Polarographic Reduction of Some Substituted Phenylthioureas

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Polarographic reduction of substituted phenylthioureas in Britton-Robinson buffers and in 0.1 M NaOH gives one well-defined, diffusion-controlled, partially irreversible, two-electron transfer oxidation waves. Below pH 5.0 ill-defined waves are obtained. The E₁/₂ shifts towards more negative value with the increase in pH and towards more positive potential with the increase in [depolarizer]. Phenylthioureas do not undergo direct oxidation but form mercuroxidum complex with mercury at d.m.e. This is further supported by the effect of substituents on E₁/₂.

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the slope and intercept of these plots is given in Table 1. The values of $K_{h,k}$ indicate the partial irreversible nature of the waves.

The effect of $pH$ on the $E_{1/2}$ of various phenylthioureas was obtained from the polarograms run in different buffers. The $E_{1/2}$ was found to shift towards more negative value with the increasing $pH$ (5.0-10.0). Such a behaviour was also observed by Fedoronko and coworkers for urea, thiourea, and isothiourea. Plots of $E_{1/2}$ versus $pH$ are linear in the $pH$ range 5.0-10.0. Below $pH$ 5.0, ill-defined waves were obtained.

Since the value of $n$ was found to be two, the anodic depolarization may involve the formation of disulphide or mercurous complex. In the former case the Nernst equation should be given by

$$E_{d,e.} = E_{1/2} - RT/nF \ln \left( [C_s]^n / [C_y] \right)$$

where $C_s$ and $C_y$ are concentrations of substituted thiourea and its disulphide respectively.

Putting $n = 2$, the above equation changes to

$$E_{d,e.} = E_{1/2} - 0.059/2 \ln \left( (i_i^2 - i_0^2)/i \right)$$

where $i$ represents the amount corresponding to the concentration of the oxidized substance and $i_0$ to the total limiting current. If the formation of disulphide is involved the plots of $E_{d,e.}$ vs $ln( (i_i^2 - i_0^2)/i)$ should be linear with slope of 0.059/2. However, it was found that the slopes of these plots are much higher (in the range 0.06-0.07) than the theoretical value. On the basis of this observation the possibility of direct oxidation of the substituted phenylthioureas was ruled out.

The second possibility of complex formation can be accounted for by considering the zwitterion formation of thioureas. These species would react with mercurous ions to give a complex. As the concentration of $Hg_{2}S_{2}^{+}$ will be controlled by the solubility product $S$ of the mercurous compound, the Nernst equation in this case can be represented as

$$E = E^o_{Hg_{2}S_{2}^{+}} + RT/2F \ln S - RT/F \ln [C_s] / 2$$

After considering the diffusion of substituted phenylthiourea ions towards the electrode surface at $i = 0$ the above equation changes to

$$E_{1/2} = E^o - RT/F \ln C_s / 2$$

where $E^o = E^o_{Hg_{2}S_{2}^{+}} + RT/2F \ln S$.

From this equation it is clear that the $E_{1/2}$ should be independent of flow rate, drop time and the height of the mercury column. This is what has been observed in the case of all these thioureas. Similar type of complex formation have also been reported by Edsberg in the case of unsubstituted thiourea.

An examination of the data in Table 1 reveals that electron donating substituents, viz. methoxy, ethoxy and methyl groups, shift the $E_{1/2}$ towards more positive potential, whereas electron withdrawing groups like chloro and bromo shifts the $E_{1/2}$ towards more negative potential. This behaviour can be explained on the basis of zwitterion formation. An electron withdrawing substituents attracts electron towards itself due to which tendency of zwitterion formation would be decreased thereby making the reaction more difficult. An electron donating group would impart a negative charge, thereby increase the zwitterion formation tendency with the result $E_{1/2}$ slightly shift towards more positive potential.

The relation between half-wave potential of substituted phenylthioureas and the Hammett substituent constant ($\sigma$) which include both polar induction effect and polar conjugation effect is shown in Fig. 1. It is observed from this plot that substituents like H, 3-CH$_3$, 4-CH$_3$, 4-CH$_2$H$_4$, 4-Br obey Hammett equation while other groups deviate from the regression line.

### Table 1 — Values of Various Kinetic Parameters for the Substituted Phenylthioureas

<table>
<thead>
<tr>
<th>No</th>
<th>R</th>
<th>$-E_{1/2}^o$ (V)</th>
<th>$\alpha$</th>
<th>$10^3 \times K_{h,k}$ (cm sec$^{-1}$)</th>
<th>$E_{1/2}^o 10^{-5}$ (cm sec$^{-1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>0.400</td>
<td>0.775</td>
<td>1.620</td>
<td>3.90</td>
</tr>
<tr>
<td>2</td>
<td>2-CH$_3$</td>
<td>0.380</td>
<td>0.775</td>
<td>1.545</td>
<td>3.27</td>
</tr>
<tr>
<td>3</td>
<td>3-CH$_3$</td>
<td>0.390</td>
<td>0.835</td>
<td>1.608</td>
<td>3.70</td>
</tr>
<tr>
<td>4</td>
<td>4-CH$_3$</td>
<td>0.395</td>
<td>0.750</td>
<td>2.525</td>
<td>3.24</td>
</tr>
<tr>
<td>5</td>
<td>4-Cl</td>
<td>0.440</td>
<td>0.797</td>
<td>1.002</td>
<td>2.98</td>
</tr>
<tr>
<td>6</td>
<td>4-Br</td>
<td>0.420</td>
<td>0.780</td>
<td>2.415</td>
<td>3.65</td>
</tr>
<tr>
<td>7</td>
<td>4-CH$_2$H$_4$</td>
<td>0.380</td>
<td>0.730</td>
<td>2.862</td>
<td>3.97</td>
</tr>
<tr>
<td>8</td>
<td>4-OC$_2$H$_4$</td>
<td>0.390</td>
<td>0.720</td>
<td>2.812</td>
<td>3.20</td>
</tr>
</tbody>
</table>

*At concentration $1 \times 10^{-2}M.*