CHAPTER VI
OXIDATION OF DMF BY AQUEOUS ALKALINE PERMANGANATE

The importance of permanganate is discussed in chapter II (p. 42 and 43). The use of dimethylformamide (DMF) as a solvent in organic syntheses is extensive. However, the mechanism of oxidation of DMF has been studied only in a few cases in acid medium\(^1,2\) and in alkaline medium\(^3\). In acid medium with different oxidants, DMF decomposes to formic acid and dimethylamine (DMA). DMA does not react further and oxidation of formic acid is essentially the only reaction in acid medium. However, in alkaline medium formic acid is unaffected, where as DMA undergoes oxidation. Literature survey reveals that there is no report on the oxidation of DMF by permanganate either in alkaline or acidic medium. It is interesting to note that DMF does not undergo oxidation in acid medium whereas readily undergoes oxidation in alkaline medium by oxidant, permanganate. This prompted us to undertake the detailed study of the title reaction to investigate the redox chemistry of permanganate in such media.
Doubly distilled conductivity water was used for preparing the solutions throughout the work. The stock solutions of permanganate and potassium manganate were prepared and standardized as described in chapter II (p.45). DMF was distilled under reduced pressure and the stock solution of DMF was prepared by appropriate dilution with water.

All other reagents were of analytical grade and their solutions were prepared by dissolving appropriate amounts of samples in water. NaOH and NaClO₄ were utilized to provide the required alkalinity and to maintain ionic strength respectively.

**Kinetic Measurements**

All kinetic runs were carried out under pseudo-first order conditions where [DMF] was nearly 20 times greater than the [MnO₄⁻] at a constant ionic strength of 1.0 mol dm⁻³. The reaction was initiated by mixing previously thermostatted solutions of MnO₄⁻ and DMF which also contained required quantities of NaOH and NaClO₄. The temperature was uniformly maintained at 26 ± 0.1 °C using Toshniwal thermostat. The
course of the reaction was followed by measuring the decrease in the absorbance of permanganate at its absorption maximum 526 nm as a function of time, using 1 cm quartz cell of Hitachi 150-20 Spectrophotometer. Previously, it was verified that there is negligible absorbance at 526 nm from other reaction species. The Beer's law for $\text{MnO}_4^-$ at 526 nm had earlier been verified in the medium employed as given in chapter II (p.46), giving $\varepsilon = 2083 \pm 50$ dm$^{-3}$ mol$^{-1}$ cm$^{-1}$. The pseudo-first order rate constants, $k_{\text{obs}}$ were determined by plots of log $[\text{MnO}_4^-]$ versus time. The first order plots in almost all cases were linear up to 80% completion of the reaction and rate constants were reproducible within ±5% error. An example run is given in Table VI(i) (p.186) and its plot is shown in Fig. VI(i) (p.187). DMF hydrolyses to DMA and formic acid in acidic medium at high temperature. But at room temperature and in alkaline medium, DMF has not undergone hydrolysis to any significant extent.

In view of modest concentration of alkali used in the reaction medium, attention was also directed on the effect of the surface of reaction vessel on the kinetics. Use of polythene/ acrylic ware and quartz polyacrylate cells gave the same results indicating that the surfaces play no significant role on reaction rates.
Table VI(i)

Oxidation of DMF by aqueous alkaline permanganate at 26 °C.

\[ [\text{MnO}_4^-] = 2.35 \times 10^{-4}; \quad [\text{DMF}] = 4.0 \times 10^{-3} \]
\[ [\text{OH}^-] = 0.50; \quad I = 1.0/\text{mol dm}^{-3} \]

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Optical density</th>
<th>([\text{MnO}_4^-] \times 10^4) mol dm(^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.488</td>
<td>2.34</td>
</tr>
<tr>
<td>0.2</td>
<td>0.476</td>
<td>2.28</td>
</tr>
<tr>
<td>0.4</td>
<td>0.466</td>
<td>2.23</td>
</tr>
<tr>
<td>0.6</td>
<td>0.456</td>
<td>2.18</td>
</tr>
<tr>
<td>0.8</td>
<td>0.446</td>
<td>2.14</td>
</tr>
<tr>
<td>1.0</td>
<td>0.437</td>
<td>2.09</td>
</tr>
<tr>
<td>2.0</td>
<td>0.392</td>
<td>1.88</td>
</tr>
<tr>
<td>3.0</td>
<td>0.347</td>
<td>1.66</td>
</tr>
<tr>
<td>4.0</td>
<td>0.304</td>
<td>1.45</td>
</tr>
<tr>
<td>5.0</td>
<td>0.263</td>
<td>1.26</td>
</tr>
<tr>
<td>6.0</td>
<td>0.225</td>
<td>1.08</td>
</tr>
<tr>
<td>7.0</td>
<td>0.191</td>
<td>0.91</td>
</tr>
<tr>
<td>8.0</td>
<td>0.162</td>
<td>0.77</td>
</tr>
<tr>
<td>10.0</td>
<td>0.118</td>
<td>0.56</td>
</tr>
<tr>
<td>12.0</td>
<td>0.094</td>
<td>0.45</td>
</tr>
</tbody>
</table>
Figure VI(i)

Pseudo-first order plots of aqueous alkaline permanganate oxidation of DMF at 26 °C.

(Conditions as in Table VI(iii) (p.191))

Time min

2 4 6 8 10

log[MnO$_4^-$]
RESULTS

Stoichiometry and Product Analysis

Different sets of reaction mixtures containing the excess permanganate concentration over DMF in presence of 0.5 mol dm$^{-3}$ alkali adjusted to 1.0 mol dm$^{-3}$ ionic strength were kept to react for 24 h at 26 ± 1.0 °C in an inert atmosphere. The remaining permanganate was then analyzed spectrophotometrically. The results indicated that one mole of DMF consumed eight moles of permanganate in accordance with equation (1). The results of the stoichiometric studies are shown in Table VI(ii) (p.189). The main reaction products were identified as formic acid, ammonia by spot test, Nessler's reagent and manganate spectrophotometrically by comparing its absorption maximum with authentic sample respectively. Such products were also reported by earlier workers with other oxidants.

Under the conditions of kinetic studies, it was observed that the formic acid does not undergo further oxidation.

\[
\begin{align*}
\text{H} & \\
\text{(CH}_3\text{)}_2\text{N} - \text{C} - \text{O} + 8\text{MnO}_4^- + 8 \text{OH}^- & \rightarrow 3\text{HCOOH} + \text{NH}_3 + \\
& + 8\text{MnO}_4^{2-} + 2\text{H}_2\text{O} \\
\end{align*}
\]

(1)
Table VI(ii)

Stoichiometry of the oxidation of DMF by aqueous alkaline permanganate.

\[ [\text{OH}^-] = 0.50 \text{ mol dm}^{-3}; \quad I = 1.0 \text{ mol dm}^{-3}. \]

<table>
<thead>
<tr>
<th>Taken [MnO_4^-] x 10^4 (mol dm^{-3})</th>
<th>[DMF] x 10^4 (mol dm^{-3})</th>
<th>Found [MnO_4^-] x 10^4 (mol dm^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.0</td>
<td>1.0</td>
<td>1.95</td>
</tr>
<tr>
<td>20.0</td>
<td>2.0</td>
<td>4.00</td>
</tr>
<tr>
<td>12.0</td>
<td>1.0</td>
<td>4.05</td>
</tr>
<tr>
<td>24.0</td>
<td>2.0</td>
<td>7.95</td>
</tr>
</tbody>
</table>

Error ± 5\%.
Reaction Order

The orders of the reaction species were determined from the slopes of $\log k_{\text{obs}}$ versus $\log$(concentration) plots by varying the concentration of DMF and alkali in turn, while keeping others constant.

Effect of Oxidant

The oxidant, permanganate concentration was varied in the concentration range of $8.0 \times 10^{-5}$ to $8.0 \times 10^{-4}$ mol dm$^{-3}$ [Table VI(iii) (p.191)] keeping all other conditions constant. Linearity of plots of $\log[\text{MnO}_4^-]$ versus time indicates the order in $[\text{MnO}_4^-]$ as unity [Fig. VI(i) (p.187)]. This was also confirmed by non-variation of pseudo-first order rate constants, [Table VI(iii) (p.191)] at various concentration of $\text{MnO}_4^-$. 

Effect of Substrate

The substrate, DMF concentration was varied in the range of $1.0 \times 10^{-3}$ to $1.0 \times 10^{-2}$ mol dm$^{-3}$ at constant concentrations of $\text{MnO}_4^-$, alkali and at fixed ionic strength of $1.0$ mol dm$^{-3}$ as in Table VI(iv) (p.192). Order of the reaction with respect to [DMF] was found to be less than unity (Fig. VI(ii) (p.193)).
Table VI(iii)

Effect of variation of $[\text{MnO}_4^-]$ on oxidation of DMF by aqueous alkaline permanganate at 26 °C.

$[\text{DMF}] = 4.0 \times 10^{-3}; \quad [\text{OH}^-] = 0.50; \quad I = 1.0/\text{mol dm}^{-3}$.

<table>
<thead>
<tr>
<th>$[\text{MnO}_4^-] \times 10^4$ mol dm$^{-3}$</th>
<th>$k_{\text{obs}} \times 10^3$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Expt.*</td>
</tr>
<tr>
<td>0.80</td>
<td>2.60</td>
</tr>
<tr>
<td>1.50</td>
<td>2.61</td>
</tr>
<tr>
<td>2.35</td>
<td>2.52</td>
</tr>
<tr>
<td>5.00</td>
<td>2.60</td>
</tr>
<tr>
<td>8.00</td>
<td>2.62</td>
</tr>
</tbody>
</table>

*Experimental and calculated

Error ±5%.
Table VI(iv)

Effect of variation of [DMF] and [OH\textsuperscript{-}] on the oxidation of DMF by aqueous alkaline permanganate at 26 °C.

\[
[MnO_4^-] = 2.35 \times 10^{-4} \text{ mol dm}^{-3}; \quad I = 1.0 \text{ mol dm}^{-3}.
\]

<table>
<thead>
<tr>
<th>[DMF] (x 10^3)</th>
<th>[OH\textsuperscript{-}]</th>
<th>(k_{\text{obs}} \times 10^3) s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>mol dm(^{-3})</td>
<td>mol dm(^{-3})</td>
<td>Expt. *</td>
</tr>
<tr>
<td>1.0</td>
<td>0.5</td>
<td>1.01</td>
</tr>
<tr>
<td>2.5</td>
<td>0.5</td>
<td>1.92</td>
</tr>
<tr>
<td>4.0</td>
<td>0.5</td>
<td>2.61</td>
</tr>
<tr>
<td>7.0</td>
<td>0.5</td>
<td>4.01</td>
</tr>
<tr>
<td>10</td>
<td>0.5</td>
<td>5.50</td>
</tr>
<tr>
<td>4.0</td>
<td>0.1</td>
<td>0.47</td>
</tr>
<tr>
<td>4.0</td>
<td>0.3</td>
<td>1.60</td>
</tr>
<tr>
<td>4.0</td>
<td>0.5</td>
<td>2.60</td>
</tr>
<tr>
<td>4.0</td>
<td>0.7</td>
<td>3.80</td>
</tr>
<tr>
<td>4.0</td>
<td>1.0</td>
<td>5.00</td>
</tr>
</tbody>
</table>

*Experimental and Calculated Error ±5%.

192
Figure VI(ii)

Order of reaction with respect to [DMF] and [OH\textsuperscript{−}] in the oxidation of DMF by aqueous alkaline permanganate.

(Conditions as in Table VI(iv) (p.192))
Effect of [Alkali]

Effect of variation of alkali concentration in the range of 0.1 to 1.0 mol dm\(^{-3}\) (Table VI(iv) (p.192)) on the reaction was studied at constant concentration of permanganate and DMF keeping constant ionic strength of 1.0 mol dm\(^{-3}\) at 26 °C. The rate constants increased with increase in concentration of alkali as in Table VI(iv) (p.192). The order of the reaction with respect to [OH\(^-\)] was determined from the slope of log \(k_{\text{obs}}\) versus log[OH\(^-\)] plot and was found to be unity [Fig. VI(ii) (p.193)].

Effect of Ionic Strength

The effect of ionic strength was studied by varying the sodium perchlorate concentration. The ionic strength of the reaction was varied from 0.50 to 3.0 mol dm\(^{-3}\) (Table VI(v) (p.195)) at a constant concentration of oxidant, reductant and alkali. It was found that the ionic strength has no significant effect on the reaction rate (Table VI(v) (p.195)).

Effect of Solvent Polarity

The relative permittivity (\(D\)) effect was studied by varying \(t\)-butanol-water content in the reaction mixture as in Table VI(v) (p.195) with all other conditions being constant. Attempts to measure the relative permittivity failed. However,
Table VI(v)

Effect of variation of ionic strength (I) and solvent polarity (D) on the oxidation of DMF by alkaline permanganate at 26 °C.

\[
\begin{align*}
\text{[MnO}_4^-\text{]} &= 2.35 \times 10^{-4}; \\
\text{[DMF]} &= 4.0 \times 10^{-3}; \\
\text{[OH}^-\text{]} &= 0.50/\text{mol dm}^{-3}.
\end{align*}
\]

<table>
<thead>
<tr>
<th>I  (mol dm(^{-3}))</th>
<th>(k_{\text{obs}} \times 10^3) (s(^{-1}))</th>
<th>(%) t-butanol</th>
<th>D (-\text{water (v/v)})</th>
<th>(k_{\text{obs}} \times 10^3) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>2.45</td>
<td>0.0</td>
<td>78.50</td>
<td>2.65</td>
</tr>
<tr>
<td>1.0</td>
<td>2.55</td>
<td>1.0</td>
<td>77.82</td>
<td>3.58</td>
</tr>
<tr>
<td>1.5</td>
<td>2.60</td>
<td>2.0</td>
<td>77.14</td>
<td>5.58</td>
</tr>
<tr>
<td>2.5</td>
<td>2.60</td>
<td>3.0</td>
<td>76.47</td>
<td>6.03</td>
</tr>
<tr>
<td>3.0</td>
<td>2.65</td>
<td>10.0</td>
<td>71.74</td>
<td>7.12</td>
</tr>
</tbody>
</table>

Error ±5%
they were computed from the values of pure liquids as reported. Earlier, the inertness of the solvent with oxidant was checked under experimental conditions employed and it was found that there was no reaction of solvent with oxidant. The rate constants, $k_{\text{obs}}$, increased with decrease in dielectric constant of the medium. The plot of $\log k_{\text{obs}}$ versus $1/D$ was linear with positive slope [Fig.VI(iii) (p.197)].

Effect of Initial Addition of Products

The addition of varying amounts of reaction products $\text{vizi.}$ $\text{MnO}_4^{2-}$, formic acid and ammonia in the concentration range of $8.0 \times 10^{-5}$ to $8.0 \times 10^{-4}$, $7.0 \times 10^{-4}$ to $7.0 \times 10^{-3}$ and $2.0 \times 10^{-4}$ to $2.0 \times 10^{-3}$ respectively, as in Table VI(vi) (p.198), did not affect the rate of the reaction to any significant extent [Table VI(vi) (p.198)].

Test for Free Radicals

To test the free radical intervention in the reaction, the reaction mixture containing acrylonitrile monomer was kept for 12 h in an inert atmosphere. Then diluting the reaction mixture with methanol, the formation of precipitate indicates the presence of free radical in the reaction.
Figure VI(iii)

Effect of variation of solvent polarity (D) on the oxidation of DMF by aqueous alkaline permanganate at 26 °C.

(Conditions as in Table VI(v) (p.195))

\[ \frac{1}{D} \times 10^2 \]

\[ \log_{10} k_{bs} \]

\[ 1.26 \quad 1.30 \quad 1.34 \quad 1.38 \quad 1.42 \]

\[ -1.9 \quad -2.1 \quad -2.3 \quad -2.5 \quad -2.7 \quad -2.9 \]
# Table VI(vi)

Effect of variation of $[\text{MnO}_4^{2-}]$, $[\text{HCOOH}]$ and $[\text{ammonia}]$ ($\text{NH}_4\text{OH}$) on oxidation of DMF by aqueous alkaline permanganate at 26 °C.

<table>
<thead>
<tr>
<th>$[\text{MnO}_4^{2-}]$ $x 10^4$ mol dm$^{-3}$</th>
<th>$[\text{HCOOH}]$ $x 10^3$ mol dm$^{-3}$</th>
<th>$[\text{NH}_4\text{OH}]$ $x 10^3$ mol dm$^{-3}$</th>
<th>$k_{\text{obs}}$ $x 10^3$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>-</td>
<td>-</td>
<td>2.50</td>
</tr>
<tr>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>2.60</td>
</tr>
<tr>
<td>2.0</td>
<td>-</td>
<td>-</td>
<td>2.45</td>
</tr>
<tr>
<td>4.0</td>
<td>-</td>
<td>-</td>
<td>2.55</td>
</tr>
<tr>
<td>8.0</td>
<td>-</td>
<td>-</td>
<td>2.59</td>
</tr>
<tr>
<td>-</td>
<td>0.7</td>
<td>-</td>
<td>2.58</td>
</tr>
<tr>
<td>-</td>
<td>1.0</td>
<td>-</td>
<td>2.65</td>
</tr>
<tr>
<td>-</td>
<td>1.5</td>
<td>-</td>
<td>2.62</td>
</tr>
<tr>
<td>-</td>
<td>2.0</td>
<td>-</td>
<td>2.70</td>
</tr>
<tr>
<td>-</td>
<td>7.0</td>
<td>-</td>
<td>2.65</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>0.2</td>
<td>2.50</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>0.5</td>
<td>2.45</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>1.0</td>
<td>2.55</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>1.5</td>
<td>2.60</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>2.0</td>
<td>2.45</td>
</tr>
</tbody>
</table>

Error ± 5%
Effect of Temperature

The temperature effect was studied at 26, 31, 36 and 41 °C at constant conditions of reactants, alkali and ionic strength. As in earlier chapter II(p.62-66), from the plot of log $k_{\text{obs}}$ versus $1/T$ [Fig. VI(iv) (p.200)], the activation parameters of the overall reaction were obtained as $\Delta H^\# = 50.0 \pm 3.0 \text{ kJ mol}^{-1}$ and $\Delta S^\# = -126 \pm 6 \text{ JK}^{-1} \text{ mol}^{-1}$.

DISCUSSION

The reaction between DMF and permanganate in alkaline medium has 8:1 stoichiometry (oxidant : Reductant) with first order dependence each on $[\text{MnO}_4^-]$ and $[\text{alkali}]$ and order of less than unity in $[\text{DMF}]$. No products effect has been observed. The direct plot of $k_{\text{obs}}$ versus $[\text{DMF}]$ gave better correlation than the reciprocal plot [Fig. VI(v) (p.201)]. The observed kinetic and other results may be explained by two path way mechanism, one a $[\text{DMF}]$ dependent and another a $[\text{DMF}]$ independent as detailed in following scheme 1.
Figure VI(iv)

Effect of temperature on the oxidation of DMF by aqueous alkaline permanganate.

\[
[MnO_4^-] = 2.35 \times 10^{-4}, \quad [DMF] = 4.0 \times 10^{-3}, \quad [OH^-] = 0.50 \quad \text{and} \quad I = 1.0/\text{mol dm}^{-3}.
\]
Figure VI(v)

Plots of $k_{obs}$ versus [DMF] and $1/k_{obs}$ versus $1/[DMF]$ 
(Conditions as in Table VI(iv) (p.192))
Path-I:

\[
(\text{CH}_3)_2N - C = O + MnO_4^- \xrightarrow{\text{H}} \text{Complex (C)}
\]

\[
C + OH^- \xrightarrow{\text{slow}} (\text{CH}_3)_2N - C = O + MnO_4^{2-} + H_2O
\]

\[
(\text{CH}_3)_2N - C = O + 7\text{MnO}_4^- + 6\text{OH}^- \xrightarrow{\text{fast}} \text{products}
\]

Path-II:

\[
\text{MnO}_4^- + OH^- \xrightarrow{\text{slow}} \text{MnO}_4^{2-} + \text{OH}
\]

\[
(\text{CH}_3)_2N - C = O + \text{OH} \xrightarrow{\text{fast}} (\text{CH}_3)_2N - C = O + H_2O
\]

\[
(\text{CH}_3)_2N - C = O + 7\text{MnO}_4^- + 6\text{OH}^- \xrightarrow{\text{fast}} \text{products}
\]

Scheme 1

The observed fractional order in [DMF] may be attributed to a formation of a complex either with alkali or permanganate. In view of first order dependence of rate on [alkali] the complex formation between OH\(^{-}\) and MnO\(_4\)^\(-\) is discarded. However,
attempt to obtain uv-vis spectral evidence for complex formation between DMF and permanganate ion are in vain. This may be due to feeble interaction. Kinetic evidence for complex formation can be obtained from non-zero intercept of plot of $1/k_{\text{obs}}$ Vs $1/\text{[DMF]}$ (Fig. VI(v) (p.201)), which is also evidenced by high negative value of $\Delta S$. Such complex formations between substrate and oxidant have been reported by earlier workers. This complex reacts with hydroxyl ion in the rate determining step to give a radical of DMF with dehydration, which reacts further with seven molecules of permanganate in subsequent fast step to give products. Since permanganate species is one electron oxidant in alkaline medium, the reaction between substrate and oxidant would afford a radical intermediate. Free radical scavenging experiment reveals such a possibility (see infra). Such type of free radicals intervention in the reaction has been observed with alkaline permanganate oxidation for various organic substrates by earlier workers\textsuperscript{9}.

In a second path, permanganate reacts with hydroxyl ion in the slow step to give the reduced product of $\text{MnO}_4^-$, and a hydroxyl free radical which reacts with DMF to give its free radical. Thus, free radical formed further reacts with seven molecules of $\text{MnO}_4^-$ in a subsequent fast step to give products.
The combined rate law for scheme 1 may be derived as follows.

Rate for path I,

\[ \text{Rate} = k_1 [C] [OH^-] \]  \hspace{1cm} (2)

\[ K_1 = \frac{[C]}{[\text{DMF}] [\text{MnO}_4^-]} \]  \hspace{1cm} (3)

\[ [C] = K_1 [\text{DMF}]_f [\text{MnO}_4^-]_f \]  \hspace{1cm} (4)

\[ \text{Rate} = k_1 K_1 [\text{DMF}]_f [\text{MnO}_4^-]_f [OH^-] \]  \hspace{1cm} (5)

Rate for path II,

\[ \text{Rate} = k_2 [\text{MnO}_4^-] [OH^-] \]  \hspace{1cm} (6)

Therefore, combined rate law,

\[ \text{Rate} = \text{Rate for path I} + \text{Rate for path II} \]

\[ \text{Rate} = K_1 [\text{DMF}]_f [\text{MnO}_4^-]_f [OH^-] + k_2 [\text{MnO}_4^-] [OH^-] \]  \hspace{1cm} (7)
Now,

\[ [\text{MnO}_4^-]_T = [\text{MnO}_4^-]_f + [C] \]
\[ = [\text{MnO}_4^-]_f + K_1 [\text{DMF}] [\text{MnO}_4^-]_f \]
\[ = [\text{MnO}_4^-]_f \left\{ 1 + K_1 [\text{DMF}] \right\} \]

\[ [\text{MnO}_4^-]_f = \frac{[\text{MnO}_4^-]_T}{(1 + K_1 [\text{DMF}])} \quad (8) \]

Similarly,

\[ [\text{DMF}]_f = \frac{[\text{DMF}]_T}{(1 + K_1 [\text{MnO}_4^-])} \quad (9) \]

Substituting equations (8) and (9) into (7) we get,

\[
\text{Rate} = - \frac{d[\text{MnO}_4^-]}{dt} = \frac{k_1 K_1 [\text{MnO}_4^-]_T [\text{DMF}]_T [\text{OH}^-]}{(1 + K_1 [\text{MnO}_4^-]) (1 + K_1 [\text{DMF}])} + k_2 [\text{MnO}_4^-] [\text{OH}^-] \]

(10)
\[
\frac{\text{Rate}}{[\text{MnO}_4^-]} = k_{\text{obs}}
\]
\[
= \frac{k_1 k_1 [\text{DMF}]_T [\text{OH}^-]}{(1 + K_1 [\text{MnO}_4^-])(1 + K_1 [\text{DMF}] )} + k_2 [\text{OH}^-]
\]

(11)

In view of low concentration of MnO<sup>-4</sup> and DMF used, the terms 
\((1 + K_1 [\text{MnO}_4^-])\) and \((1 + K_1 [\text{DMF}] )\) were approximated to unity. Therefore equation (11) becomes,

\[
k_{\text{obs}} = K_1 k_1 [\text{DMF}] [\text{OH}^-] + k_2 [\text{OH}^-]
\]

(12)

Equation (12) may be rearranged to the form (13) which is suitable for verification.

\[
\frac{k_{\text{obs}}}{[\text{OH}^-]} = K_1 k_1 [\text{DMF}] + k_2
\]

(13)

According to equation (13), the plot of \(k_{\text{obs}}/[\text{OH}^-]\) versus [DMF] is expected to be linear which is verified in Fig. VI(vi) (p.207). The slope and intercept of such plot lead to the values of \(K_1 k_1\) and \(k_2\) at 26°C as \(1.0 \pm 0.05 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}\) and \(1.0 \pm 0.04 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}\) respectively. These
Figure VI(vi)

Plot of $k_{\text{obs}}/[$OH$^{-}$] versus [DMF]

(Conditions as in Table VI(iv) (p.192))
constants are used to calculate the rate constants under various conditions of experiments. There is a reasonable agreement between calculated and observed rate constants [(Table VI(iii and iv) (p.191 and 192)]. The value of $k_2$ obtained in our work is in close agreement with earlier reports.\textsuperscript{11}

The negligible effect of ionic strength on the rate may be attributed to involvement of neutral species \textit{viz.}, DMF in the reaction. However, increasing the content of $t$-butanol in the reaction medium leads to an increase in the rate of the reaction, contrary to the expected slower reaction between like ions in the media of lower relative permittivity. The increasing effect may be attributed to substantial formation of the active reaction species, which overcomes the effect of low relative permittivity effect of decreasing the rate, so that there is an increase in the rate of reaction.\textsuperscript{12}

The values of $\Delta H^\#$ and $\Delta S^\#$ were both favourable for electron transfer processes. The favourable enthalpy was due to release of energy on solution changes in the transition state. The values of $\Delta S^\#$ within the range for radical reactions have been ascribed\textsuperscript{13} to the nature of electron pairing and electron unpairing processes, and to the loss of
degrees of freedom, formerly available to the reaction on the formation of rigid transition state.

Findings of Chapter VI

The reaction between dimethylformamide and alkaline permanganate is first order each in [permanganate] and [OH⁻] whereas less than unity in [DMF]. Formic acid and ammonia were the main oxidation products of DMF. A mechanism based on the experimental results, involving two paths, one DMF dependent and another DMF independent is proposed. The constants involved in the mechanism are evaluated. There is a good agreement between the observed and calculated rate constants at varying conditions of experiments.
REFERENCES

1. S.S.Krishnamurthy and S.Sundarajan,
   Chem. Abstr., 1971, 74, 35136d.

2. S.Langlois and A.Broche,
   D.Saxena K.S.Gupta,
   H.Singh and S.P.Srivastava,

3. G.H.Hugar and S.T.Nandibewoor,
   G.H.Hugar and S.T.Nandibewoor,

4. J.A.Riddick and E.E.Troops Jr.,
5. S. Langlois and A. Broche,
D. Saxena K. S. Gupta,
H. Sngh and S. P. Srivastava,
J. Indian Chem. Soc., 1971, 48, 725;
B. Erwing and E. A. Symons,

6. F. Feigl,

7. A. I. Vogel,

8. G. H. Hugar and S. T. Nandibewoor,
9. G.H. Hugar and S.T. Nandibewoor,


S.M. Tuwar, S.T. Nandibewoor and J.R. Raju,
*J. Indian Chem. Soc.*, 1992, 69, 651;

S.M. Tuwar, S.T. Nandibewoor and J.R. Raju,

J. Devi, S. Kothari and K.K. Banerji,

10. M. Jaky, Z. Szeverenyi and L.I. Simandi,


K.A.K. Lott and M.C.R. Symons,

R.B. Chougale, G.A. Hiremath and S.T. Nandibewoor,
*Polish J. Chem.*, 1997, 71, 1471;

R.G. Panari, R.B. Chougale and S.T. Nandibewoor,

R.G. Panari, R.B. Chougale and S.T. Nandibewoor,

R.G. Panari, R.B. Chougale and S.T. Nandibewoor,

11. M.C.R. Symons,

12 S.T. Nandibewoor and V.A. Morab,


13. C. Walling,

Free Radicals in Solution, New York, 1957, p. 38