CHAPTER V

FREE RADICAL INTERVENTION IN THE OXIDATION OF 
SULPHANILIC ACID BY DIPERIODATOCUPRATE(III) (DPC) 
COMPLEX. A KINETIC AND MECHANISTIC APPROACH

The importance of periodate and tellurate complexes of copper in its trivalent state is explained in Chapter IV (p. 115).

Sulphanilic acid (p-aminobenzenesulphonie acid) is an important and interesting compound, which finds a number of applications in the syntheses of organic dyes\textsuperscript{1}. The amide of sulphanilic acid (sulphanilamide) and certain related substituted amides are of considerable medical importance as the sulfa drugs. Although they have been supplanted to a wide extent by the antibiotics such as penicillin, terramycin, chloromycetin and aureomycin, the sulfa drugs still have their medical uses, and make up a considerable portion of the output of the pharmaceutical industry\textsuperscript{2}. Several studies have been reported on the oxidation of sulphanilic acid by other oxidants such as peroxomonophosphoric acid\textsuperscript{3}, periodate\textsuperscript{4}, hydrogen peroxide\textsuperscript{5}, cerium(IV)\textsuperscript{6}, persulphate (peroxodisulphate)\textsuperscript{7,8}. Different workers have identified different products by different oxidants for the oxidation of sulphanilic acid.\textsuperscript{1,8} The study of sulphanilic acid becomes important because of its biological significance and selectivity towards the oxidants. The literature survey reveals that there are no reports on the oxidation of sulphanilic acid by diperiodatocuprate(III) (DPC). In view of the multiple equilibria of DPC,
involving the different copper(III) periodate species and medical importance of sulphanilic acid, a detailed study of the title reaction is undertaken to arrive a plausible mechanism in such a media.

EXPERIMENTAL

Materials

All chemicals used were of analytical reagent grade. Double distilled water was used throughout. The solution of sulphanilic acid (Merck) was prepared by dissolving appropriate amount of sample in warm very dilute alkaline solution. The copper(III) periodate, copper(II) and periodate solutions were prepared and standardised as given in the Chapter IV (p.116 and 117). Since periodate is present in excess in DPC, the possibility of oxidation of sulphanilic acid by periodate in alkaline medium at 25°C was checked. It was found that there was no significant reaction under the experimental conditions employed compared to the DPC oxidation of sulphanilic acid. Potassium hydroxide and potassium nitrate were employed to maintain the required alkalinity and ionic strength respectively in reaction solutions.

Kinetic procedure

The oxidation of sulphanilic acid by DPC was followed under pseudo-first order conditions where sulphanilic acid concentration was in excess over DPC concentration at 25 ± 0.1°C. The reaction was initiated by mixing the required quantities of previously thermostatted solutions of sulphanilic acid and DPC, which also contained potassium hydroxide, potassium nitrate and periodate.
solutions to maintain the required alkalinity, ionic strength and periodate. The total concentration of hydroxide was calculated considering the potassium hydroxide present in DPC as well as the potassium hydroxide additionally added. Similarly, the total meta-periodate concentration was calculated by considering meta-periodate present in the solution of DPC and additionally added. The course of reaction was followed by measuring the absorbance of unreacted DPC in the reaction mixture in a 1 cm quartz cell located in the thermostatted compartment of a Peltier Accessory (temperature control) attached Varian CARY 50 Bio UV-VIS spectrophotometer at its maximum absorption, 415 nm, as a function of time. It was observed that there is negligible interference from other species present in the reaction mixture at this wavelength. The obedience of Beer’s law by DPC at 415 nm was verified and the molar absorbance coefficient, ε was found to be 6231 ± 311 dm³ mol⁻¹ cm⁻¹ at this wave length (Chapter IV (p.118)). An example run is given in Table V (i) (p.152). The first order rate constants, k_{obs}, were obtained from the plots of log(a−x) versus time, where ‘a’ and ‘x’ are the initial concentration and change in concentration of diperiodatocuprate(III) at time t, respectively. The plots were linear over 80 % completion of the reaction and the rate constants were reproducible within ± 5 %. The spectral changes during the reaction are similar to that of the oxidation of L-asparatic acid by DPC (Fig.IV(iii) p.122)) and it was observed that the concentration of DPC decreases at 415 nm.

The effect of dissolved oxygen on the rate of reaction was studied by
Oxidation of sulphanilic acid by diperiodatocuprate(III) in aqueous alkaline medium at 25 °C

**Example run**

\[
[DPC] = 1.0 \times 10^{-4}; \quad [\text{Sulphanilic acid}] = 1.0 \times 10^{-3}; \quad [OH^-] = 0.05; \quad [IO_4^-] = 1.0 \times 10^{-5}; \quad I = 0.50 / \text{mol dm}^{-3}
\]

<table>
<thead>
<tr>
<th>Time (sec)</th>
<th>Absorbance (A)</th>
<th>((a - x) = (A_t - A_0))</th>
<th>(2 + \log (a - x))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.7343</td>
<td>0.6348</td>
<td>1.8026</td>
</tr>
<tr>
<td>20</td>
<td>0.6915</td>
<td>0.5920</td>
<td>1.7723</td>
</tr>
<tr>
<td>40</td>
<td>0.6297</td>
<td>0.5302</td>
<td>1.7244</td>
</tr>
<tr>
<td>60</td>
<td>0.5890</td>
<td>0.4895</td>
<td>1.6898</td>
</tr>
<tr>
<td>80</td>
<td>0.5410</td>
<td>0.4415</td>
<td>1.6449</td>
</tr>
<tr>
<td>100</td>
<td>0.5057</td>
<td>0.4062</td>
<td>1.6087</td>
</tr>
<tr>
<td>120</td>
<td>0.4726</td>
<td>0.3731</td>
<td>1.5718</td>
</tr>
<tr>
<td>140</td>
<td>0.4429</td>
<td>0.3434</td>
<td>1.5358</td>
</tr>
<tr>
<td>160</td>
<td>0.4213</td>
<td>0.3218</td>
<td>1.5076</td>
</tr>
<tr>
<td>180</td>
<td>0.3845</td>
<td>0.2850</td>
<td>1.4549</td>
</tr>
<tr>
<td>200</td>
<td>0.3589</td>
<td>0.2594</td>
<td>1.4140</td>
</tr>
<tr>
<td>0.0995</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
</tbody>
</table>

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preparing the reaction mixture and following the reaction in an atmosphere of the nitrogen. No significant difference between the results was observed in the presence and absence of nitrogen. In view of the modest concentration of alkali used in the reaction medium, attention was also given to the effect of the surface of the reaction vessel on the kinetics. The use of polythene or acrylic ware and quartz or polyacrylate cells gave the same results, indicating that the surface does not have any significant effect on the rate.

Regression analysis of the experimental data to obtain the regression coefficient, $r$ and standard deviation, $S$ of points from the regression line was performed using a Pentium-IV personal computer.

RESULTS

Stoichiometry and product analysis

Different sets of reaction mixtures containing excess DPC over sulphanilic acid at constant concentration of hydroxyl ion, periodate and potassium nitrate were kept for 2 hours in a closed vessel under nitrogen atmosphere. The remaining concentration of DPC was estimated by spectrophotometrically at 415 nm. The results indicate 1:4 stoichiometry as given in equation (1) (Table V (ii) (p.154)).

\[
\text{NH}_2\text{I} + 4\text{H}_2\text{SO}_4 + 4\text{Cu}^{(II)} + 4\text{OH}^- \rightarrow \text{NH}_2\text{I} + 4\text{Cu}^{(II)} + 3\text{H}_2\text{O} + 4\text{H}_2\text{SO}_4
\] (1)
Table V (ii)

Stoichiometry of oxidation of sulphanilic acid by DPC in aqueous alkaline medium at 25 °C

\[ \text{[OH']} = 0.1; \quad \text{[IO}_4'^{-} \text{]} = 1.0 \times 10^{-5}; \quad I = 0.50 / \text{mol dm}^{-3} \]

<table>
<thead>
<tr>
<th>[DPC] x 10^4 (mol dm^-3)</th>
<th>[ASP] x 10^4 (mol dm^-3)</th>
<th>Found [DPC] x 10^6 (mol dm^-3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>1.0</td>
<td>0.01</td>
</tr>
<tr>
<td>10.0</td>
<td>2.0</td>
<td>2.08</td>
</tr>
<tr>
<td>12.0</td>
<td>2.5</td>
<td>2.10</td>
</tr>
<tr>
<td>8.0</td>
<td>1.0</td>
<td>4.02</td>
</tr>
<tr>
<td>8.0</td>
<td>2.0</td>
<td>0.02</td>
</tr>
<tr>
<td>6.0</td>
<td>1.0</td>
<td>2.02</td>
</tr>
</tbody>
</table>
The reaction product was extracted with ether and recrystallised from aqueous alcohol and the purity was checked by HPLC. This is identified as p-nitroso benzenesulphonic acid by its I.R. spectrum (KBr), which showed a band at (υ) 1554 cm⁻¹ due to N→O stretching of acid, a broad band at 1220 cm⁻¹ due to S=O of SO₃H stretching. N→O and SO₃H groups are confirmed by spot tests⁹. Copper(II) sulphate was identified by spot test¹⁰ and UV-Vis spectra. It was observed that p-nitroso benzenesulphonic acid does not undergo further oxidation under the present kinetic conditions.

**Reaction order**

The reaction orders were determined from the slope of the plots of log_{k_{obs}} versus log (concentration) by varying the concentrations of reductant and alkali in each while keeping all other concentrations and conditions constant.

**Effect of [diperiodatocuprate(III)]**

The concentration of diperiodatocuprate(III) was varied in the range, 2.50 x 10⁻² to 2.0 x 10⁻⁴ mol dm⁻³ at fixed concentration of sulphanilic acid, alkali, periodate and ionic strength. The non-variation in the pseudo-first order rate constants at various concentrations of DPC indicates the order in DPC concentration as unity (Table V (iii) (p.157). The plots of log (a - x) versus time are linear and parallel in this study and as in the case of Chapter IV (p.121).
Effect of [sulphanilic acid]

The substrate, sulphanilic acid was varied in the concentration range of $5.0 \times 10^{-4}$ to $5.0 \times 10^{-3}$ mol dm$^{-3}$ at 25°C keeping all other conditions constant (Table V (iii) (p.157)). The $k_{obs}$ values increased with increase in concentration of sulphanilic acid. From the plot of log $k_{obs}$ versus log[sulphanilic acid] the value of slope was found to be less than unity, indicating less than unit order dependence on concentration of sulphanilic acid (Fig. V (i) (p.158)) ($r = 0.9991$, $S = 0.011$)

Effect of [alkali]

The effect of concentration of alkali on the rate of reaction was studied at constant concentrations of sulphanilic acid, DPC, periodate and ionic strength at 0.5 mol dm$^{-3}$ at 25°C. The rate constants increased with increase in hydroxyl ion concentration (Table V (iv) (p.159)). The order was found to be less than unity (Fig. V (ii) (p.160)) ($r = 0.9917$, $S = 0.03$)

Effect of [periodate]

The effect of concentration of IO$_4^-$ was observed by varying the concentration from $1.0 \times 10^{-5}$ to $1.5 \times 10^{-4}$ mol dm$^{-3}$ at constant concentrations of DPC, sulphanilic acid, alkali and potassium nitrate. It was found that the added periodate has no effect on the rate of the reaction (Table V (iv) (p.159))

Effect of initially added products

The initially added products, such as copper(II) and p-nitroso benzenesulphonic
Table V (iii)

Effect of variation of concentration of DPC and sulphanilic acid on diperiodatocuprate(III) oxidation of sulphanilic acid in an aqueous alkaline medium at 25 °C

\([\text{IO}_4^-] = 1.0 \times 10^{-5}; \quad \text{[OH}^-] = 0.10; \quad I = 0.50 / \text{mol dm}^{-3}\]

<table>
<thead>
<tr>
<th>[DPC] x 10^4 (mol dm(^{-3}))</th>
<th>[sulphanilic acid] x 10^3 (mol dm(^{-3}))</th>
<th>(k_{\text{obs}} \times 10^3 (s^{-1}))</th>
<th>Found</th>
<th>Calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>1.0</td>
<td>4.21</td>
<td>4.61</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>1.0</td>
<td>4.33</td>
<td>4.61</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>1.0</td>
<td>4.44</td>
<td>4.61</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>1.0</td>
<td>4.01</td>
<td>4.61</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>1.0</td>
<td>4.14</td>
<td>4.61</td>
<td></td>
</tr>
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<td>1.0</td>
<td>0.5</td>
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<td>2.78</td>
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</tr>
<tr>
<td>1.0</td>
<td>1.0</td>
<td>4.44</td>
<td>4.61</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
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<td>5.42</td>
<td>5.84</td>
<td></td>
</tr>
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<td>1.0</td>
<td>2.0</td>
<td>6.43</td>
<td>6.85</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>5.0</td>
<td>9.50</td>
<td>9.70</td>
<td></td>
</tr>
</tbody>
</table>
Figure V (i)

Order with respect to sulphanilic acid concentration on the diperiodatocuprate(III) oxidation of sulphanilic acid in aqueous alkaline medium at 25 °C

(Conditions as in Table V (iii) (p.157))
Table V (iv)

Effect of variation of OH' and IO₄⁻ ion concentrations on diperiodatocuprate(III)
oxidation of sulphanilic acid in aqueous alkaline medium at 25 °C

[DPC] = 1.0 x 10⁻⁴;  [sulphanilic acid] = 1.0 x 10⁻³;  I = 0.50 / mol dm⁻³

<table>
<thead>
<tr>
<th>[OH⁻]</th>
<th>[IO₄⁻] x 10⁻⁵</th>
<th>kₒbs x 10⁻³ (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(mol dm⁻³)</td>
<td></td>
</tr>
<tr>
<td>0.02</td>
<td>1.0</td>
<td>1.95</td>
</tr>
<tr>
<td>0.05</td>
<td>1.0</td>
<td>3.57</td>
</tr>
<tr>
<td>0.10</td>
<td>1.0</td>
<td>4.44</td>
</tr>
<tr>
<td>0.15</td>
<td>1.0</td>
<td>5.50</td>
</tr>
<tr>
<td>0.20</td>
<td>1.0</td>
<td>6.25</td>
</tr>
<tr>
<td>0.05</td>
<td>1.0</td>
<td>4.44</td>
</tr>
<tr>
<td>0.05</td>
<td>2.0</td>
<td>4.41</td>
</tr>
<tr>
<td>0.05</td>
<td>4.0</td>
<td>4.42</td>
</tr>
<tr>
<td>0.05</td>
<td>8.0</td>
<td>4.41</td>
</tr>
<tr>
<td>0.05</td>
<td>15.0</td>
<td>4.71</td>
</tr>
</tbody>
</table>
Figure V (ii)

Order with respect to hydroxyl ion concentration on the diperiodatocuprate(III) oxidation of sulphanilic acid in aqueous alkaline medium at 25 °C

(Conditions as in Table V (iv) (p.159))
acid did not show any significant effect on the rate of the reaction.

**Effect of ionic strength and dielectric constant**

The effect of ionic strength was studied by varying the potassium nitrate concentration in the reaction medium. The ionic strength of the reaction medium was varied from 0.05 to 0.50 mol dm$^{-3}$ at constant concentration of DPC, sulphanilic acid, IO$_4^-$ and alkali concentrations. The effect of dielectric constant (D) was studied by varying the t-butyl alcohol-water content in the reaction mixture with all other conditions being constant. It was found that both the ionic strength and dielectric constant do not have any significant effect on the rate of reaction.

**Test for free radicals**

To test the intervention of free radicals, the reaction mixture was mixed with acrylonitrile monomer and kept for 2 hours under nitrogen atmosphere. On dilution with methanol, a white precipitate of polymer was formed, indicating the intervention of free radicals in the reaction. The blank experiment of either DPC or sulphanilic acid with acrylonitrile alone did not induce polymerization under the same experimental conditions as those induce with the reaction mixture. Initially added acrylonitrile decreases the rate of reaction indicating the intervention of free radical. The similar results are also available in the literature$^{11}$.

**Effect of temperature**

The activation parameters for the reaction were calculated by using linear regression analysis as given in Chapter II, (p.49). The rate of reaction was
measured at four different temperatures under varying sulphanilic acid concentration keeping other conditions constant. The rate constants were found to increase with increase in temperature. The rate constants $k$, of the slow step of Scheme 1 (p.167) were obtained from the intercept of $1/k_{obs}$ versus $1/[\text{sulphanilic acid}]$ ($r = 0.9937$, $S = 0.013$) plot at four different temperatures and were used to calculate the activation parameters. The values of $k$ are given in Table V (v) p.163). From the Arrhenius plot of log$k$ ($Y^{*}\text{cal}$) versus $1/T$ ($r = 0.9999$, $S <0.0001$) $E_a$ was obtained and from which the activation parameters, $\Delta H^\#$, $\Delta S^\#$ and $\Delta G^\#$ are calculated and are given in Table V (v) p.163).

The thermodynamic quantities for the first and second equilibrium steps in Scheme 1 can be evaluated as follows: The sulphanilic acid and hydroxyl ion concentrations were varied (Table V (iii) (p.157; (iv) (p.159)) at four different temperatures. From the slopes and intercepts, of the plots of $1/k_{obs}$ versus $1/[\text{OH}^-]$ ($r = 0.998$, $S = 0.0124$) and $1/k_{obs}$ versus $1/[\text{sulphanilic acid}]$ ($r = 0.9937$, $S = 0.013$) the values of $K_4$ and $K_5$ (dm$^3$ mol$^{-1}$) are calculated at different temperatures 298, 303, 308, and 313 K and are given in Table V (vi) p.165). The vant Hoff’s plots were drawn for the variation of $K$’s with temperature [i.e., log $K_4$ versus $1/T$ and log $K_5$ versus $1/T$]. The values of the enthalpy of reaction $\Delta H$, entropy of reaction $\Delta S$ and free energy of reaction $\Delta G$, were calculated and are given in Table V (vi) (p.165).
(a) Effect of temperature on the slow step of the mechanism of oxidation of sulphanilic acid by diperiodatocuprate(III) in an aqueous alkaline medium

\[
[DPC] = 1.0 \times 10^{-4}; \quad [\text{sulphanilic acid}] = 1.0 \times 10^{-3}; \\
[\text{OH}^-] = 0.05; \quad [\text{IO}_4^-] = 1.0 \times 10^{-4}; \\
I = 0.50 \text{ mol dm}^{-3}
\]

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>(k \times 10^2) (s(^{-1}))</th>
<th>(\log k) (Y)</th>
<th>(1/T \times 10^3) (X)</th>
<th>(Y_{calc})</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>1.34</td>
<td>-1.8729</td>
<td>3.36</td>
<td>-1.8976</td>
</tr>
<tr>
<td>303</td>
<td>1.48</td>
<td>-1.8297</td>
<td>3.30</td>
<td>-1.7770</td>
</tr>
<tr>
<td>308</td>
<td>2.14</td>
<td>-1.6696</td>
<td>3.25</td>
<td>-1.6799</td>
</tr>
<tr>
<td>313</td>
<td>2.70</td>
<td>-1.5685</td>
<td>3.20</td>
<td>-1.5763</td>
</tr>
</tbody>
</table>

*Calculated,

(b) Activation parameters with respect to slow step of Scheme 1.

<table>
<thead>
<tr>
<th>Activation parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_a) (kJ mol(^{-1}))</td>
<td>38.3 ± 1.4</td>
</tr>
<tr>
<td>(\Delta S^\circ) (JK(^{-1}) mol(^{-1}))</td>
<td>-161 ± 11</td>
</tr>
<tr>
<td>(\Delta H^\circ) (kJ mol(^{-1}))</td>
<td>35.7 ± 1</td>
</tr>
<tr>
<td>(\Delta G^\circ) (kJ mol(^{-1}))</td>
<td>85 ± 4</td>
</tr>
<tr>
<td>log A</td>
<td>6.8 ± 0.2</td>
</tr>
</tbody>
</table>
Figure V (iii)

Effect of temperature on the oxidation of sulphanilic acid by diperiodatocuprate(III) in aqueous alkaline medium

(Conditions as in Table V (v) (p. 163))
Table V (vi)

Thermodynamic quantities, $K_4$ and $K_5$ with respect to the oxidation of sulphanilic acid by diperiodatocuprate(III) in aqueous alkaline medium

$$[	ext{DPC}] = 1.0 \times 10^{-4}; \quad [	ext{sulphanilic acid}] = 1.0 \times 10^{-3};$$

$$[\text{OH}^-] = 0.05; \quad [\text{IO}_4^-] = 1.0 \times 10^{-4};$$

$I = 0.50 / \text{mol dm}^{-3}$

(a) The values with respect to first ($K_4$) and second ($K_5$) steps of Scheme 1

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$K_4$ (dm$^3$ mol$^{-1}$)</th>
<th>$K_5 \times 10^{-3}$ (dm$^3$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>9.4</td>
<td>1.082</td>
</tr>
<tr>
<td>303</td>
<td>17.2</td>
<td>1.051</td>
</tr>
<tr>
<td>308</td>
<td>21.6</td>
<td>1.024</td>
</tr>
<tr>
<td>313</td>
<td>27.5</td>
<td>1.008</td>
</tr>
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</table>

(b) Thermodynamic quantities with respect to first and second steps of Scheme 1

<table>
<thead>
<tr>
<th>Thermodynamic quantities</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>First step</td>
<td>Second step</td>
</tr>
<tr>
<td>$\Delta H$ (kJ mol$^{-1}$)</td>
<td>$53.7 \pm 2.1$</td>
</tr>
<tr>
<td>$\Delta S$ (JK$^{-1}$ mol$^{-1}$)</td>
<td>$-3.71 \pm 0.18$</td>
</tr>
<tr>
<td>$\Delta G$ (kJ mol$^{-1}$)</td>
<td>$200 \pm 10$</td>
</tr>
</tbody>
</table>
DISCUSSION

The water soluble Copper(III) periodate complex is reported\textsuperscript{12,13}, to be [Cu(HIO\textsubscript{6})(OH)\textsubscript{2}]\textsuperscript{7-}. However, in an aqueous alkaline medium and at a high pH range as employed in the study, periodate is unlikely to exist as HIO\textsubscript{6}\textsuperscript{4-} (as present in the complex) as is evident from its involvement in the multiple equalibria\textsuperscript{14} (2) to (4) depending on the pH of the solution.

\[
\begin{align*}
    \text{H}_3\text{IO}_6 & \rightleftharpoons \text{H}_4\text{IO}_6^- + \text{H}^+ & K_1 = 5.0 \times 10^{-4} \\
    \text{H}_4\text{IO}_6^- & \rightleftharpoons \text{H}_3\text{IO}_6^{2-} + \text{H}^+ & K_2 = 4.9 \times 10^{-9} \\
    \text{H}_3\text{IO}_6^{2-} & \rightleftharpoons \text{H}_2\text{IO}_6^{3-} + \text{H}^+ & K_3 = 5.0 \times 10^{-4}
\end{align*}
\]

Periodic acid exists as H\textsubscript{3}IO\textsubscript{6} in acid medium and as H\textsubscript{4}IO\textsubscript{6} at pH 7. In alkaline conditions, the main species are expected to be H\textsubscript{3}IO\textsubscript{6}\textsuperscript{2-} and H\textsubscript{2}IO\textsubscript{6}\textsuperscript{3-}. At higher concentrations, periodate also tends to dimerise\textsuperscript{15}. Hence, at the pH employed in this study, the soluble copper(III) periodate complex exists as diperiodatocuprate(III), [Cu(OH)\textsubscript{2}(H\textsubscript{2}IO\textsubscript{6})\textsubscript{2}]\textsuperscript{3-} in aqueous alkaline medium, a conclusion also supported by literature\textsuperscript{12}. The reaction between DPC and sulphanilic acid in alkaline medium has the stoichiometry 4:1 with a first order dependence on DPC, apparent less than unit order in alkali and sulphanilic acid. Periodate has no effect in on the rate of the reaction. So, deprotonated DPC complex is considered to be the active species of copper(III) complex. Added acrylonitrile monomer undergoes polymerization under inert atmosphere.
indicating the presence of free radical formation in the reaction mixture. In composite equilibrium steps sulphanilic acid binds to deprotonated DPC species to form a complex (C). Then this complex (C) reacts in slow step to form an intermediate free radical species, which undergoes successive reactions with deprotonated DPC in fast steps to yield the products. All the experimental results support the following mechanism.

\[
[Cu ((H_2IO_6)_2 (OH)_2)]^3+ OH^- \rightleftharpoons [Cu (H_2IO_6) (H_2IO_6) (OH)_2]^4- + H_2O
\]

Scheme 1

\[
\begin{align*}
&\text{NH}_2 \quad \text{SO}_3\text{H} \\
&\text{SO}_3\text{H} \quad \text{NH}_2
\end{align*}
\]
The probable structure of the complex is given by

![Chemical Structure](image)

The spectral evidence for the complex (C) formation between oxidant and substrate was obtained from UV-VIS spectra of the oxidant and mixtures of substrate and oxidant. A bathochromic shift of about 6 nm from 238 to 244 nm is observed, and hyperchromicity is also observed at 244 nm. The literature supports the formation of such type of complex. The formation of the complex (C) is also proved kinetically by the non-zero intercept of the plot of $1/k_{obs}$ versus $1/[\text{sulphanilic acid}]$ (Michaelis-Menten) ($r = 0.9937$, $S = 0.013$) (Fig. (V) (iv) (p.173)). The observed modest enthalpy of activation and a relatively low value of the entropy of activation as well as a higher rate constant of the slow step indicate that the oxidation presumably occurs via inner-sphere mechanism. This conclusion is supported by earlier observation. Since Scheme 1 is in accordance with the generally well accepted principle of non-complementary oxidations taking place in sequence of one-electron steps, the reaction between the substrate and oxidant would afford a radical intermediate. A free radical scavenging experiment...
revealed such a possibility. This type of radical intermediate has also been observed in literature\textsuperscript{18}.

The rate law of the reaction can be derived from Scheme 1 as below.

\[
\text{Rate} = -\frac{d[DPC]}{dt} = k [C] \quad (5)
\]

But from the second step of Scheme 1 we have,

\[
[C] = K_4 [SA] [Cu (H_3IO_6) (H_3IO_6) (OH)_{2f}]^+ \quad (6)
\]

Substituting the value of \(C\) in equation (5), we get

\[
\text{Rate} = k K_4 [SA] [Cu (H_3IO_6) (H_3IO_6) (OH)_{2f}]^+ \quad (7)
\]

From the first step of Scheme 1,

\[
[Cu (H_3IO_6) (H_3IO_6) (OH)_{2f}]^+ = K_4 [DPC]_r [OH^-]_r \quad (8)
\]

Substituting the equation (8) in the equation (7) we get,

\[
\text{Rate} = k K_4 K_5 [SA]_r [DPC]_r [OH^-]_r \quad (9)
\]

Now, \([DPC]_r = [DPC]_r + [Cu (H_3IO_6) (H_3IO_6) (OH)_{2f}]^+ + [C]\)

\[
= [DPC]_r + K_4 [OH^-]_r [DPC]_r + K_5 [SA] [C]
\]

\[
= [DPC]_r + K_4 [OH^-]_r [DPC]_r + K_4 K_5 [SA] [OH^-]_r [DPC]_r
\]
\[
[DPC]_f = \frac{[DPC]_t}{1 + K_4 [OH^-] + K_4 K_5 [SA] [OH^-]}
\]

Where 't' and 'f' stands for total and free,

\[
[OH^-]_t = [OH^-]_f + [A] + [C] = [OH^-]_f + K_4 [OH^-]_f [DPC] + K_5 [SA] [A] = [OH^-]_f + K_4 [OH^-]_f [DPC] + K_4 K_5 [SA] [OH^-]_f [DPC]_f
\]

Therefore,

\[
[OH^-]_f = \frac{[OH^-]_t}{1 + K_4 [DPC] + K_4 K_5 [SA] [DPC]}
\]

Similarly,

\[
[SA]_t = [SA]_f + [C] = [SA]_f + K_4 [SA] [A] = [SA]_f + K_4 K_5 [OH^-] [DPC] [SA]_f
\]

Therefore,

\[
[SA]_f = \frac{[SA]_t}{1 + K_4 K_5 [OH^-] [DPC]}
\]
Substituting the values of equation (10), (11) and (12) in equation (9) and omitting subscripts t and f, we get,

\[
- \frac{d[DPC]}{dt} = \frac{k K_4 K_5 [SA][DPC][OH']}{{(1 + K_4 K_5 [OH'][DPC])} \{1 + K_4[DPC] + K_4 K_5[SA][DPC]\} \times \{1 + K_4[OH'] + K_4 K_5[SA][OH']\}}
\]

The terms such as \((1+K_4 K_5[DPC][OH'])\) and \((1+ K_4[DPC] + K_4 K_5[SA][DPC])\) in the denominator of equation (13) approximate to unity in view of low concentration of DPC used in the experiment. Therefore equation (13) becomes equation (14)

\[
Rate = \frac{d[DPC]}{dt} = \frac{k K_4 K_5 [SA][DPC][OH']}{{1 + K_4[OH'] + K_4 K_5[SA][OH']}}
\]

or

\[
Rate \frac{[DPC]}{[DPC]} = k_{obs} = \frac{k K_4 K_5 [SA][OH']}{{1 + K_4[OH'] + K_4 K_5[SA][OH']}}
\]

Thus, equation (14) can be rearranged to the following form, which is used for the verification.

\[
\frac{1}{k_{obs}} = \frac{1}{k K_4 K_5 [SA][OH']} + \frac{1}{k K_5 [SA]} + \frac{1}{k}
\]

According to equation (15), other conditions being constant, the plots of \(1/k_{obs}\) versus \(1/[SA]\) \((r = 0.9937, S = 0.013)\), \(1/k_{obs}\) versus \(1/[OH']\) \((r = 0.9975, S = 0.012)\) should be linear (Fig.V (iv) (p.173)). From the slopes and intercepts, the values of \(K_4\), \(K_5\) and \(k\) could be derived as \(9.4 \pm 0.5\), \(1082 \pm 50\) mol dm\(^{-3}\) and 171.
1.34 ± 0.10 x 10^2 s^{-1} respectively. Using these constants, the rate constants were calculated over different experimental conditions and there is a reasonable agreement between the calculated and experimental values Table V (iii) (p.157); (iv) (p.159), which fortifies the proposed mechanism.

The moderate values of ΔH^* and ΔS^* were both favorable for electron transfer processes. The negative value of ΔS^* indicates that the complex(C) is more ordered than the reactants^{19}.

**Importance of Chapter V**

Among various species of DPC in alkaline medium, deprotonated DPC is considered as the active species for the title reaction. It becomes apparent that in carrying out this reaction, the role of pH in the reaction medium is crucial. The rate constant of the slow step and other equilibrium constants involved in the mechanism evaluated and activation parameters with respect to the slow step of the reaction were computed. The overall mechanistic sequence described here is consistent with product and kinetic studies.
Figure V (iv)

Verification of rate law (14) in the form of (15)

(Conditions as in Table V (iii) (p.157) and Table V (iv) (p.159))
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