<td>13.80</td>
<td>0.54</td>
<td>1.20</td>
<td>2.52</td>
<td>3.38</td>
</tr>
</tbody>
</table>

which is attributed to the oxidation of the product at the first peak. The first peak is attributed to the reduction of nitro group. During the second scan of the cycle and on repeating the cycle a new cathodic peak at more positive potentials to the first peak is noticed in all the supporting electrolytes except in the buffers of pH 1.5 and 11.70. This new cathodic peak can be attributed to the reduction of the product formed at the anodic peak. The redox couple is observed to be irreversible as evidenced by the separation of their peak potentials.

The reduction of the nitro group is irreversible, diffusion-controlled and adsorption-free as evidenced from the linear plots of \( i_p \) versus \( v' \) which pass through origin. A.C. polarographic results also show the reduction to be adsorption-free. The peak potential values increase linearly with pH until pH 6.85 and remain practically constant thereafter. Typical cyclic voltammetric data are presented in Table 2.

(c) Chronoamperometric results

Chronoamperometric measurements have been carried out at the step potentials chosen from the diffusion-controlled regions of the first reduction peak corresponding to the reduction of nitro group. The linear and horizontal plots of \( i_p \) versus \( i' \) indicate the diffusion-controlled, adsorption-free, electrode process for the nitro group. Typical chronoamperometric data are presented in Table 2.

(d) Chronopotentiometric results

Two consecutive chronopotentiograms were obtained for the reduction of 4-chloro-3-nitrobenzophenone indicating the reduction of nitro and
carbonyl groups respectively. The $i_o$ and $i_T$ values are constant for the reduction of nitro group providing evidence for the diffusion-controlled nature of the process. Typical data are presented in Table 2.

**Mechanism of reduction**

(a) Polarographic reduction

Under polarographic conditions, the nitro group is found to undergo reduction to the hydroxylamine stage in all the supporting electrolytes except in 0.1 M HCl. In 0.1 M HCl, the process is observed to lead to the formation of corresponding amine. The plots of $E_{dme}$ versus $k_{th}$ are linear indicating one rate-determining step in the reduction process throughout the entire pH range. The involvement of protons in the rate-determining step is evidenced by the plot of $E_i$ versus pH. Since the number of electrons involved in the overall electrode process is four, the mechanism shown in Scheme 1 can be proposed in acid buffers. Step (1) is pH dependent and hence $E_i$ values increase linearly with pH until pH 6.85. After pH 6.85, the $E_i$ values are independent of pH of solution and therefore the reduction follows the mechanism shown in Scheme 2.

(b) Cyclic voltammetric and chronopotentiometric reduction

The variation of peak potential values with pH is found similar to the variation of $E_i$ with pH. In cyclic voltammetry, the appearance of anodic peak when the scan is reversed can be attributed to the oxidation of the -NHOH group formed at the first peak to nitroso group. During the second scan of the cycle, a new anodic peak is observed at more positive potentials to the first peak due to the reduction of nitroso derivative formed at the electrode surface to -NHOH group.

Spectral analysis (UV and IR) showed the controlled potential electrolysis product to be the corresponding azo compound. Due to the short time available in cyclic voltammetry and d.c. polarography (in comparison to the controlled potential electrolysis), the formation of azo compound is not possible at d.m.e. or HMDE. On the other hand, in controlled potential electrolysis, the hydroxylamine formed on the electrode surface will be oxidized to the corresponding nitroso derivative in solution and the azo compound can be formed by condensation of hydroxylamine and nitroso derivative as shown in Scheme 3.
v) DMF-water. This increases the delocalization of negative charge over the ring which in turn decreases the fraction of negative charges at the carbon bearing chlorine.

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References