CHAPTER IV

RESULTS AND DISCUSSION

Section 1

Results of Vanadium(v) oxidation of acetophenones.

Table 1

Rate dependence on acetophenone concentration.

\[ 10^3 [V(v)] = 4.72 \text{ M}, \quad [\text{HClO}_4] = 0.90 \text{ M}, \quad \text{HOAc}:\text{H}_2\text{O} = 85:15(\text{v/v}) \]

Temperature = 40°C

\[
\begin{array}{|c|c|c|c|c|c|}
\hline
[\text{acetophenone}] \text{ in M} & 0.1 & 0.2 & 0.3 & 0.4 & 0.45 & 0.5 \\
\hline
k \times 10^5 \text{ in Sec}^{-1} & 0.732 & 1.793 & 2.60 & 3.05 & 3.22 & 4.21 \\
\hline
\end{array}
\]

\[
\begin{array}{|c|c|c|c|c|}
\hline
\frac{k \times 10^5}{[\text{ketone}]} & 7.32 & 3.94 & 8.6 & 7.6 & 7.15 & 8.40 \\
\hline
\end{array}
\]

Table 2

Rate dependence on \([V(v)]\)

\[ [\text{Acetophenone}] = 0.5 \text{ M}, \quad [\text{HClO}_4] = 0.90 \text{ M}, \quad \text{HOAc}:\text{H}_2\text{O} = 85:15(\text{v/v}) \]

Temperature = 40°C

\[
\begin{array}{|c|c|c|c|c|}
\hline
10^3 [V(v)] \text{ in M} & 14.25 & 9.25 & 7.25 & 4.22 \\
\hline
k \times 10^5 \text{ in Sec}^{-1} & 3.31 & 3.42 & 3.36 & 4.21 \\
\hline
\end{array}
\]
Table - 3
Rate dependence on $[\text{HClO}_4]$  
$10^3 [v(v)] = 47.5 \text{ M}, [\text{Acetophenone}] = 0.5 \text{ M}, \text{HOAc:H}_2\text{O} = 75:25(v/v)$  
Temperature $= 40^\circ\text{C}$

<table>
<thead>
<tr>
<th>$[\text{HClO}_4]$ in M</th>
<th>0.45</th>
<th>0.75</th>
<th>0.90</th>
<th>1.16</th>
<th>1.20</th>
<th>1.50</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k \times 10^5$ in Sec$^{-1}$</td>
<td>1.05</td>
<td>1.37</td>
<td>1.65</td>
<td>2.12</td>
<td>2.73</td>
<td>4.62</td>
</tr>
</tbody>
</table>

Table - 4
Rate dependence on $[\text{ClO}_4^-]$ with $[\text{HClO}_4]$ constant.  
$[\text{Acetophenone}] = 0.5 \text{ M}, 10^3 [v(v)] = 47.5 \text{ M}, [\text{HClO}_4] = 0.9 \text{ M}, \text{HOAc:H}_2\text{O} = 75:25(v/v)$, Temperature $= 40^\circ\text{C}$

<table>
<thead>
<tr>
<th>$[\text{ClO}_4^-]$ in M</th>
<th>0.9</th>
<th>1.05</th>
<th>1.2</th>
<th>1.35</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k \times 10^5$ in Sec$^{-1}$</td>
<td>1.65</td>
<td>1.5</td>
<td>1.6</td>
<td>1.62</td>
</tr>
</tbody>
</table>

Table - 5
Rate dependence on $[\text{HClO}_4]$ keeping $[\text{ClO}_4^-]$ constant.  
$[\text{Acetophenone}] = 0.5 \text{ M}, 10^3 [v(v)] = 47.5 \text{ M}, [\text{ClO}_4^-] = 1.5 \text{ M}, \text{HOAc:H}_2\text{O} = 75:25(v/v)$, Temperature $= 40^\circ\text{C}$

<table>
<thead>
<tr>
<th>$[\text{HClO}_4]$ in M</th>
<th>0.90</th>
<th>1.05</th>
<th>1.20</th>
<th>1.35</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k \times 10^5$ in Sec$^{-1}$</td>
<td>1.32</td>
<td>2.32</td>
<td>3.41</td>
<td>4.05</td>
</tr>
</tbody>
</table>
### Table 6
Rate dependence on solvent composition.

\[
\text{[Acetophenone]} = 0.5 \text{ M}, \; 10^3 [V(v)] = 47.5 \text{ M}, \; [\text{HClO}_4] = 1.25 \text{ M}, \\
\text{Temperature} = 40^\circ\text{C}
\]

<table>
<thead>
<tr>
<th>% H\text{OAc}</th>
<th>65</th>
<th>70</th>
<th>75</th>
<th>80</th>
<th>82.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k \times 10^5) in Sec(^{-1})</td>
<td>1.98</td>
<td>2.37</td>
<td>3.59</td>
<td>5.04</td>
<td>7.06</td>
</tr>
<tr>
<td>(\frac{10^3}{D})</td>
<td>33.5</td>
<td>37.5</td>
<td>41.0</td>
<td>45.0</td>
<td>47.5</td>
</tr>
</tbody>
</table>

### Table 7
Values of rate data, energy of activation and entropy of activation for the V(v) oxidation of substituted acetophenones.

\[
\text{[Ketone]} = 0.3 \text{ M}, \; 10^3 [V(v)] = 43.5 \text{ M}, \; [\text{HClO}_4] = 1.5 \text{ M}, \\
\text{H\text{OAc}:H}_2\text{O} = 75:25 (v/v)
\]

<table>
<thead>
<tr>
<th>Nature of substituent</th>
<th>(k \times 10^5) in Conc(^{-1}) Sec(^{-1})</th>
<th>E in Kcals per mole</th>
<th>(-\Delta S^\circ) in e.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(35^\circ\text{C})</td>
<td>(40^\circ\text{C})</td>
<td>(45^\circ\text{C})</td>
</tr>
<tr>
<td>H</td>
<td>-</td>
<td>8.33</td>
<td>11.36</td>
</tr>
<tr>
<td>p-OMe</td>
<td>2.05</td>
<td>7.20</td>
<td>9.93</td>
</tr>
<tr>
<td>p-Cl</td>
<td>-</td>
<td>10.03</td>
<td>12.91</td>
</tr>
<tr>
<td>p-NO(_2)</td>
<td>-</td>
<td>10.1</td>
<td>14.1</td>
</tr>
</tbody>
</table>
DISCUSSION ON VANADIUM(V) OXIDATION OF ACETOPHENONE

The vanadium(v) oxidation of acetophenone has been studied in perchloric acid medium. The concentration of ketone used is always in large excess. The reaction did not proceed at all at higher concentration of V(v) and hence no stoichiometry could be determined.

The oxidation has been found to be first order with respect to $[V(v)]$ and also to the $[\text{Ketone}]$ (Fig.1). The ratio of the first order rate constant and the concentration of ketone is constant (Table-1). Plot of $1/k$ vs. $\frac{1}{[\text{Ketone}]}$ has been prepared (Fig.2) in order to see the possibility of kinetically discernible complexation. No intercept has been obtained. The oxidation has also been studied at various $[\text{HClO}_4]$ and the results are incorporated in table 3. The values of $k/ [\text{HClO}_4]$ are constant and so the reaction is also first order with respect to perchloric acid concentration.

At a fixed $[\text{HClO}_4]$, perchlorate ion concentration was varied by addition of sodium perchlorate and the rate constant was found to be unaltered (Table-4). So V(v) oxidation of acetophenone is unaffected by ionic strength effect. Cristol and coworkers have also not observed any effect of sodium perchlorate in perchloric acid catalysed reactions. However, at a fixed $[\text{ClO}_4^-]$ of 1.5 M there was a slight enhancement in rate when $[\text{HClO}_4]$ was varied (Table-5).
The rate expression for vanadium(v) oxidation of acetophenone, therefore, may be written as: rate = 
\[ k_3 \left[ \text{ketone} \right] \left[ V(v) \right] \left[ \text{HClO}_4 \right] \] . Vanadium(v) in aqueous perchloric media has been described as \( \text{VO}_2^+ \) (aq) and \( \text{V(OH)}_4^+ \). In perchloric acid solution the following equilibria (\( K_1 \) and \( K_2 \)) exist.

\[
\text{VO}_2^+ + 2\text{H}^+ \rightleftharpoons \text{V(OH)}_2^+^3 \quad \text{\( K_1 \)}
\]

\[
\text{V(OH)}_4^+ + \text{H}^+ \rightleftharpoons \left[ \text{V(OH)}_3 \right]^{++} \quad \text{\( K_2 \)}
\]

Since the rate increases with increasing acidity, the species \( \left[ \text{V(OH)}_2 \right]^{+3} \) and \( \left[ \text{V(OH)}_3 \right]^{++} \) may be important in the oxidation of acetophenones.

Further the oxidation has been studied at different acetic acid-water mixtures. Increase in acetic acid concentration increases the rate of reaction (Table-6). The increased rate in higher concentration of acetic acid may be explained as due to the formation of a stronger electrophile by replacing hydroxyl hydrogen by an acetyl group, which would then further decrease the electron density on the central vanadium ion. The possibility of the formation of such acetyl group containing oxidising species in acetic acid medium and its nature as a powerful oxidising agent has also been indicated in case of chromic acid oxidation of organic compounds. Moreover the pioneering work of Kolthoff and co-workers show that acids like HClO\(_4\) is stronger in HOAc than in water, although they are only
slightly dissociated into free ions in HOAc. So all these effects may have a cumulative effect in increasing the rate of oxidation. A plot of log $k$ vs. $1/D$ (Fig. 3) in accordance to the Amis equation,$^{47}$ has been prepared and a straight line has been obtained, with a slope of 35.4 for $Ze\mu/2.303kT^2$, where the terms have their usual significance. The value of $'r'$ has been computed to be 4.38 to 5.36 Å considering bi and tri positive vanadium ion as the oxidising species. This value of $'r'$ has a reasonable magnitude.

The oxidation has also been studied with substituted acetophenones. The order of reactivity of the substituents is $p$-$NO_2 > p$-$Cl > H > p$-$OEt$. This order of reactivity has been observed in most of the vanadium(v) and cerium(iv) oxidation of aromatic ketones containing Ar-CO group. The energy and entropy of activation values have been calculated (Table-7). The values of $\Delta S^\ddagger$ are highly negative. Since the oxidation takes place by transfer of electrons from the substrate to the oxidant, this high negative $\Delta S^\ddagger$ value may be due to curtailment of vibrational and rotational degrees of freedom and freezing of solvent molecules.$^{48}$ A straight line plot of log $k$ vs. log $[HClO_4]$ indicates participation of water molecules in the oxidation. Approximately a loss of 2.2 eu can be accounted for by arresting the translational degrees of freedom of a molecule of water. In the reaction a loss of 10 to 20 eu has been indicated. Therefore 4 to 8 molecules of water are frozen around the transition state. The validity of this assumption is due to the fact that the oxidation
proceeds by an outer sphere process and possibly ClO^ acts as an electron transport agent.

The rate data show that the energy of activation values are in reverse order to the reactivity. The plot of \( \Delta H^\ddagger \) vs. \( \Delta S^\ddagger \) gives a straight line (Fig. 4) with 'b' value of 630°K. The oxidation, therefore, is both energy and entropy controlled obeying Leffler's compensation law, supporting the validity of a straight line Hammett plot with a rho value of +0.12 at 50°C.

The product analysis shows the formation of benzoic acid or substituted benzoic acids. No experimental evidence has been adduced for the formation of a transient free radical, since polymerisation of acrylonitrile or reduction of mercuric chloride was not affected. Sengupta et al. have also made a similar observation.

On the basis of informations gained in the present investigation, the following scheme may be proposed as the most probable mechanism for the V(v) oxidation of acetophenones.

\[
\begin{align*}
\text{C}_6\text{H}_5\text{-C} = \text{O} & \overset{V(v)}{\longrightarrow} \text{C}_6\text{H}_5\text{-C} = \text{O}^+ \\
\text{C}_6\text{H}_5\text{-C} = \text{O}^+ & \overset{\text{slow}}{\longrightarrow} \text{C}_6\text{H}_5\text{-C} = \text{O}^+ + \text{CH}_3 \\
\text{C}_6\text{H}_5\text{-C} = \text{O}^+ & \overset{\text{H}_2\text{O}}{\longrightarrow} \text{C}_6\text{H}_5\text{COOH} \\
\text{CH}_3 + \text{H}_2\text{O} & \overset{V(v)}{\longrightarrow} \text{CH}_3\text{OH} + \text{H}^+
\end{align*}
\]

Evidence for the methyl free radical has been furnished from photolysis of acetophenone and decarboxylation of acetate free radical. This free radical does not have a sufficient lifetime to react with added acrylonitrile or HgCl₂.
Section - 3

Results of Vanadium oxidation of phenacyl bromides.

Table - 1
Rate dependence on V(v) concentration.

\[ 10^3 [\text{PhBr}] = 45.0 \text{ M}, \ [\text{H}_2\text{SO}_4] = 4.0 \text{ M}, \text{ HOAc:H}_2\text{O} = 50:50(v/v) \]

Temperature = 40°C

<table>
<thead>
<tr>
<th>[10^3 [V(v)]]</th>
<th>34.5</th>
<th>28.75</th>
<th>23.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k \times 10^4) in min(^{-1})</td>
<td>25.02</td>
<td>26.65</td>
<td>24.32</td>
</tr>
</tbody>
</table>

Table - 2
Rate dependence on [Phenacyl bromide]

\[ 10^3 [V(v)] = 18.25 \text{ M}, \ [\text{H}_2\text{SO}_4] = 2.5 \text{ M}, \text{ HOAc:H}_2\text{O} = 50:50(v/v) \]

Temperature = 40°C

<table>
<thead>
<tr>
<th>[10^3 [\text{PhBr}]]</th>
<th>31.25</th>
<th>50</th>
<th>75</th>
<th>93.75</th>
<th>125.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10^4 x k) in min(^{-1})</td>
<td>8.06</td>
<td>9.82</td>
<td>14.34</td>
<td>16.12</td>
<td>25.19</td>
</tr>
<tr>
<td>(10^4 x k) in min(^{-1})</td>
<td>2.57</td>
<td>1.96</td>
<td>1.97</td>
<td>1.72</td>
<td>2.01</td>
</tr>
</tbody>
</table>

\[ \text{PhBr} \text{ in M} \]
### Table 3

Rate dependence on $[\text{H}_2\text{SO}_4]$  

$10^3[V(v)] = 13.83$ M, $10^3[\text{PhBr}] = 125.0$ M, H\text{OAc}:H\text{O} = 50:50 (v/v)  

Temperature = 40°C  

<table>
<thead>
<tr>
<th>$[\text{H}_2\text{SO}_4]$ in M</th>
<th>4.5</th>
<th>4.0</th>
<th>3.5</th>
<th>2.5</th>
<th>2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k \times 10^4$ in min$^{-1}$</td>
<td>106.4</td>
<td>70.63</td>
<td>56.80</td>
<td>26.82</td>
<td>16.12</td>
</tr>
</tbody>
</table>

### Table 4

Rate dependence on $[\text{HClO}_4]$ and $[\text{PhBr}]$ at different temperatures  

$10^3[V(v)] = 31.75$ M, H\text{OAc}:H\text{O} = 50:50 (v/v)  

<table>
<thead>
<tr>
<th>$10^3[\text{PhBr}]$ in M</th>
<th>125.0</th>
<th>93.7</th>
<th>62.5</th>
<th>106.25</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp.</td>
<td>$[\text{HClO}_4]$ in M</td>
<td>2.2</td>
<td>3.0</td>
<td>3.4</td>
</tr>
<tr>
<td>40°C</td>
<td>$k \times 10^3$ in min$^{-1}$</td>
<td>14.30</td>
<td>28.66</td>
<td>31.01</td>
</tr>
<tr>
<td>40°C</td>
<td></td>
<td>11.85</td>
<td>23.66</td>
<td>24.95</td>
</tr>
<tr>
<td>40°C</td>
<td></td>
<td>8.81</td>
<td>24.95</td>
<td>34.43</td>
</tr>
<tr>
<td>45°C</td>
<td></td>
<td>13.20</td>
<td>34.43</td>
<td>47.74</td>
</tr>
</tbody>
</table>

### Table 5

Rate dependence on solvent composition.  

$10^3[V(v)] = 32.25$ M, $10^3[\text{PhBr}] = 62.5$ M, $[\text{H}_2\text{SO}_4] = 2.0$ M  

<table>
<thead>
<tr>
<th>% \text{HOAc}</th>
<th>70</th>
<th>65</th>
<th>60</th>
<th>50</th>
<th>45</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^4 \times k$ in min$^{-1}$</td>
<td>20.01</td>
<td>15.5</td>
<td>12.49</td>
<td>3.1</td>
<td>5.83</td>
<td>4.05</td>
</tr>
<tr>
<td>$10^3/D$</td>
<td>37.5</td>
<td>33.5</td>
<td>31.7</td>
<td>26.04</td>
<td>24.10</td>
<td>22.38</td>
</tr>
</tbody>
</table>
Table - 6

Rate dependence on p-NO₂PhBr concentration at different Temp.

\[10^3 [\text{V(v)}] = 6.0 \text{ M}, [\text{HClO}_4] = 3.0 \text{ M}, \text{H}^+\text{Ac}:\text{H}_2\text{O} = 50:50(\text{v/v})\]

<table>
<thead>
<tr>
<th>(10^3 [\text{p-NO}_2\text{PhBr}] \text{ in M} )</th>
<th>30.0</th>
<th>25.0</th>
<th>20.0</th>
<th>15.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature in °C</td>
<td>k x 10⁵ in Sec⁻¹</td>
<td>3.38</td>
<td>2.73</td>
<td>2.33</td>
</tr>
<tr>
<td>35</td>
<td></td>
<td>4.06</td>
<td>3.57</td>
<td>3.00</td>
</tr>
<tr>
<td>40</td>
<td></td>
<td>6.00</td>
<td>5.61</td>
<td>4.17</td>
</tr>
</tbody>
</table>

Table - 7

Values of the equilibrium constant for the complex formation and its rate of decomposition at various acidities and temperature for phenacyl bromide and p-nitro phenacyl bromides and the thermodynamic parameters for equilibrium and activation.

<table>
<thead>
<tr>
<th>Nature of substituent</th>
<th>[\text{HClO}_4] in M</th>
<th>(K\text{ in Conc}^{-1})</th>
<th>(\Delta\text{H in Kcal per e.u.})</th>
<th>(\Delta\text{S in Kcal per e.u.})</th>
<th>(10^3 k\text{ in min}^{-1})</th>
<th>(\Delta\text{G}^\circ\text{ in Kcal per mole})</th>
<th>(\Delta\text{F}^\circ\text{ in Kcal per mole})</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>2.2</td>
<td>5.6</td>
<td>-13.4</td>
<td>-55.4</td>
<td>3.3</td>
<td>-20.0</td>
<td>65.0</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>9.2</td>
<td>4.5</td>
<td>3.7</td>
<td>10.0</td>
<td>20.0</td>
<td>65.0 19.0</td>
</tr>
<tr>
<td></td>
<td>3.4</td>
<td>2.3</td>
<td>-14.7</td>
<td>-23.6</td>
<td>4.1</td>
<td>13.2</td>
<td>23.0 24.8</td>
</tr>
<tr>
<td>p-NO₂</td>
<td>3.0</td>
<td>25.4</td>
<td>16.6</td>
<td>11.5</td>
<td>-14.7</td>
<td>-23.6</td>
<td>7.3 13.2 22.0 21.6</td>
</tr>
</tbody>
</table>

- 32 -
Phenacyl bromide consumed two equivalent of V(v) in 3.0 M HClO₄ at 35°C and the reaction can be represented stoichiometrically by the following equation:

\[ \text{C}_6\text{H}_5\text{COCH}_2\text{Br} + 2\text{V}(v) \rightarrow \text{C}_6\text{H}_5\text{COOH} + \text{CH}_2\text{O} + \text{Br}^- + 2\text{V}(iv) \]...

The rates were studied at constant substrate concentration and varying \([\text{V}(v)]\) (Table-1). The first order rate constants were found to be the same (Fig.1). The rates were studied at constant \([\text{V}(v)]\) and [acid] but varying substrate concentration. The rates increased with increase in the concentration of the substrate (Table-2). A plot of \(1/k_1\) against \(1/|\text{PhBr}|\) did not pass through the origin (Fig.2).

The first order rate equation, \(t = \frac{2.303}{k_1} \log \frac{a}{(a-x)}\) was used to evaluate the rate constants \((k_1)\), where \(a = \) initial concentration of the \(\text{V}(v)\), \((a-x) = \) concentration of the \(\text{V}(v)\) after a lapse of time \(t\). Duplicate experiments were reproducible to within \(\pm 3\%\). The energy of activation was calculated from the slope of the plot of \(\log k_2\) against \(1/T\). The heat, entropy and free energy of activation were then evaluated.

The acid dependence of the reaction rates were studied at a series of runs at different acid concentrations and different substrate concentration (Table-3 & 4). These results suggest that the values of \(k_1\) increases with increasing \([\text{HClO}_4]\) and \([\text{H}_2\text{SO}_4]\). A plot of \(\log k\) vs. \(\log [\text{Acid}]\) was found to be
straight line for both perchloric and sulphuric acid (Fig.5) obeying the equation \( \log k = 0.17 \times 10^{-4} - 3 \log [\text{HClO}_4] \) and \( \log k = 0.66 \times 10^{-4} - 2 \log [\text{H}_2\text{SO}_4] \). A plot of rate constant vs. \([\text{Acid}]^2\) or \(3\) gave a straight line but did not pass through the origin indicating complexation of the oxidant with acid, when the actual concentration of the acid is less than actually taken. A linear log-log plot, however, suggests participation of a molecule of water.

Rate constants and reciprocals of dielectric constants \(D\) are recorded in table-5. Dielectric constants of acetic acid-water mixture are of Radhakrishna Murty and Pati. Plots of \(\log k_2\) against \(1/D\) gave a straight line with a slope of +45.0, (Fig.3). Therefore, the oxidation is between an ion and a dipole. The positive ions may be designated as \(\text{[V(OH)HSO}_4]^+\), \(\text{[V(OH)HSO}_4]^++\), \(\text{[V(OH)_2HSO}_4]^+\) as suggested by Littler and Waters. Vanadium(\(v\)) in acetic acid aqueous media has been described as \(\text{V}^{2+}\) and \(\text{V(OH)}^{2+}\). The following equilibria have been suggested in perchloric and sulphuric acid medium.

\[
2. \quad \text{V}^{2+} + 2\text{H}^+ \rightleftharpoons \text{[V(OH)]}_2^{+3} \quad \ldots K_1
\]

\[
3'. \quad \text{V}^{2+} + \text{H}_3\text{O}^+ \rightleftharpoons \text{[V(OH)H]}_3^{++} \quad \ldots K_2
\]

\[
4. \quad \text{[V(OH)]}_2^{+3} + \text{HSO}_4^- \rightleftharpoons \text{[V(OH)HSO}_4^+]^{++} \quad \ldots K_3
\]

\[
5. \quad \text{[V(OH)]}_3^{++} + \text{HSO}_4^- \rightleftharpoons \text{[V(OH)HHSO}_4^+]^+ \quad \ldots K_4
\]

The equilibria 2 and 3 occur in perchloric acid and 4 and 5 in sulphuric acid. At lower acidities, the rate constants for perchloric acid and sulphuric acid are almost same.
but at higher acidities the rate constants in HClO₄ are more than the sulphuric acid.

Since a plot of $k_{obv}^{-1}$ vs. $[\text{Br}^{-}]$, did not pass through the origin, the values of equilibrium constants (K), the rate of decomposition of the complex ($k_2$) were determined at various temperatures and acidities. The values are given in table-7.

The decrease in free energy of formation of the complex was calculated from the relationship $-\Delta G = -RT\ln K$. The enthalpy change $\Delta H$ associated with the equilibrium constant $K$ was calculated from the slope of the plot (Fig.6) of log $K$ against 1/T, which was used to evaluate the entropy change from the relation $\Delta G = \Delta H - T\Delta S$. The thermodynamic parameters are presented in table-7.

Similarly from the values of $k_2$ at various temperatures, the energy and entropy of activation values of the decomposition process of the complex were determined and given in table-7.

The values of rate constants at different substrate concentration have been determined for p-nitro phenacyl bromide (Table-6). With this compound also there is kinetic evidence of complexation. The thermodynamic parameters of the formation and the activation parameters of its decomposition are determined (Table-7). The rate of the reaction is found to be almost 2.5 to 3 times faster with p-NO₂ compound in comparison to its unsubstituted product. The values of energy of activation are also in accordance with reactivity.
The values of $\Delta^\dagger$ are negative indicating a rigid transition state.

Vanadium(v) is an one electron exidant and so produces free radicals out of the substrate and gets converted to V(iv). The formation of free radical is not indicated in the present context since no polymerisation with acrylonitrile or no reduction of mercuric chloride was observed. Therefore the reaction is believed to proceed through an ionic intermediate and V(v) probably acts as a two electron oxidant according to the following scheme (eqn.6) in perchloric acid. This observation has also been made by Sengupta and his coworkers.\(^5\)

$$V(v) + 2e \rightarrow V(iii), V(iii) + V(v) \rightarrow 2V(iv) \quad \text{(6)}$$

Therefore, two molecules of vanadium(v) will be absorbed per mole of the substrate, which has been found to be the case. The order of oxidation with respect to [acid] is ca 2.0 for sulphuric acid but ca 3.0 for perchloric acid. Therefore, in sulphuric acid, probably $[V(OH)_2]^3+$ and $[V(OH)_2HSO_4]^{++}$ are active species, where in perchloric acid both $[V(OH)_2]^3+$ and $[V(OH)_3]^{++}$ are active.

The values of equilibrium constant and the rate of decomposition of the complex suggests that the complex has a rigid structure and is formed by an exothermic process. The decomposition rate of the complex, however, is faster for phenacyl bromide than for p-nitro, although the reverse was the case for the composite rate constant. The complex formation, however, is facilitated by nitro substituent. From these considerations and from the fact that a molecule
of water participates in the transition state, the following mechanism can be suggested for the oxidation. Vanadium(v) forms octahedral complexes and there is a weak dipole-dipole type of interaction between the metal ion and water molecules. Therefore the complexation will occur by replacement of water molecule.

\[
\text{C}_6\text{H}_5\text{COCH}_2\text{Br} + [\text{V(OH)}_3(\text{H}_2\text{O})_3]^{++} \xrightarrow{K} \text{C}_6\text{H}_5\text{C}=\text{O} + \text{CH}_2\text{Br} + \text{V}^{\text{iii}} ; \text{CH}_2 = \text{Br} + \text{H}_2\text{O} \xrightarrow{k_2} \text{CH}_2\text{Br} \quad \text{...(2)}
\]

\[
\text{V}^{\text{iii}} + \text{V}^{(v)} \xrightarrow{\text{fast}} 2\text{V}^{(iv)} \quad \text{...(3)}
\]

\[
\text{CH}_2 = \text{Br} + \text{H}_2\text{O} \xrightarrow{\text{fast}} \text{CH}_2\text{O} + \text{Br}^- + 2\text{H}^+ \quad \text{...(4)}
\]

The transition state can be represented as,
The mechanism appears to be similar to V(v) oxidation of pinacols, which also proceed through C-C bond cleavage, but by a free radical pathway.

The oxidation does not appear to proceed through enol intermediate because (i) the substituent effect is opposite to the acid catalysed enolisation (halogenation), (ii) the equilibrium constant values for the formation of the complex is more with p-nitro than with the unsubstituted compound.
Section - 5

RESULTS OF VANADIUM OXIDATION OF CHALKONES.

Table - 1
Rate dependence on Chalkone concentration.

\[ \text{Rate dependence on Chalkone concentration.} \]

\[ 10^2 \left[ \text{V(v)} \right] = 1 \text{ M}, \ [\text{HClO}_4] = 3 \text{ M}, \ \text{HOAc}:\text{H}_2\text{O} = 68.3:31.7(v/v) \]

\[ \text{Temperature} = 35^\circ\text{C} \]

\[
\begin{array}{cccc}
10^2 [\text{chalkone}] \text{ in M} & 4.00 & 5.00 & 6.00 & 7.50 \\
k_1 \times 10^5 \text{ in Sec}^{-1} & 11.04 & 14.01 & 17.55 & 19.99 \\
\frac{k_1 \times 10^5}{[\text{chalkone}] \times 10^5} & 2.76 & 2.8 & 2.93 & 2.66 \\
\end{array}
\]

Table - 2
Rate dependence on \( \left[ \text{V(v)} \right] \)

\[ 10^2 [\text{chalkone}] = 5 \text{ M}, \ [\text{HClO}_4] = 3 \text{ M}, \ \text{HOAc}:\text{H}_2\text{O} = 68.3:31.7(v/v) \]

\[ \text{Temperature} = 35^\circ\text{C} \]

\[
\begin{array}{ccc}
10^2 \left[ \text{V(v)} \right] \text{ in M} & 1.0 & 2.0 & 2.5 \\
k_1 \times 10^5 \text{ in Sec}^{-1} & 2.83 & 2.69 & 3.20 \\
\end{array}
\]

Table - 3
Rate dependence on \([\text{HClO}_4]\)

\[ 10^2 [\text{chalkone}] = 7.5 \text{ M}, \ 10^2 \left[ \text{V(v)} \right] = 1 \text{ M}, \ \text{HOAc}:\text{H}_2\text{O} = 55.1:44.9(v/v) \]

\[ \text{Temperature} = 35^\circ\text{C} \]

\[
\begin{array}{cccc}
[\text{HClO}_4] \text{ in M} & 4.0 & 3.0 & 2.5 & 2.0 \\
k_1 \times 10^5 \text{ in Sec}^{-1} & 54.69 & 19.99 & 3.31 & 0.767 \\
\end{array}
\]
Table - 4
Rate dependence on solvent composition.

\(10^2 [\text{chalcone}] = 5 \text{ M}, \quad [\text{V} (\text{v})] \times 10^2 = 1.5 \text{ M}, \quad [\text{HClO}_4] = 3 \text{ M}\),

Temperature = 35°C

<table>
<thead>
<tr>
<th>% of HOAc</th>
<th>55.8</th>
<th>58.3</th>
<th>60.8</th>
<th>63.3</th>
<th>68.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_1 \times 10^5) in (\text{Sec}^{-1})</td>
<td>0.576</td>
<td>0.763</td>
<td>0.96</td>
<td>1.27</td>
<td>2.5</td>
</tr>
<tr>
<td>(10^3 / D)</td>
<td>28.5</td>
<td>30.0</td>
<td>31.2</td>
<td>32.5</td>
<td>36.3</td>
</tr>
</tbody>
</table>

Table - 5
Rate constants for substituted chalcones.

\(10^3 [\text{chalcone}] = 25 \text{ M}, \quad [\text{V} (\text{v})] \times 10^3 = 5 \text{ M}, \quad [\text{HClO}_4] = 3 \text{ M}\),

\(\text{HOAc:H}_2\text{O} = 68.3:31.7(v/v)\)

<table>
<thead>
<tr>
<th>Substituents</th>
<th>(k \times 10^3) Conc(^{-1}) Sec(^{-1}) at 30°C</th>
<th>E in K.cals per mole</th>
<th>(-\Delta S_{35^\circ C}) in e.u.</th>
<th>(\Delta F^\ddagger) in K.cals per mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-Cl</td>
<td>1.92</td>
<td>3.26</td>
<td>3.84</td>
<td>5.76</td>
</tr>
<tr>
<td>p-Cl</td>
<td>2.86</td>
<td>4.45</td>
<td>8.06</td>
<td>14.56</td>
</tr>
<tr>
<td>0-OMe*</td>
<td>7.08</td>
<td>9.52</td>
<td>-</td>
<td>15.65</td>
</tr>
<tr>
<td>H</td>
<td>- 4.09</td>
<td>6.39</td>
<td>10.7</td>
<td>19.16</td>
</tr>
<tr>
<td>0-NO(_2)</td>
<td>9.21</td>
<td>12.23</td>
<td>17.27</td>
<td>57.56</td>
</tr>
<tr>
<td>p-NO(_2)</td>
<td>23.2</td>
<td>31.62</td>
<td>37.46</td>
<td>-</td>
</tr>
<tr>
<td>p'-Cl</td>
<td>- 3.07</td>
<td>4.50</td>
<td>6.14</td>
<td>13.62</td>
</tr>
<tr>
<td>p'-OMe</td>
<td>- 0.39</td>
<td>0.32</td>
<td>0.61</td>
<td>23.95</td>
</tr>
<tr>
<td>p'-NO(_2)</td>
<td>- 0.53</td>
<td>0.86</td>
<td>1.32</td>
<td>15.66</td>
</tr>
</tbody>
</table>

\(\text{*} [\text{HClO}_4] = 2.5 \text{ M}\)

Table - 6
Effect of different cations on the rate.

\(10^3 [\text{cation}] = 4 \text{ M}, \quad [\text{HClO}_4] = 3 \text{ M}, \quad [\text{chalcone}] 10^2 = 5 \text{ M}, \quad [\text{V} (\text{v})] 10^2 = 1 \text{ M}\)

Temperature = 35°C

<table>
<thead>
<tr>
<th>Cation</th>
<th>(\text{Ag}^+)</th>
<th>(\text{Cu}^{2+})</th>
<th>(\text{Hg}^{2+})</th>
<th>(\text{Cd}^{2+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_1 \times 10^5) in (\text{Sec}^{-1})</td>
<td>3.84</td>
<td>1.73</td>
<td>3.07</td>
<td>1.34</td>
</tr>
<tr>
<td>(k \times 10^3) Conc(^{-1}) Sec(^{-1})</td>
<td>0.77</td>
<td>0.35</td>
<td>0.61</td>
<td>0.27</td>
</tr>
</tbody>
</table>
DISCUSSION ON VANADIUM(V) OXIDATION OF CHALKONES.

The vanadium(v) oxidation of chalkones has been studied in acetic acid-water mixture. The concentration of the substrate is always in excess. These reaction types are better studied in excess of the substrate unlike the conditions maintained by Ogata et al.56 who used excess of oxidant. It appears that in the presence of excess of chalcone, all side reactions are suppressed. The oxidation has been found to be first order (Fig.1) with respect to the concentration of chalcone and also to the concentration of vanadium(v). The ratio of the first order rate constant and the concentration of the ketone is constant (Table-1).

The plot (Fig.2) of 1/k vs. 1/[ketone] does not indicate kinetic evidence for the complex formation between chalcone and vanadium(v) as the straight line passes through the origin. The oxidation has also been studied at various [HClO₄] and the results are incorporated in table-3. The values of first order rate constants increase with increasing concentrations of perchloric acid. To know the order of oxidation with respect to [HClO₄], a plot of log k vs. log[HClO₄] has been prepared and a slope of about 3 has been obtained. Therefore, considering perchloric acid concentration to be same as the hydrogen ion concentration at the solvent composition studied, the rate expression for the present oxidation can be formulated as:

\[
\text{Rate} = k \left[\text{chalcone}\right] \left[V(v)\right] \left[H^+\right]^3
\]
**Solvent influence:**

The rate of the reaction has been found to increase with increasing acetic acid content in the solvent mixture (Table-4). The plot of log k vs. 1/D (Fig.3) has been found to be linear with a positive slope. This dependence of rate on the solvent composition have been examined in light of the observations of Hughes and Ingold. They have suggested that the activation energies of ion-molecule reactions should increase and that rates should decrease with increasing ionising power of the medium as a consequence of the charge dispersal in going from the reacting ion to the transition state and the resulting increased difference in solvation energy. The same argument has also been advanced by Kamlet and Glover.

According to Amis, for an ion-dipole reaction involving a positive ionic reactant the rate would decrease with increasing dielectric constant of the medium. Using the Amis equation for a head on approach of an ion to a dipolar molecule, the slope of the line obtained by plotting log k against the reciprocal of the dielectric constant of the medium gives a value for the term in the equation, $\frac{Ze^4}{2.303kT\mu^2}$. The value of 'r' for this reaction has been computed to be 6 or 9 Å depending upon whether the oxidising ion is bipositive or tripositive. This reasonable value for 'r' is consistent with a reaction in which one of the reacting species is a positively charged complex and the other one is a dipole.

The role of solvent in the reaction can not be explained exclusively on the basis of dielectric constants.
Following Hughes and Ingold, with the species indicated there is a greater dispersal of charge in the transition state which is possibly more solvated. A preferential solvation by water can not be excluded. Rabinson and Stokes\textsuperscript{60} clearly state that the bulk dielectric constant is entirely different from the dielectric constant in the region of an ion; this being specifically so in low dielectric media. The studies of Ingold and co-workers\textsuperscript{61} and of Hudson and Brown\textsuperscript{62} pointed out that the solvent-solute interaction is a more probable factor influencing the rate, the dielectric constant becoming only a secondary factor.

Another aspect of the solvent influence is the consideration of the electrophilic and nucleophilic behaviour of the solvent. The life time of the carbonium ion is increased in solvents of nucleophilic type. In acetic acid-water mixture, the greater the proportion of acetic acid, the greater is its nucleophilic behaviour. This oxidation reaction appears to proceed through a carbonium ion intermediate and hence the reaction rate is likely to be favoured in a medium containing large proportion of acetic acid.

The increased rate in higher concentration of acetic acid may be explained as due to the formation of a stronger electrophile by replacing hydroxyl hydrogen by an acetyl group which would then further decrease the electron density on the central vanadium ion. Such acetyl group containing oxidising species in acetic acid medium are known to be powerful oxidising agents\textsuperscript{63}. The present oxidation has been carried out in
presence of perchloric acid. The perchloric acid has been shown to be "stronger" in acetic acid than in water and further perchlorate ion is one in which the degree of 'tightness' is relatively low in acetic acid. Therefore both these effects may simultaneously operate and the rate of oxidation is expected to increase.

Effect of substituents:

The order of reactivity of the different substituents in the benzene ring of the styryl group is: p-NO₂ > o-NO₂ > p-Cl > o-Cl and the benzene ring of the benzoyl group is: p'-Cl > p'-NO₂ > p'-OMe. The rate of oxidation of 4-methoxy compound is so fast that it could not be measured even at very low acidity and acetic acid content. The rate of oxidation of 2-methoxy compound was also fast and hence the acidity has been lowered. This is suggestive of a carbonium ion mechanism. Since both p-NO₂ and p-OMe group increase the rate of oxidation and p-OMe > p-NO₂, it appears that two different mechanisms operate for both the compounds. A free radical mechanism could explain such a substituent effect but a free radical is believed not to be formed due to (a) lack of induced acrylonitrile polymerisation and (b) dependence of rate on dielectric constant. The log k vs. 1/D plot suggests a positive ion-dipole or ion-ion (similar type) type of reaction. The data recorded in table-5 indicates that the substituents in the benzoyl group generally lower the rate of oxidation.

The dipolar nitrogroup is a potential nucleophile but reactions in which it functions as such are rare. The
most clearcut examples are found in reactions of nitrobenzene derivatives which involve intra-molecular oxygen transfer between the nitrogroup and an ortho side chain. Recent interest in this type of neighbouring group interaction has centred on the ability of aromatic nitrogroup to participate in the solvolytic reactions of orthosubstituents. Tenant and Spence have also reported such a participation of the ortho nitro group. The reaction rate due to ortho nitro group is probably enhanced due to this type of internal nucleophilic activity.

Oxidising species:

Although acid independent route in V(v) oxidation has been observed by several workers, no acid independent route is expected in this oxidation as the substrate is a feebly basic one. A plot of log k versus log [HClO₄] intersects the acid axis and hence there is no acid independent route. Vanadium(v) in acidic aqueous solution has been described as VO₂⁺ and [V(OH)₄]⁻¹. In perchloric acid media, the following equilibria exist:

\[
\begin{align*}
    VO_2^+ + 2H^+ & \rightleftharpoons K_1 V(OH)_2^+ \\
    V(OH)_4^+ + H^+ & \rightleftharpoons K_2 V(OH)_3^{++} + H_2O
\end{align*}
\]

Since the rate of oxidation depends on \([H^+]^3\), both the species \([V(OH)_2]^+\) and \([V(OH)_3]^++\) may be considered equally important in the oxidation of chalones.

Effect of cations:

It is interesting to note the effect of cations on the rate of oxidation. Since Ag⁺ is known to form π com-
plexes with olefinic compounds, it was presumed that the rate of oxidation would be lowered down in presence of Ag⁺. This was in fact observed and therefore, the rate of oxidation was also carried with a few transition metal ions. In all cases the rate suppression has been observed. The general picture of rate suppression in case of d⁹ and d¹⁰ metal ions is,

\[
\text{Cu}^{++} > \text{Cd}^{++} > \text{Ag}^+ > \text{Hg}^{+2}
\]

The rate picture with Cd⁺² ion is different from Ag⁺ and Hg⁺² ions although all of them are d¹⁰ ions. Crystallographic studies show that many of the compounds of Ag⁺ and Hg⁺² contain linearly co-ordinated metal ions. For example, in HgCl₂ each Hg⁺² ion is surrounded by two collinear near neighbour chloride ions and four more neighbours at much greater distances. Similarly Ag₂O has a unique crystal structure in which metal ions are linearly co-ordinated and hence it indicates sp covalent bonding. Although Ag⁺ and Hg⁺² ions are known to form sp bonds, Zn⁺⁺ and Cd⁺² ions do not form such bonds. The sp energy separation in Ag⁺ and Hg⁺² ions follow a different stereochemistry than Cd⁺². Cu⁺² also does not form a linear complex like Cd⁺². The divalent Cu⁺² ion having an electronic configuration of \((t_2g)^6 (e_g)^3\) has got an octahedral environment with four short and two long bonds. So possibly chalkone with its \(\Pi\) orbitals, overlaps with the \(d^2\) or \(d_{x^2-y^2}\) orbital, since \((e_g)^3\) configuration is doubly degenerate.

**Mechanism:**

A plot of \(1/k\) versus \(1/[\text{chalkone}]\) does not indicate
the formation of a complex between the substrate and the oxidant. Both nitro and methoxy substituents increase the rate of the reaction. This type of substituent effect can be explained by a free radical pathway or by the carbonium ion mechanism. However, the free radical pathway does not appear to occur since the induced polymerisation of acrylonitrile is absent in this case.

The molecular geometry of chalkone and p-methoxy chalkone has been elucidated by Robinovitch. The molecule as a whole is not planar, the maximum deviation from the mean plane, in p-methoxy chalkone, being 0.2\textdegree. The molecule may be divided into three planar parts, the two benzene rings which are planar to within 0.007\textdegree and the $C = C - C = 0$ bridge with maximum out of plane deviation of 0.03\textdegree. Deviation of the whole molecule from planarity can best be described in terms of the relative tilts of the two benzene rings from the plane of $C = C - C = 0$ bridge, amounting to 4.5\textdegree and 11.5\textdegree (in p-methoxy chalkone) and 16.9\textdegree in chalkone. The molecular geometry of two chalkones are represented by I and II.
The bond angle and bond distance values indicate a greater single bond character in p-methoxy chalcone than in chalcone. The greater reactivity of p-methoxy compound is therefore due to the greater ease of availability of π electrons.

The following mechanism can be proposed basing on the above evidences.

(a) \( \text{C}_6\text{H}_5\text{C}-\text{CH} = \text{CH}-\text{C}_6\text{H}_5 \xrightarrow{V(v)} \text{C}_6\text{H}_5\text{C}-\text{CH} = \text{CH}-\text{C}_6\text{H}_5 \) (i)

(b) \( \text{C}_6\text{H}_5\text{C} = \text{CH} \xrightarrow{V(v)} \text{C}_6\text{H}_5\text{C} + \text{C}_6\text{H}_5\text{CH} = \text{CH} \) (ii)

(c) \( \text{C}_6\text{H}_5\text{CH} = \text{CH} \xrightarrow{\text{H}_2\text{O}} \text{C}_6\text{H}_5\text{CH} = \text{CH}-\text{OH} \xrightarrow{\text{C}_6\text{H}_5\text{CH}-\text{COOH}} \)

(d) \( \text{C}_6\text{H}_5\text{C} = \text{C}_6\text{H}_5\text{COOH} \)

The stoichiometry, the product analysis, the effect of substituents and the rate expression support this mechanism.
Section - 7

RESULTS OF VANADIUM(V) OXIDATION OF ACETONAPHTHONES.

Table - 1

Rate dependence on $[\text{V(v)}]$  

<table>
<thead>
<tr>
<th>$[\text{V(v)}]$ x $10^3$ in M</th>
<th>16.7</th>
<th>5.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k x 10^2$ in litres mole$^{-1}$ min$^{-1}$</td>
<td>7.5</td>
<td>6.4</td>
</tr>
</tbody>
</table>

$[\text{BK}] = 0.02$ M, $[\text{H}_2\text{SO}_4] = 3.0$ M, Temperature = 40°C

$[\text{V(v)}]$ x $10^3$ in M 4.0 10.0 15.0 25.0 40.0 50.0  

$k x 10^2$ in Conc$^{-1}$ min$^{-1}$ 18.4 11.43 6.43 6.34 5.05 3.67

Table - 2

Rate dependence on $[\text{BK}]$  

<table>
<thead>
<tr>
<th>$[\text{BK}]$ x $10^3$ in M</th>
<th>2.5</th>
<th>3.25</th>
<th>3.5</th>
<th>3.6</th>
<th>3.75</th>
<th>4.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k x 10^2$ in Conc$^{-1}$ min$^{-1}$</td>
<td>2.2</td>
<td>6.63</td>
<td>8.77</td>
<td>9.76</td>
<td>13.96</td>
<td>24.3</td>
</tr>
</tbody>
</table>

$[\text{BK}] = 0.05$ M, $[\text{BK}] = 0.02$ M, Temperature = 40°C

Table - 3

Rate dependence on $[\text{H}_2\text{SO}_4]$  

<table>
<thead>
<tr>
<th>$[\text{H}_2\text{SO}_4]$ in M</th>
<th>37.5</th>
<th>45.0</th>
<th>50.0</th>
<th>62.5</th>
<th>75.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k x 10^2$ in Conc$^{-1}$ min$^{-1}$</td>
<td>10.45</td>
<td>13.5</td>
<td>20.1</td>
<td>37.05</td>
<td>522.5</td>
</tr>
</tbody>
</table>

$[\text{BK}] = 0.025$ M, $[\text{BK}] = 0.01$ M, $[\text{H}_2\text{SO}_4] = 4.0$ M, Temp. = 40°C
Table - 5

\[ \{v(v)\} = 0.01 \text{ M}, \quad \{\text{HClO}_4\} = 3 \text{ M}, \quad \text{Temperature} = 40^\circ\text{C} \]

\begin{array}{cccccc}
[BK] \times 10^3 \text{ in M} & 100.0 & 75.0 & 60.0 & 50.0 \\
k \times 10^2 \text{ in litre mole}^{-1} \text{ min}^{-1} & 15.95 & 17.0 & 13.12 & 13.71
\end{array}

Table - 6

Change of cation

\[ \{BK\} = 0.1 \text{ M}, \quad \{\text{H}_2\text{SO}_4\} = 2.2 \text{ M}, \quad \text{Temperature} = 40^\circ\text{C} \]

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Concentration in M</th>
<th>( k \times 10^2 ) in Conc(^{-1}) min(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{V}_2\text{O}_5</td>
<td>0.0196</td>
<td>3.58</td>
</tr>
<tr>
<td>\text{Na}_3\text{V}_4\text{O}_4</td>
<td>0.0157</td>
<td>3.07</td>
</tr>
</tbody>
</table>

Table - 7

\[ \{BK\} = \alpha\text{-acetonaphthone} \]

Rate dependence on \( \{LK\} \).

\[ \{v(v)\} = 0.01 \text{ M}, \quad \{\text{H}_2\text{SO}_4\} = 2.2 \text{ M}, \quad \text{Temperature} = 40^\circ\text{C} \]

\begin{array}{cccccc}
[LK] \times 10^3 \text{ in M} & 50.0 & 60.0 & 75.0 \\
k \times 10^2 \text{ in litre mole}^{-1} \text{ min}^{-1} & 3.92 & 3.82 & 3.70
\end{array}

Table - 8

Rate dependence on temperature.

\[ \{\text{ketone}\} = 0.075 \text{ M}, \quad \{v(v)\} = 0.01 \text{ M}, \quad \{\text{H}_2\text{SO}_4\} = 2.2 \text{ M}, \quad \text{H}_2\text{OAc}=37.5\% \]

<table>
<thead>
<tr>
<th>Ketone</th>
<th>( k \times 10^2 ) in litre mole(^{-1}) min(^{-1} ) at 35°C</th>
<th>40°C</th>
<th>45°C</th>
<th>50°C</th>
<th>E in Kcals/ mol</th>
<th>( \Delta S ) in Kcals/ mol</th>
<th>( \Delta F ) in Kcals/ mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>LK</td>
<td>1.00</td>
<td>1.47</td>
<td>2.62</td>
<td>4.12</td>
<td>19.12</td>
<td>-14.4</td>
<td>23.7</td>
</tr>
<tr>
<td>BK</td>
<td>0.464</td>
<td>0.75</td>
<td>1.62</td>
<td>3.57</td>
<td>31.32</td>
<td>+31.1</td>
<td>21.4</td>
</tr>
</tbody>
</table>
DISCUSSION ON VANADIUM(V) OXIDATION OF ACETONAPHTHOINES.

The reaction has been found to obey second order rate equation (Fig. 7), when the concentration of the oxidant is lower than that of the substrate. When the substrate concentration is lower, the first order rate equation is obeyed (Table 1 and 2). Such types of observations have been made by Krishna and Tiwari and Aditya et al. Not much investigation has been done in the latter category but in the former category, the reaction is first order both with respect to the oxidant and the substrate. This has been verified at very high concentration of ketone (10 times) when first order plots were obtained.

The rate of oxidation depends on acid concentration. The rate increases with increasing concentration of sulphuric acid (Table-3). Solution of $\text{V}_2\text{O}_5$ in sulphuric acid are supposed to contain $[\text{V}0(\text{SO}_4)_2]^-$ and $[\text{V}0(\text{SO}_4)_3]^{3-}$. At higher concentration of the acid, these oxo-complexes are not protonated. The resistance of mono oxo-complexes to protonation is ascribed to the fact that the remaining lone pair on oxygen is in a $sp^3$ hybrid orbital (since the two $2p$ orbitals of the oxygen are used for bond formation to the metal atom). It considerable s character makes it less suitable for bonding purposes. So the complex dependence of log $k$ on sulphuric acid may be due to the varying nature of the oxidant. Probably at lower acid concentration, the species $[\text{V}0(\text{SO}_4)_2]^-$ becomes important, whereas at
higher acid concentration \([\text{V}_0(\text{SO}_4)_2]^-\) becomes important. A log-log plot of \(k\) against sulphuric acid concentration has a slope of 4.0 and 9.75. They are the square of the sulphuric acid concentration used for the formation of \([\text{V}_0(\text{SO}_4)_2]^-\) and \([\text{V}_0(\text{SO}_4)_3]^-\) species. A plot of log \(k\) against \([\text{H}_2\text{SO}_4]\) gives a curve which is consistent with the reaction mechanism,

\[
\text{S} + \text{H}^+ \rightarrow \text{SH}^+ \rightarrow \text{Product}
\]

under the conditions such that the concentration of \(\text{SH}^+\) is significant.

The rate of oxidation is higher by 3 times in perchloric acid than in sulphuric acid. This increase in the rate suggests an electron transfer mechanism rather than atom transfer one\textsuperscript{76}.

The rate of oxidation is found to increase with increasing percentage of acetic acid in a non-linear fashion (Table-4). So the reaction appears to take place either between a non-polar molecule and an ion or between two oppositely charged ions. The effect of dielectric constant on the rate of reaction between polar and ionic species can be represented by the following equation\textsuperscript{77}

\[
\ln k = \ln k_o + \frac{N_2^2 e^2}{2 \varepsilon RT} \left(\frac{1}{r} - \frac{1}{r^*}\right)
\]

In this case \(r^* > r\) and thus the correction term will be positive and the rate constant will increase as the dielectric constant \(\varepsilon\) decreases. The rate constant between oppositely charged ions can be represented by the Brönsted-Christian-
Since \( z_A \cdot z_B \) is negative, \( \ln k \) will increase with decreasing dielectric constant. In these equations, \( e \) = electronic charge, \( R \) = gas constant, \( T \) = temperature in \(^o\text{K}\) and \( r^* \) = the radius of the activated complex. \( k_0 \) is the value of the rate constant \( k \) in a hypothetical medium of infinite dielectric constant.

The oxidation rate constant is less for beta- than for alpha-acetonaphthones at a sulphuric acid concentration of 2.2 M. This is in contrast to the observation of Rout et al\(^{78}\) for the Ce(IV) oxidation of these ketones in sulphuric acid medium. It has been explained that the decrease in rate constant of alpha-acetonaphthone is due to the steric interference of the H-atom at position eight in the naphthalene ring. If \( V(\text{v}) \) does not suffer from this steric interaction; then the ratio of ionic radii of Ce(IV) and \( V(\text{v}) \) should correspond to the ratio of the rate constants of alpha and beta-acetonaphthones. The ratio of the ionic radii is 1.5 and the ratio of rate constants is 1.7. This agreement suggests that \( V(\text{v}) \) approaches the reaction site without being sterically hindered.

The self polarizability of the carbon atoms in the alpha-position \( |\tau_\alpha| = 0.443/|\beta| \) is larger than that of carbon atoms at beta-position \( |\tau_\beta| = 0.405/|\beta| \) and this explains the known fact that both electrophilic and nucleophilic reagents
preferably attack the alpha-position. Moreover, the free radicals will also most readily react with the alpha-position, since the latter has a free valence of 0.452 as compared with a free valence of 0.404 at beta-position. Hence, the greater reactivity of the alpha-acetonaphthone with V(V) than its beta-analogue is quite expected.

The rate of oxidation has been studied at various temperatures for alpha and beta-acetonaphthones. The values of energy of activation and entropy of activation have been calculated from a plot (Fig. 6) of log k vs. 1/T, (Table-9). Since it has not been possible to determine the course of oxidation completely, no structure can be assigned to the transition state. So no plausible explanation can be offered to the energy and entropy of activation values of these acetonaphthones.

**Mechanism:**

Analysis of the product, stoichiometry leads to suggest the following mechanism for the oxidation.

\[ \beta\text{-acetonaphthone:} \]

\[(a) \quad \begin{array}{c} \text{COCH}_3 \\ \text{O}^{+} \end{array} \xrightarrow{V(V)} \begin{array}{c} \text{CO} \\ \text{C} \end{array} \text{CH}_3 \]

\[(b) \quad \begin{array}{c} \text{C} \\ \text{C} \end{array} \xrightarrow{\text{H}_2\text{O}} \begin{array}{c} \text{C} \end{array} \Rightarrow \begin{array}{c} \text{C} \end{array} \text{C}^{+} + \text{C} \text{H}_3 \]

\[(c) \quad \begin{array}{c} \text{C} \end{array} \xrightarrow{\text{H}_2\text{O}} \begin{array}{c} \text{COOH} \end{array} \]

(d) $2\text{CH}_3 \rightarrow \text{C}_2\text{H}_6$

(e) 

(f)

(\(\alpha\)-H is more active than \(\beta\)-H since the former is a benzylic -H and also establishes conjugation with \(\text{CH} = \text{CH} - \text{CO} - \text{system.}\))
RESULTS OF VANADIUM(V) OXIDATION OF INDANE 1:3 DIONE.

**Table 1**
Rate dependence on \([V(V)]\)  
\([I.D] = 1 \times 10^{-3} \text{M, } [H^+] = 0.525 \text{ M, } \mu = 2, \text{ HOAc: H}_2\text{O} = 50:50 (v/v)\)  
Temperature = 45°C

<table>
<thead>
<tr>
<th>(10^3[V(V)]) in M</th>
<th>0.60</th>
<th>0.72</th>
<th>0.80</th>
<th>0.88</th>
<th>1.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_1 \times 10^5) in sec(^{-1})</td>
<td>3.34</td>
<td>4.60</td>
<td>5.75</td>
<td>6.90</td>
<td>7.44</td>
</tr>
</tbody>
</table>

**Table 2**
Rate dependence on the concentration of Indane 1:3 dione  
\([V(V)] = 1 \times 10^{-2} \text{M, } [H^+] = 0.525 \text{ M, } \mu = 2, \text{ HOAc: H}_2\text{O} = 50:50 (v/v)\)  
Temperature = 45°C

<table>
<thead>
<tr>
<th>(10^3[I.D]) in M</th>
<th>0.50</th>
<th>0.75</th>
<th>1.00</th>
<th>1.20</th>
<th>1.30</th>
<th>1.50</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_1 \times 10^5) in sec(^{-1})</td>
<td>2.13</td>
<td>4.35</td>
<td>7.44</td>
<td>11.84</td>
<td>12.83</td>
<td>15.03</td>
</tr>
</tbody>
</table>

**Table 3**
Rate dependence on the [ketone] in HClO\(_4\) medium  
\(10^3[V(V)] = 1 \text{ M, } [H^+] = 0.39 \text{ M, } \mu = 0.5, \text{ HOAc: H}_2\text{O} = 50:50 (v/v)\)  
Temperature = 45°C

<table>
<thead>
<tr>
<th>([I.D] \times 10^3) in M</th>
<th>0.50</th>
<th>1.00</th>
<th>1.20</th>
<th>1.50</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_1 \times 10^5) in sec(^{-1})</td>
<td>8.72</td>
<td>17.50</td>
<td>21.36</td>
<td>23.54</td>
</tr>
</tbody>
</table>
Table - 4
Rate dependence on ionic strength (by addition of $\text{(NH}_4)_2\text{SO}_4$

\[ [\text{V}(\nu)] = 1 \times 10^{-2} \text{M}, \quad [\text{I}.\text{D}] = 1 \times 10^{-3} \text{M}, \quad [\text{H}^+] = 0.525 \text{ M}, \]
$\text{HOAc:HO}_2\text{O} = 50:50 (\text{v/v}), \text{ Temperature} = 45^\circ \text{C}$

<table>
<thead>
<tr>
<th>( \mu ) in M</th>
<th>2.0</th>
<th>2.25</th>
<th>2.5</th>
<th>2.75</th>
<th>3.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 \times 10^5 ) in Sec(^{-1} )</td>
<td>7.44</td>
<td>13.31</td>
<td>13.42</td>
<td>23.78</td>
<td>39.15</td>
</tr>
</tbody>
</table>

Table - 5
Rate dependence on the $[\text{H}_2\text{SO}_4]$

\[ [\text{V}(\nu)] = 1 \times 10^{-2} \text{M}, \quad [\text{I}.\text{D}] = 1 \times 10^{-3} \text{M}, \quad \text{HOAc:HO}_2\text{O} = 1:1 (\text{v/v}), \text{T} = 45^\circ \text{C} \]

<table>
<thead>
<tr>
<th>( [\text{H}^+] ) in M</th>
<th>0.5</th>
<th>0.75</th>
<th>1.0</th>
<th>1.25</th>
<th>1.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 \times 10^5 ) in Sec(^{-1} )</td>
<td>7.50</td>
<td>9.20</td>
<td>11.17</td>
<td>13.32</td>
<td>13.42</td>
</tr>
</tbody>
</table>

Table - 6
Rate dependence on the concentration of added salt, at 45°C.

\[ [\text{V}(\nu)] = 1 \times 10^{-2} \text{M}, \quad [\text{I}.\text{D}] = 1 \times 10^{-3} \text{M}, \mu = 2, \text{HOAc:HO}_2\text{O} = 1:1 (\text{v/v}) \]

<table>
<thead>
<tr>
<th>Salt</th>
<th>NaClO(_4)</th>
<th>NaCl</th>
<th>MgSO(_4)</th>
<th>HgCl(_2)</th>
<th>(NH(_4))(_2)SO(_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 \times 10^5 ) in Sec(^{-1} )</td>
<td>41.45</td>
<td>18.42</td>
<td>22.37</td>
<td>16.12</td>
<td>7.44</td>
</tr>
</tbody>
</table>

Table - 7
Rate constants at different temperatures in $\text{H}_2\text{SO}_4$ medium

\[ [\text{V}(\nu)] = 1 \times 10^{-2} \text{M}, \quad [\text{I}.\text{D}] = 1 \times 10^{-3} \text{M}, \quad [\text{H}^+] = 0.525 \text{ M}, \mu = 2, \text{HOAc:HO}_2\text{O} = 1:1 (\text{v/v}) \]

<table>
<thead>
<tr>
<th>Temperature in °C</th>
<th>35</th>
<th>40</th>
<th>45</th>
<th>50</th>
<th>E in Kcals</th>
<th>$-\Delta S$ in per mole e.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 \times 10^5 ) in Sec(^{-1} )</td>
<td>2.46</td>
<td>4.93</td>
<td>7.44</td>
<td>12.93</td>
<td>19.45</td>
<td>16.7</td>
</tr>
</tbody>
</table>

Table - 8
Rate constants at different temperatures in $\text{HClO}_4$ medium

\[ [\text{V}(\nu)] = 1 \times 10^{-2} \text{M}, \quad [\text{I}.\text{D}] = 1 \times 10^{-3} \text{M}, \mu = 0.5, \quad [\text{H}^+] = 0.39 \text{ M}, \text{HOAc:HO}_2\text{O} = 1:1 (\text{v/v}) \]

<table>
<thead>
<tr>
<th>Temperature in °C</th>
<th>35</th>
<th>40</th>
<th>45</th>
<th>50</th>
<th>E in Kcals</th>
<th>$-\Delta S$ in per mole e.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 \times 10^5 ) in Sec(^{-1} )</td>
<td>5.48</td>
<td>10.46</td>
<td>15.75</td>
<td>23.03</td>
<td>15.78</td>
<td>26.91</td>
</tr>
</tbody>
</table>
DISCUSSION ON VANADIUM(V) OXIDATION OF INDANE 1:3 DIONE.

The vanadium(v) oxidation of Indane 1:3 dione has been done in acetic acid-water mixture both in presence of sulphuric acid and perchloric acid. The rate data have been very well fitted to the first order rate expression (Fig.1). The first order rate constants are found to increase with increasing concentration of vanadium(v) (Table-1). This increase in rate constant is probably due to increase in ionic strength in the medium. A plot of log k versus log \([V(v)]\) yields a straight line with a slope of Ca 1.3. Almost the same slope is obtained when log k is plotted against ionic strength calculated on the basis of increase in the sodium vanadate concentration in the reaction medium.

The values of first order rate constant \((k_1)\) have been found to increase with increasing substrate concentration (Table-2 & 3). A plot of log \(k_1\) vs. log \([\text{substrate}]\) gave a straight line with a slope of 1.7 in sulphuric acid medium. But in perchloric acid medium the slope is 1.0. The actual order of oxidation is therefore one with respect to substrate. In sulphuric acid medium, however, the reaction kinetics becomes complicated owing to the complexation of vanadium cations by sulphate groups.

The rate of oxidation has also been found to increase with increasing ionic strength (Table-4). The ionic strength has been changed by addition of ammonium sulphate.
A plot of log k vs. $\sqrt[2]{\mu}$ (Fig. 8) gave two straight lines whereas a plot of log k vs. $\mu$ gave a straight line with a slope of ca 0.7 in accordance with the equation,

$$\ln k = \ln k_o + \left[ \frac{8 N \text{Ne}^2}{1000 \text{DRT}} \right] \frac{z^2 d}{\mu}$$

for the reaction between an ion and a dipole or between two dipoles. The value of $k_o$ has been determined to be $0.29 \times 10^{-5}$ Sec$^{-1}$ by extrapolation to zero ionic strength. Since $V(v)$ exists as a cation in acid solution the reaction occurs between an ion and a dipole. The diketone, therefore, does not react in its protonated form or in its enol form and it is as such attacked by vanadium cation. Using the dielectric constant value for the 50% acetic acid-water (v/v) mixture, the value of $z^2 d$ has been computed to be 3.05 A$^0$ at 45°C. The value of $d$ the minimum distance of approach of the two reacting species, have been calculated for the probable charged species of vanadium and these have been found to be of reasonable magnitude.

The rate constant increased with increasing concentration of sulphuric acid (Table-5). A plot of k vs. $[H_2SO_4]$ gave a straight line up to 1.25 M and the line had an intercept at $k = 3.7 \times 10^{-5}$ Sec$^{-1}$. Therefore, the existence of a non-acid catalysed path for the oxidation of the ketone with $V^{5+}$ as the oxidising species has been indicated. The deviation of the straight line beyond 1.25 M can be understood from the fact that the redox potential of the $V(v)$ - $V(iv)$ couple increases with acidity in the region from pH 1.5 to 2 M acid as
would be expected if the species concerned are $V^{2+}(aq)$ and $V^{3+}(aq)$\textsuperscript{81}. At higher acidities the activity of water is reduced and thus influences the redox equilibrium:

$$VO_2^+ + 2H^+ + e \rightarrow V^{3+} + H_2O.$$ 

The rate of oxidation has also been studied in the presence of various salts at a constant ionic strength. The $ClO_4^-$ is found to catalyse the reaction. In general, divalent cations have an accelerating effect on the rate of the reaction. The $Na^+$ ion catalyses the reaction more than $Hg^{2+}$. The alkali metal cations are known to serve as charge carriers in some reactions of organic radical ions in solvents of low dielectric constant\textsuperscript{82}. The greater rate of reactivity with $ClO_4^-$ may also be a consequence of this phenomenon.

The oxidation has also been studied at various temperatures both in sulphuric and perchloric acid medium. Arrhenius equation (Fig.6) has been found to be obeyed in both the cases. The energy of activation values have been calculated to be 19.45 and 15.73 Kcals/mole in sulphuric and perchloric acid medium respectively. In sulphuric acid medium the vanadium cations gets complexed and therefore need more energy of activation for reaction. This difference of 3.67 Kcals/mole may roughly be ascribed to the energy difference between the complexed and uncomplexed $V(v)$ species. The values of entropy of activation have also been calculated. The difference in $\Delta S$ values is ca. 10 e.u. If this difference in energy and entropy is solely ascribed to the complexation of
V(v) with sulphate ions only, then the value of the equilibrium constant K can be calculated to be 148 at 45°C.

**Mechanism:**

Studies on stoichiometry reveals that one mole of the diketone absorbs five moles of vanadium(v). Addition of acrylonitrile (0.1 M in the reaction mixture of V(v) = 0.01 M and ketone = 0.001 M), completely inhibits the reaction. This indicates that the reaction proceeds through a stable free radical intermediate. A plot of 1/k vs. 1/[ketone] species shows no kinetic evidence for the complexation between vanadium species and the diketone. The straight line in the above plot passed through the origin both in sulphuric and perchloric acid medium. Therefore the oxidation of indane 1:3 dione by vanadium(v) possibly occurs by an outer sphere process. In this process the electron transfer occurs through intervening solvent molecules, so that in the transition state solvent reorganisation takes place and hence there occurs an entropy decrease.

Basing on these studies, the following probable mechanisms can be proposed.

**Path A**

\[
\begin{align*}
\text{V}^{3+} \text{O}_2^+ \text{H}_2\text{O}^+ & \rightarrow \text{C}_\text{H}_2^+ \\
\text{C}_\text{H}_2 & \rightarrow \text{C}_\text{H}_2^+ \\
\text{C}_\text{H}_2 & \rightarrow \text{COOH} \\
\text{COOH} & \rightarrow \text{C}_\text{H}_2^+ \\
\end{align*}
\]
Both phthalic acid and formaldehyde have been isolated as products in the reaction. The first step i.e. removal of an electron from the \( \text{>C = 0} \) group is consistent with (a) ionisation potential value and (b) vanadium(v) oxidation of cyclohexanone by an outer sphere process\(^{33}\). In the third step of the proposed process, an -ketoalcohol is shown to be formed as an intermediate. The isolation of this compound is difficult, since it reacts 200 times faster than the ketone by vanadium(v)\(^{34}\).

Consistent with these observations but not involving removal of electron from the \( \text{>C = 0} \) group in the first step, another pathway can be proposed. This alternative pathway is initiated with the removal of electron from the C-H bond, since this bond is weakened due to the adjacent keto groups.

Path B

---

\[
\text{COOH} \quad \xrightarrow{\text{V(v)}} \quad \text{COOH} \\
\text{COOH} \quad \xrightarrow{\text{CH}_2\text{OH}} \quad \text{COOH} + \text{CH}_2\text{OH} \\
\text{COOH} \quad \xrightarrow{\text{H}_2\text{O}} \quad \text{COOH}
\]

\[
\text{CH}_2\text{OH} \quad \xrightarrow{\text{V(v)}} \quad \text{CH}_2\text{OH} \quad \xrightarrow{\text{H}_2\text{O}} \quad \text{CH}_2\text{O}
\]
The compound obtained in stage (12) is a keto aldehyde and may be oxidised like formaldehyde absorbing two moles of $V(\text{v})$\textsuperscript{35}, giving a keto acid. The oxidation of keto acids are too fast\textsuperscript{36}. The oxidation of pyruvic acid\textsuperscript{37} studied with Mn(iii) and two moles of Mn(iii) are found to be absorbed for each mole of the substrate. Therefore the keto acid produced in stage (13) may also absorb 2 moles of $V(\text{v})$ to give phthalic acid. Therefore in the scheme one mole of indane 1:3 dione absorbs eight moles of $V(\text{v})$ to give rise to products. Experimentally five moles of $V(\text{v})$ have been found to be absorbed per
mole of the diketone. Therefore the oxidation proceeds to the extent of 75% by path A and 25% by path B. In other words the abstraction of an electron from a nonbonding orbital is three times more powerful than from a σ orbital (C-H bond). On examination of the ionisation potential data of the hydrocarbons and the corresponding ketones, the values of $I/I_0$ comes to 1.1.

The value of $\log k_n/k_\sigma$, (where $k_n$ = percentage oxidation by involving 'n' electrons and $k_\sigma$ = percentage oxidation by involving σ electrons of indane 1:3 dione) comes out to be 0.48. These two results agree in its direction and the magnitudes are not comparable since in the former hydrocarbons are taken for C-H ionisation potential values, whereas in the later it is actually a activated C-H bond.

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Section -11

RESULTS OF VANADIUM(V) OXIDATION OF DEOXYBENZOIN.

Table - 1

Rate dependence on \([V(v)]\)

\[
[DB] = 0.05 \text{ M}, [\text{HClO}_4] = 0.42 \text{ M}, \text{HOAc:H}_2\text{O} = 50:50 (v/v)
\]

Temperature = 35°C

<table>
<thead>
<tr>
<th>(10^3[V(v)] \text{ in M} )</th>
<th>5.0</th>
<th>4.0</th>
<th>3.0</th>
<th>2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10^5 \times k \text{ in Sec}^{-1} )</td>
<td>9.46</td>
<td>8.16</td>
<td>10.37</td>
<td>9.79</td>
</tr>
</tbody>
</table>

Table - 2

Rate dependence on the concentration of deoxybenzoin.

\(10^3[V(v)] = 3.0 \text{ M}, [\text{HClO}_4] = 0.42 \text{ M}, \text{HOAc:H}_2\text{O} = 50:50 (v/v)\)

Temperature = 35°C

\[
[DB] \text{ in M}
\]

<table>
<thead>
<tr>
<th>([DB] \text{ in M} )</th>
<th>0.05</th>
<th>0.04</th>
<th>0.02</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10^5 \times k \text{ in Sec}^{-1} )</td>
<td>10.37</td>
<td>3.7</td>
<td>6.61</td>
</tr>
<tr>
<td>(10^3 \times k \text{ in Sec}^{-1} )</td>
<td>2.07</td>
<td>2.18</td>
<td>3.305</td>
</tr>
</tbody>
</table>

\[ [\text{HClO}_4] = 0.9 \text{ M} \]

<table>
<thead>
<tr>
<th>([DB] \text{ in M} )</th>
<th>0.05</th>
<th>0.03</th>
<th>0.02</th>
<th>0.012</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10^5 \times k \text{ in Sec}^{-1} )</td>
<td>24.00</td>
<td>13.23</td>
<td>8.9</td>
<td>5.27</td>
</tr>
<tr>
<td>(10^3 \times k \text{ in Sec}^{-1} )</td>
<td>4.3</td>
<td>4.401</td>
<td>4.45</td>
<td>4.4</td>
</tr>
</tbody>
</table>
### Table - 3

Rate dependence on addition of salts.

\[ \text{[DB]} = 0.05 \text{ M, } [\text{HCIO}_4] = 0.42 \text{ M, } \text{HOAc}:\text{H}_2\text{O} = 50:50(\text{v/v}) \]

\[ 10^3 [V(v)] = 3.0 \text{ M, Temperature } = 35^\circ \text{C} \]

<table>
<thead>
<tr>
<th>Salt</th>
<th>0.2</th>
<th>0.16</th>
<th>0.12</th>
<th>0.08</th>
<th>0.06</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaClO_4</td>
<td>9.9</td>
<td>9.93</td>
<td>10.79</td>
<td>10.71</td>
<td>-</td>
</tr>
<tr>
<td>Na_2SO_4</td>
<td>12.79</td>
<td>12.0</td>
<td>12.23</td>
<td>12.2</td>
<td>12.2</td>
</tr>
</tbody>
</table>

### Table - 4

Rate dependence on solvent composition.

\[ 10^3 [V(v)] = 3.0 \text{ M, } [\text{HCIO}_4] = 0.42 \text{ M, Temperature } = 35^\circ \text{C} \]

<table>
<thead>
<tr>
<th>[DB] in M</th>
<th>% HOAc (v/v)</th>
<th>70</th>
<th>60</th>
<th>56</th>
<th>54</th>
<th>50</th>
<th>40</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.04</td>
<td>10^5 x k in Sec^{-1}</td>
<td>29.5</td>
<td>15.85</td>
<td>14.2</td>
<td>11.62</td>
<td>3.7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.02</td>
<td>8.91</td>
<td>-</td>
<td>6.61</td>
<td>-</td>
<td>-</td>
<td>5.48</td>
<td>4.27</td>
<td></td>
</tr>
</tbody>
</table>

### Table - 5

Rate constants at different temperatures and the energy and entropy of activation values.

\[ 10^3 [V(v)] = 3.0 \text{ M, [DB]} = 0.02 \text{ M, } [\text{HCIO}_4] = 0.42 \text{ M,} \]

\[ \text{HOAc}:\text{H}_2\text{O} = 50:50(\text{v/v}) \]

<table>
<thead>
<tr>
<th>Temperature in °C</th>
<th>35</th>
<th>40</th>
<th>45</th>
<th>E in Kcals per mole</th>
<th>$\Delta S^\ddagger$ in e.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^5 x k$ in Conc^{-1} Sec^{-1}</td>
<td>4.45</td>
<td>2.91</td>
<td>16.33</td>
<td>26.49</td>
<td>6.66</td>
</tr>
</tbody>
</table>
DISCUSSION ON VANADIUM(V) OXIDATION OF DEOXYBENZOIN.

The V(v) oxidation of deoxybenzoin has been done and the oxidation has been found to be of first order (Fig.1) with respect to both the $[\text{V}(\text{v})]$ and the [ketone]. (Table 1 and 2 respectively). To examine the possibility of any salt effect the oxidation has been studied in presence of NaClO$_4$ and Na$_2$SO$_4$. It is observed that addition of sodium perchlorate does not produce any effect on the rate constant i.e. the reaction is not affected by ionic strength effect. But when Na$_2$SO$_4$ is added, the reaction rate is enhanced and this enhanced rate data remains constant in all the concentration of the salt. This enhancement of rate due to the addition of SO$_4^{2-}$ may be due to the complexation of V(v) with SO$_4^{2-}$, thus making the central metal atom a better electrophile. Perhaps this would be the reason for the rate increase in sodium sulphate.

The reaction has also been studied at different HOAc:H$_2$O composition and at different [DB]. The plots of log k vs. 1/D (Fig.3) are straight lines indicating the linear dependence of the oxidation on the dielectric constant. The values of the slope are 13.25 and 45.0 at 0.02 and 0.04 M deoxybenzoin. The values of log $k_0$ are also $31.50 \times 10^{-5}$ and $17.48 \times 10^{-5} \text{Sec}^{-1}$ respectively. It is interesting to note that at situations of infinite dielectric constant i.e. in solvents of very high ionising power the order of the reaction would approach zero i.e. the reaction would be independent of the concentration of the
ketone. Moreover the dependence of the rate of oxidation to
dielectric constant is not independent of substrate.

The reaction has also been studied at various [HClO₄].
As before the rate increases with increasing concentration
of perchloric acid. The plot of log k vs. log [HClO₄] (Fig.5)
has been found to be a straight line with a slope ≈ 1.0.
Therefore the oxidation is first order with respect to [HClO₄].

Therefore the oxidising species in the present oxidation
appears to be V(OH)₃⁺² formed by the reaction, VO₂⁺ + H⁺ +
H₂O → [V(OH)₃]⁺². To examine if there is any acid independent
route a plot of k vs. [HClO₄] has also been prepared. Although
a linearity in the relationship is indicated yet there does
not appear to be an acid independent route i.e. VO₂⁺ does not
behave as an effective oxidising agent.

Determination of stoichiometry has indicated the
absorption of 2.5 moles of vanadium(v) per mole of deoxyben-
zoin. Analysis of the product with 2.5 to 3 moles of V(v) per
mole of deoxybenzoin has shown the formation of benzoic acid,
benzil and dibenzyl, whereas with 0.25 moles of V(v) per mole
of deoxybenzoin (kinetic condition), benzoic acid and benzoin
was isolated along with a little of dibenzyl and unconverted
deoxybenzoin. Since dibenzyl happened to be the product of
oxidation, the polymerisation was checked up with acrylonitrile
with success. The polymerisation of deoxybenzoin happened to
be proceeding very slowly. In the absence of deoxybenzoin the
polymerisation of acrylonitrile was very slow.
All these results lead to suggest the following mechanism for the oxidation of deoxybenzoin.

(A) 

\[
\begin{align*}
C_6H_5C=CH_2C_6H_5 & \xrightarrow{V(v)} C_6H_5\overset{0}{\longrightarrow}C_6H_5\overset{0}{\longrightarrow}CH_2C_6H_5 \\
C_6H_5\overset{0}{\longrightarrow}C=O & \rightarrow C_6H_5\overset{0}{\longrightarrow}C=O + C_6H_5CH_2 \\
2C_6H_5CH_2 & \rightarrow C_6H_5CH_2CH_2C_6H_5 \\
C_6H_5\overset{0}{\longrightarrow}C=O & \rightarrow C_6H_5COOH \\
\end{align*}
\]

This mechanism explains the stoichiometry and also product analysis.

(B) 

\[
\begin{align*}
C_6H_5C=CH_2C_6H_5 & \xrightarrow{V(v)} C_6H_5\overset{0}{\longrightarrow}C=O \overset{C=O}{\longrightarrow}CH-C_6H_5 \\
C_6H_5\overset{0}{\longrightarrow}C=CHC_6H_5 & \xrightarrow{H_2O,V(v)} C_6H_5\overset{0}{\longrightarrow}C=CH-C_6H_5 + H^+ \\
C_6H_5\overset{0}{\longrightarrow}C=CH\overset{0}{\longrightarrow}C_6H_5 & \xrightarrow{H_2O,2V(v)} C_6H_5\overset{0}{\longrightarrow}C=O-C-C_6H_5 \\
\end{align*}
\]

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