CHAPTER 3

RESULTS AND DISCUSSION

Though the subject of metalloporphyrin catalysis in various oxidation reactions has been focused widely in the last two decades, information available regarding the stability of the catalyst towards the oxidants such as hydrogen peroxide, peracetic acid, Oxone® and m-chloroperbenzoic acid is rather scanty. The importance of oxidation catalysis versus stability of the catalyst has been taken into consideration here in the oxidation reactions such as epoxidation, N-oxidation and S-oxidation. The present work deals with the following aspects.

1. Kinetics and mechanism of oxidation of isobutyl 3-butenoate by hydrogen peroxide in acetonitrile solvent in the presence of F$_{20}$TPPFeCl as a catalyst.
2. Kinetics and mechanism of degradation of F$_{20}$TPPFeCl by hydrogen peroxide in acetonitrile solvent both in the presence and absence of a substrate.
3. Kinetics and mechanism of interaction of F$_{20}$TPPFeCl with peracetic acid in the medium of acetonitrile solvent in the presence as well as in the absence of a substrate.
4. Kinetics and mechanism of oxidation of 2-chloropyridine to 2-chloropyridine N-oxide by peracetic acid in acetonitrile solvent in the presence of F$_{20}$TPPFeCl as a catalyst.
5. Kinetics and mechanism of degradation of $F_{20}TPPFeCl$ by Oxone® in the medium of acetonitrile and water solvent in the presence as well as in the absence of a substrate.

6. Kinetics and mechanism of oxidation of 4,4'-diacetyldiamino diphenylsulfoxide to 4,4'-diacetyldiamino diphenylsulfone by Oxone® catalyzed by $F_{20}TPPFeCl$ in methanol and water as solvents.

7. Kinetics and mechanism of degradation of $F_{20}TPPFeCl$ by m-chloroperbenzoic acid in acetonitrile solvent both in the presence and absence of a substrate.

8. Kinetics and mechanism of oxidation of isobutyl 3-butenoate by m-chloroperbenzoic acid in the medium of acetonitrile in the presence of $F_{20}TPPFeCl$ as a catalyst.

In all the above cases of study, suitable mechanism and rate law are proposed in the light of the observed facts.

3.1 A KINETIC STUDY OF IRON(III)PORPHYRIN MEDIATED BIOMIMETIC EPOXIDATION BY $H_2O_2$

Hydrogen peroxide is an extremely advantageous source of oxygen. Unfortunately, only few catalysts have been discovered to date that allow for the selective oxygenation of fine chemicals with this oxidant. Significant challenges still remain, e.g. the major problems in hydrogen peroxide catalytic oxidations are the stability of the catalysts involved to the reaction conditions. Hence it was thought of interest to follow the title study.
3.1.1 Oxidation of Isobutyl 3-butenolate

The substrate isobutyl 3-butenolate was efficiently oxidized (epoxidized) by this catalyst and oxidant and UV-Visible overlays showed loss of isobutyl 3-butenolate peak at 270 nm (due to the loss of the chromophore on epoxidation) in the presence of hydrogen peroxide in the medium of acetonitrile. It should be admitted here that the reaction was sluggish in the absence of catalyst. A plot of absorbance vs time is shown in Figures 3.1 and 3.2 and similar plots were obtained for the same reaction at the various concentrations of catalyst, hydrogen peroxide and isobutyl 3-butenolate.

3.1.2 Effect of Varying [substrate]

Reaction orders have been determined by monitoring the disappearance of isobutyl 3-butenolate at 270 nm in reactions catalyzed by $F_{20}$TPPFeCl at the early stage of the epoxidation reaction where the relationship between olefin conversions vs time is linear. We determined the dependence of the reaction rate on various concentrations of olefin keeping the concentrations of catalyst and oxidant constant (Table 3.1). Reaction order determinations were based on the measurements of initial rates at various concentrations of substrate with the order being the slope of a plot made between the logarithms of initial reaction rate at various concentrations of the reactant vs the logarithm of the reactant concentration. The rate of the reaction approximately remained constant with increase in the concentration of substrate and hence the dependence of rate on [isobutyl 3-butenolate] was zero order.
Figure 3.1  Plot of absorbance vs time for the F_{20}TPPFeCl- catalyzed oxidation of isobutyl 3-butenolate in acetonitrile at 25°C. (a) [isobutyl 3-butenolate] = 3.0 \times 10^{-3} \text{ mol dm}^{-3}, [H_2O_2] = 5.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ and } [F_{20}TPPFeCl] = 9.4 \times 10^{-6} \text{ mol dm}^{-3} \text{ and (b) [isobutyl 3-butenolate] = 1.25 \times 10^{-3} \text{ mol dm}^{-3}, [H_2O_2] = 5.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ and } [F_{20}TPPFeCl] = 9.4 \times 10^{-6} \text{ mol dm}^{-3}. The absorbance was recorded at 270 nm.
Figure 3.2  Plot of absorbance vs time for the $F_{20}TPPFeCl$- catalyzed oxidation of isobutyl 3-butenoate in acetonitrile at 25°C to show the first 20% of the reaction. (a) [isobutyl 3-butenoate] = 3.0×10^{-3} \text{ mol dm}^{-3}, [H_2O_2] = 5.0×10^{-3} \text{ mol dm}^{-3} and $[F_{20}TPPFeCl]$ = 9.4×10^{-6} \text{ mol dm}^{-3}$ and (b) [isobutyl 3-butenoate] = 1.25 × 10^{-3} \text{ mol dm}^{-3}, [H_2O_2] = 5.0 × 10^{-3} \text{ mol dm}^{-3} and $[F_{20}TPPFeCl] = 9.4 × 10^{-6} \text{ mol dm}^{-3}$. The absorbance was recorded at 270 nm.
Table 3.1 Values of observed rate constant, $k_{obs}$ for $\text{F}_{20}\text{TPPFeCl}$ catalyzed oxidation of Isobutyl 3-butenoate by $\text{H}_2\text{O}_2$ in acetonitrile at 25°C.

Dependence of the rate on [substrate]

$[\text{H}_2\text{O}_2] = 2.5 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{F}_{20}\text{TPPFeCl}] = 23.5 \times 10^{-6} \text{ mol dm}^{-3}$

<table>
<thead>
<tr>
<th>Entry</th>
<th>[isobutyl 3-butenoate] ($\times 10^{3} \text{ mol dm}^{-3}$)</th>
<th>$k_{obs}$ ($\times 10^{4} \text{ /sec}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.25</td>
<td>26.63</td>
</tr>
<tr>
<td>2</td>
<td>3.0</td>
<td>48.45</td>
</tr>
<tr>
<td>3</td>
<td>6.0</td>
<td>48.88</td>
</tr>
<tr>
<td>4</td>
<td>15.0</td>
<td>29.28</td>
</tr>
<tr>
<td>5</td>
<td>25.0</td>
<td>33.45</td>
</tr>
</tbody>
</table>
3.1.3 **Effect of Varying [oxidant]**

Oxidation of isobutyl 3-butenolate by hydrogen peroxide was investigated with several initial concentrations of oxidant, keeping the concentrations of catalyst and substrate constant (Table 3.2). The rate of the reaction was found to increase with increase in concentration of the oxidant. The order of the reaction with respect to the oxidant was found to be one as evidenced by the linear plot of \( \log k_{\text{obs}} \) vs \( \log [\text{H}_2\text{O}_2] \) with a slope of unity (Figure 3.3).

3.1.4 **Effect of Varying [catalyst]**

Considerable increase in the rate was observed when the concentration of the catalyst, \( \text{F}_{20}\text{TPPFeCl} \) in the reaction mixture was increased keeping the concentrations of substrate and oxidant constant (Table 3.3). From the plot of \( \log k_{\text{obs}} \) vs \( \log [\text{F}_{20}\text{TPPFeCl}] \), it was found that with respect to \( \text{F}_{20}\text{TPPFeCl} \) the order of the reaction is one (Figure 3.4).

3.1.5 **Rate Law**

From all the above experimental results, it is seen here that with respect to \( \text{H}_2\text{O}_2 \) and \( \text{F}_{20}\text{TPPFeCl} \), the order of the reaction was found to be one. In contrast, the dependence on [isobutyl 3-butenolate] was approximately zero order and overall we propose the rate equation:

\[
\frac{d [\text{epoxide}]}{dt} = \frac{-d [\text{isobutyl 3-butenolate}]}{dt} = k [\text{H}_2\text{O}_2] [\text{F}_{20}\text{TPPFeCl}] \quad (3.1)
\]

\[
= k [\text{H}_2\text{O}_2] [\text{F}_{20}\text{TPPFeCl}] \quad (3.2)
\]
Table 3.2  Values of observed rate constant, $k_{obs}$ for the $\text{F}_{20}\text{TPPFeCl}$ catalyzed oxidation of Isobutyl 3-butenoate by $\text{H}_2\text{O}_2$ in acetonitrile at 25°C.

Dependence of the rate on [oxidant]

[isobutyl 3-butenoate] = $10 \times 10^{-3}$ mol dm$^{-3}$\quad [F$_{20}$TPPFeCl] = $23.5 \times 10^{-6}$ mol dm$^{-3}$

<table>
<thead>
<tr>
<th>Entry</th>
<th>$[\text{H}_2\text{O}_2]$ ($\times 10^3$ mol dm$^{-3}$)</th>
<th>$k_{obs}$ ($\times 10^4$/ sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>2.5</td>
<td>43.84</td>
</tr>
<tr>
<td>7</td>
<td>3.0</td>
<td>54.25</td>
</tr>
<tr>
<td>8</td>
<td>3.75</td>
<td>68.52</td>
</tr>
<tr>
<td>9</td>
<td>5.0</td>
<td>90.78</td>
</tr>
<tr>
<td>10</td>
<td>7.5</td>
<td>136.17</td>
</tr>
<tr>
<td>11</td>
<td>12.5</td>
<td>227.02</td>
</tr>
</tbody>
</table>
Figure 3.3 Reaction order with respect to hydrogen peroxide in F_{20}TPPF{FeCl-catalyzed oxidation of isobutyl 3-butenoate in acetonitrile at 25°C
Table 3.3  Values of observed rate constant, $k_{obs}$ for the $\text{F}_{20}\text{TPPFeCl}$ catalyzed oxidation of Isobutyl 3-butenoate by $\text{H}_2\text{O}_2$ in acetonitrile at 25°C.

**Dependence of the rate on $[\text{F}_{20}\text{TPPFeCl}]$**

$[\text{isobutyl 3-butenolate}] = 10 \times 10^{-3} \text{ mol dm}^{-3}$  \hspace{1cm} $[\text{H}_2\text{O}_2] = 2.5 \times 10^{-3} \text{ mol dm}^{-3}$

<table>
<thead>
<tr>
<th>Entry</th>
<th>$[\text{F}_{20}\text{TPPFeCl}]$ ($\times 10^{6}$ mol dm$^{-3}$)</th>
<th>$k_{obs}$ ($\times 10^{4}$/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>4.7</td>
<td>8.75</td>
</tr>
<tr>
<td>13</td>
<td>9.4</td>
<td>16.23</td>
</tr>
<tr>
<td>14</td>
<td>14.1</td>
<td>26.25</td>
</tr>
<tr>
<td>15</td>
<td>18.8</td>
<td>35.02</td>
</tr>
<tr>
<td>16</td>
<td>21.15</td>
<td>40.13</td>
</tr>
<tr>
<td>17</td>
<td>4.7</td>
<td>8.80*</td>
</tr>
</tbody>
</table>

* Contained 0.005 mol dm$^{-3}$ benzoic acid
Figure 3.4  Reaction order with respect to $F_{20}$TPPFeCl in $F_{20}$TPPFeCl-catalyzed oxidation of isobutyl 3-butenoate in acetonitrile at 25°C
3.1.6 Mechanism

The form of equations (3.1) and (3.2) given in section 3.1.5 is consistent with the generally accepted mechanism of metalloporphyrin-catalyzed oxidation shown in Scheme 3.1, which involves slow rate-limiting conversion of the catalyst to an oxidized intermediate, which then transfers oxygen to the substrate, isobutyl 3-butenoate in a fast step. The general mechanism shown in Scheme 3.1 for metalloporphyrin-catalyzed epoxidation is widely accepted. However the nature of the ‘oxidized intermediate’ has been the subject of much debate when formed from reaction with hydrogen peroxide or hydroperoxides.

\[
\begin{align*}
F_{20} \text{TPPFeCl} + H_2O_2 & \xrightarrow{\text{slow}} \text{oxidized intermediate} \xrightarrow{\text{fast}} \text{product} \\
& \quad \downarrow H_2O
\end{align*}
\]

Scheme 3.1

3.1.7 Nature of the Intermediate Species

One school of thought favors an oxoferryl species (por)Fe^{IV}=O formed by the homolysis of the oxidant (Battioni 1986 and 1988, Gopinath 1991 and Panicucci 1990), the other an oxoperferryl species (por)Fe^{V}=O, more likely, (por\{+)Fe^{IV}=O formed by heterolysis (Traylor 1995) (Scheme 3.2).

\[
\begin{align*}
\text{homolytic pathway} & \quad \text{(por) Fe}^{IV}=O \\
\text{(por) Fe}^{IV}=O & \quad \text{compound II} \\
\text{heterolytic pathway} & \quad \text{(por}\{+)Fe^{IV}=O \\
\text{(por}\{+)Fe^{IV}=O & \quad \text{compound I}
\end{align*}
\]

Scheme 3.2
If the reaction proceeds through a radical pathway, a free radical inhibitor should quench the reaction. 2,6-di-tert-butyl-p-cresol has been employed by Guo et al (1999) to prove that the oxidation reactions catalyzed by metalloporphyrins involve radical pathway by their ability to quench substantially the reaction. In our work, benzoic acid, a radical inhibitor in the atmosphere of nitrogen did not quench the reaction rate (vide entry 17 in Table 3.3). Secondly the highly symmetric peroxidic bond of hydrogen peroxide is more liable to homolytic cleavage (Meunier 1988 and Lane 2003). Homolytic pathway of such an epoxidation reaction has also been supported by the literature data (Murata 1990, He 1991 and Meunier 1992). The 'epoxidation factor' is therefore difficult to reconcile with anything other than involvement of the (por)Fe^{IV}=O species in our oxidation of isobutyl 3-butenoate.
3.2 A KINETIC STUDY OF OXIDATIVE DEGRADATION OF F$_{20}$TPPFeCl BY H$_2$O$_2$

We believe that the oxidative destruction of the catalyst, a point often overlooked in such studies is also significant in the chemistry of metalloporphyrins. Even with a reactive substrate such as isobutyl 3-butenolate which left some unbleached catalyst by TLC analysis at the reaction end, a degree of catalyst bleaching was found upon analysis of the reaction by UV-Visible spectroscopy.

3.2.1 Stability of F$_{20}$TPPFeCl in acetonitrile

Before studying the degradation of the catalyst by H$_2$O$_2$ in the absence of a suitable substrate, first we studied the behavior of F$_{20}$TPPFeCl ($1.88 \times 10^{-4}$ mol dm$^{-3}$) in acetonitrile by following UV-Visible spectroscopy (between 250 and 1100 nm). In acetonitrile, a far greater stability was exhibited by F$_{20}$TPPFeCl, which under the conditions studied in the kinetic runs below, showed no degradation.

3.2.2 Interaction of F$_{20}$TPPFeCl with H$_2$O$_2$

We then turned our attention to the oxidation of F$_{20}$TPPFeCl in the absence of substrate. Treatment of micromolar F$_{20}$TPPFeCl with millimolar H$_2$O$_2$ in acetonitrile resulted in bleaching of the former as shown by the disappearance of the Soret band of the metalloporphyrin at 411 nm (Figure 3.5).

3.2.3 Shift of $\lambda_{\text{max}}$ of F$_{20}$TPPFeCl

On closer inspection, the bleaching was seen to be preceded by a rapid shift of the 424 nm peak to one at 411 nm before slower bleaching. Here it is a reasonable supposition to treat this rapid initial shift as the first one of
Figure 3.5 Bleaching of the soret band of iron porphyrin (23.5 × 10⁻⁶ mol dm⁻³) at 411 nm on reaction with hydrogen peroxide (5.0 × 10⁻³ mol dm⁻³). (Spectral scans were taken at 60 sec. intervals)
consecutive reactions in which F$_{20}$TPPFeCl absorbing at 424 nm is converted to the one absorbing at 411 nm prior to the latter’s decomposition (Scheme 3.3). The initial F$_{20}$TPPFeCl ($\lambda_{\text{max}}$=424 nm) was seen to be transformed into an intermediate with $\lambda_{\text{max}}$ of 411 nm before slower bleaching (Figure 3.6). It is reasonable to assume that the compound absorbing at 411 nm is rapidly formed from the one at 424 nm and stoichiometrically equivalent to the latter.

\[
\text{F}_{20}\text{TPPFeCl} \quad \text{1}\textsuperscript{st} \text{Step} \quad \text{intermediate} \quad \text{2}\textsuperscript{nd} \text{Step} \quad \text{bleached product}
\]

\[
(\text{at 424 nm}) \quad \quad \quad \quad (\text{at 411 nm})
\]

\textbf{Scheme 3.3}

Attention was firstly concentrated on the slow second reaction. To determine the reaction order, the kinetics was analyzed omitting the few seconds involving the rapid 424 nm to 411 nm shift.

\textbf{3.2.4 Effect of Varying [F$_{20}$TPPFeCl] in the Absence of Substrate}

Reaction orders have been determined by monitoring the disappearance of F$_{20}$TPPFeCl at 411 nm. Oxidation of F$_{20}$TPPFeCl by H$_2$O$_2$ was investigated at several initial concentrations of F$_{20}$TPPFeCl keeping the other variable such as the concentration of H$_2$O$_2$ constant. A plot of log (absorbance) vs time (Figure 3.7) gave a straight line ($r = 0.996$), indicating a first order dependence of the rate on [F$_{20}$TPPFeCl]. Linearity was not well maintained beyond the plotted limits of the iron porphyrin concentration. Pseudo first order rate constant in each time was calculated from gradient of such a straight line by the method of least squares and is given in Table 3.4.
Figure 3.6  UV-Visible spectra showing the shift of the 424 nm peak to one at 411nm for the H₂O₂ oxidation of F₂₀TPPFeCl. (Spectral scans were taken at 5 sec. intervals with the Scan speed of 900 nm / min.)
Figure 3.7  Plot of log (absorbance) vs time in porphyrin destruction in the absence of substrate
Table 3.4  Values of observed rate constant, $k_{obs}$ for the oxidation of $F_{20}$TPPFeCl by $H_2O_2$ in acetonitrile at 25°C in the absence of substrate.

Dependence of the rate on $[F_{20}$TPPFeCl$]$

$$[H_2O_2] = 2.5 \times 10^{-3} \text{ mol dm}^{-3}$$

<table>
<thead>
<tr>
<th>Entry</th>
<th>$[F_{20}$TPPFeCl$]$ ($\times 10^6$ mol dm$^{-3}$)</th>
<th>$k_{obs}$ ($\times 10^4$ / sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>4.7</td>
<td>18.0</td>
</tr>
<tr>
<td>19</td>
<td>9.4</td>
<td>13.0</td>
</tr>
<tr>
<td>20</td>
<td>14.1</td>
<td>9.0</td>
</tr>
<tr>
<td>21</td>
<td>18.8</td>
<td>5.0</td>
</tr>
<tr>
<td>22</td>
<td>21.15</td>
<td>3.0</td>
</tr>
</tbody>
</table>
3.2.5 Effect of Varying $[\text{H}_2\text{O}_2]$ in the Absence of Substrate

The reaction was followed at 25°C by varying the concentration of oxidant at constant $\text{F}_{20}\text{TPPFeCl}$ (Table 3.5). The order of the reaction was found to be one with respect to the oxidant as evidenced by the linear plot of log $k_{\text{obs}}$ vs log [oxidant] with a slope of unity (Figure 3.8).

3.2.6 Effect of Varying $[\text{F}_{20}\text{TPPFeCl}]$ in the Presence of Substrate

Reaction orders have been determined by monitoring the disappearance of $\text{F}_{20}\text{TPPFeCl}$ at 411 nm in the presence of substrate with the concentration, $10.0 \times 10^{-3}$ mol dm$^{-3}$. Oxidation of $\text{F}_{20}\text{TPPFeCl}$ by $\text{H}_2\text{O}_2$ was investigated at several initial concentrations of $\text{F}_{20}\text{TPPFeCl}$ keeping the other variable such as the concentration of $\text{H}_2\text{O}_2$ constant. The kinetic analysis of the catalyst destruction in the presence of substrate was consistent with the same in the absence of substrate. A plot of log (absorbance) vs time (Figure 3.9) gave a straight line ($r = 0.994$), which indicates that a first order dependence of the rate on $[\text{F}_{20}\text{TPPFeCl}]$. Pseudo first order rate constants are given in Table 3.6.

3.2.7 Effect of Varying $[\text{H}_2\text{O}_2]$ in the Presence of Substrate

The reaction order with respect to the oxidant was found to be one for $\text{F}_{20}\text{TPPFeCl}$-degradation when the reaction was carried out in the presence of substrate ($10 \times 10^{-3}$ mol dm$^{-3}$). A plot of log $k_{\text{obs}}$ vs log [oxidant] gave a straight line with a slope of unity (Figure 3.10). Pseudo first order rate constants are given in Table 3.7.
Table 3.5  Values of observed rate constant, $k_{\text{obs}}$ for the oxidation of F$_{20}$TPPFFeCl by H$_2$O$_2$ in acetonitrile at 25°C in the absence of substrate.

Dependence of the rate on [oxidant]

\[
[F_{20}\text{TPPFFeCl}] = 23.5 \times 10^{-6} \text{ mol dm}^{-3}
\]

<table>
<thead>
<tr>
<th>Entry</th>
<th>$[\text{H}_2\text{O}_2]$ ($\times 10^3 \text{ mol dm}^{-3}$)</th>
<th>$k_{\text{obs}}$ ($\times 10^4 / \text{ sec}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>2.5</td>
<td>3.1</td>
</tr>
<tr>
<td>24</td>
<td>3.0</td>
<td>4.2</td>
</tr>
<tr>
<td>25</td>
<td>3.75</td>
<td>5.4</td>
</tr>
<tr>
<td>26</td>
<td>5.0</td>
<td>7.0</td>
</tr>
<tr>
<td>27</td>
<td>7.5</td>
<td>11.0</td>
</tr>
<tr>
<td>28</td>
<td>12.5</td>
<td>16.5</td>
</tr>
</tbody>
</table>
Figure 3.8 Reaction order with respect to hydrogen peroxide in porphyrin destruction in the absence of substrate
Figure 3.9  Plot of log (absorbance) vs time in porphyrin destruction in the presence of substrate
Table 3.6  Values of observed rate constant, $k_{\text{obs}}$ for the oxidation of $\text{F}_{20}\text{TPPFeCl}$ by $\text{H}_2\text{O}_2$ in acetonitrile at 25°C in the presence of substrate.

**Dependence of the rate on $[\text{F}_{20}\text{TPPFeCl}]$**

$[\text{H}_2\text{O}_2] = 2.5 \times 10^{-3} \text{ mol dm}^{-3}$  
$[\text{substrate}] = 10 \times 10^{-3} \text{ mol dm}^{-3}$

<table>
<thead>
<tr>
<th>Entry</th>
<th>$[\text{F}_{20}\text{TPPFeCl}]$ ($\times 10^6 \text{ mol dm}^{-3}$)</th>
<th>$k_{\text{obs}}$ ($\times 10^4 / \text{ sec}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>29</td>
<td>4.7</td>
<td>0.225</td>
</tr>
<tr>
<td>30</td>
<td>9.4</td>
<td>0.160</td>
</tr>
<tr>
<td>31</td>
<td>14.1</td>
<td>0.130</td>
</tr>
<tr>
<td>32</td>
<td>18.8</td>
<td>0.070</td>
</tr>
<tr>
<td>33</td>
<td>21.15</td>
<td>0.045</td>
</tr>
</tbody>
</table>
Figure 3.10 Reaction order with respect to hydrogen peroxide in porphyrin destruction in the presence of substrate (10 × 10^{-3} mol dm^{-3})

$y = 1.0347x - 1.7866$

$R^2 = 0.9888$
Table 3.7  Values of observed rate constant, $k_{obs}$ for the oxidation of \( \text{F}_{20}\text{TPPFeCl} \) by \( \text{H}_2\text{O}_2 \) in acetonitrile at 25°C in the presence of substrate.

**Dependence of the rate on [oxidant]**

\[
\text{[F}_{20}\text{TPPFeCl]} = 23.5 \times 10^{-6} \text{ mol dm}^{-3} \quad \text{[Substrate]} = 10 \times 10^{-3} \text{ mol dm}^{-3}
\]

<table>
<thead>
<tr>
<th>Entry</th>
<th>([\text{H}_2\text{O}_2]) ((\times 10^3) mol dm(^{-3}))</th>
<th>(k_{obs}) ((\times 10^4) / sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>34</td>
<td>2.5</td>
<td>0.038</td>
</tr>
<tr>
<td>35</td>
<td>3.0</td>
<td>0.053</td>
</tr>
<tr>
<td>36</td>
<td>3.75</td>
<td>0.068</td>
</tr>
<tr>
<td>37</td>
<td>5.0</td>
<td>0.088</td>
</tr>
<tr>
<td>38</td>
<td>7.5</td>
<td>0.138</td>
</tr>
<tr>
<td>39</td>
<td>12.5</td>
<td>0.210</td>
</tr>
</tbody>
</table>
3.2.8  **Nature of the Intermediate**

The initial F\textsubscript{20}TPPFeCl (\(\lambda_{\text{max}}=424\) nm) was seen to be transformed into an intermediate with \(\lambda_{\text{max}}\) of 411 nm before slower bleaching. It is reasonable to assume that the compound absorbing at 411 nm is rapidly formed from the one at 424 nm and stoichiometrically equivalent to the later. Now the question arises as to the nature of the intermediate (\(\lambda_{\text{max}}=411\)nm). Despite a wealth of literature reports on high-valent oxidized intermediates (Groves 1983, 1986 and 1988, Hashimoto 1987, Gold 1988, Yamaguchi 1992, Meunier 2000, Dey 2002), a definitive description of the UV-Visible changes associated with the formation of high-valent iron-oxo porphyrin complexes is hard to find, particularly with respect to the ‘Soret band’. The situation is complicated by solvent variations and variations due to ligation by solvent and added ligands. Furthermore ligation can be differential for the various oxidized states.

Much evidence points to the key species in the degradation of metalloporphyrrin being the iron (IV) oxo radical cation porphyrin species i.e. (F\textsubscript{20}TPP \(\cdot^+\))Fe\textsuperscript{IV}\(=\)O, but it is improbable that our compound is this species. Firstly, the UV-Visible spectrum was not typical of (F\textsubscript{20}TPP \(\cdot^+\))Fe\textsuperscript{IV}\(=\)O. In particular there was no evidence for the absorption above 600 nm typical of the radical cation (Groves 1986, Sugimoto 1988, Colclough 1994). The UV-Visible spectrum (Figure 3.5) suggests, particularly with the small peak at 550 nm, that the intermediate is the oxoferryl species, (F\textsubscript{20}TPP)Fe\textsuperscript{IV}\(=\)O (Colclough 1994 and the references therein).

3.2.9  **Mechanism and Rate Law**

From all the foregoing evidences it is evident that in the absence of substrate the intermediate formed before slower bleaching is *compound II* (Scheme 3.4). *Compound II* is slowly bleached by interaction with \(\text{H}_2\text{O}_2\).
Based on the above results, the rate law can be derived as:

\[
\text{rate} = \frac{-d [F_{20}TPPFeCl]}{dt} = k_2 [\text{Compound II}] [H_2O_2] \quad (3.3)
\]

**3.2.10 Destruction of the Catalyst**

In the catalytic process of hydrogen peroxide activation, metalloporphyrins are converted into highly active oxidant species (intermediate), which, directly or indirectly, can promote the destruction of the catalyst. Some general ways for the catalyst degradation have been considered by Leanord et al (1991). One possibility is the intramolecular decomposition of the highly active species i.e. interaction between two active species thereby leading to catalyst destruction (path ‘a’ in Scheme 3.5) by a process similar to the described ring destruction in supported metalloporphyrins (Leanord 1991, Gilmartin 1995). Other processes of macrocycle destruction of intermolecular nature are the oxidation of another molecule of catalyst by the active intermediate species (path b). Lastly, there is a chance of direct interaction of the active species with oxidant (Traylor 1993, Cunningham 2001 and 2002), which also can destroy the catalyst (path c).
3.2.11 Mechanism of Degradation of $F_{20}$TPPFeCl

Decomposition by oxidation of the porphyrin ring is the least well characterized, but an important mode appears to involve reaction of the unoxidized metalloporphyrin with an oxidized form such as (por)Fe$^{IV} = O$ (intermolecular, path b) (Nappa 1985, Leanord 1991). However, according to Bell (1991), being bimolecular, this mode can be suppressed by the use of sterically hindered metalloporphyrins similar to that of $F_{20}$TPPFeCl. Moreover in the present work, the rate of porphyrin destruction decreased with increase of [porphyrin]. So the intermolecular pathway of macromolecular destruction is ruled out as a major decomposition route.
Furthermore, an intramolecular ‘self-oxidation’ (path a), for example by rearrangement of the \((\text{por})\text{Fe}^{\text{IV}}=\text{O}\) to an iron porphyrin-N-oxide (Groves 1986 and Leanord 1991), would show a first-order dependence on [porphyrin] only. Instead, the kinetic dependence of the decomposition of \((\text{por})\text{Fe}^{\text{IV}}=\text{O}\) on the \([\text{H}_2\text{O}_2]\) indicates an oxidative decomposition of \((\text{por})\text{Fe}^{\text{IV}}=\text{O}\) which probably involves oxidation of the porphyrin by \(\text{H}_2\text{O}_2\) (path c). This is despite the presence of the strongly electron-withdrawing pentafluorophenyl meso-substituents.

3.2.12 Overview of Epoxidation by \(\text{H}_2\text{O}_2\) and \(\text{F}_{20}\text{TPPFeCl}\)

In the \(\text{H}_2\text{O}_2\) oxidation of isobutyl 3-butenoate with \(\text{F}_{20}\text{TPPFeCl}\) as catalyst, the rate-determining step is formation of an oxidized metalloporphyrin intermediate, \textit{oxoferryl species}, \((\text{F}_{20}\text{TPP})\text{Fe}^{\text{IV}}=\text{O}\). Degradation of the metallo porphyrin takes place both in the presence and absence of substrate despite the catalyst is substituted with strong electronegative substituents. The key species in the degradation of metalloporphyrin by \(\text{H}_2\text{O}_2\) is also \textit{oxoferryl species}. Finally, this intermediate decomposes via direct oxidation by \(\text{H}_2\text{O}_2\) to give a bleached product.
3.3 A KINETIC STUDY OF OXIDATIVE DEGRADATION OF $F_{20}TPPFeCl$ BY AcOOH

N-oxidation of pyridine derivatives has been widely investigated (Edwards 1966, Murray 1985, 1995 and 1996, Zhu 1995, Goti 1996, Yamazaki 1997 and Copéret 1998) but not in detail with $F_{20}TPPFeCl$. The substrate, 2-chloropyridine was oxidized (N-oxidized) by this catalyst and oxidant. In metalloporphyrin catalyzed oxidation reactions, the generally accepted mechanism is one that involves slow rate-limiting conversion of the catalyst to an oxidized intermediate, which then transfers oxygen to the substrate in a fast step. Hence we first turned our attention to study the interaction between the oxidant and porphyrin and then the oxidation of a substrate catalyzed by porphyrin. The study of interaction between porphyrin and oxidant was helpful in making the mechanism of oxidation of the substrate catalyzed by porphyrin. The importance of oxidation catalysis versus stability of the catalyst has been taken into consideration here.

3.3.1 Oxidation of $F_{20}TPPFeCl$ by AcOOH in the absence of substrate

In acetonitrile, $F_{20}TPPFeCl$ was highly stable, which did not show any degradation under the conditions studied in the kinetic runs below. UV-Visible spectra of the reaction between iron porphyrin and AcOOH revealed that the initial $F_{20}TPPFeCl$ with Soret $\lambda_{\text{max}}$ 424 nm was converted to a new iron porphyrin with Soret $\lambda_{\text{max}}$ 411 nm and this species subsequently decayed with the fade of band at 411 nm (Figure 3.11). In our work, initial few seconds, which involve the speedy shift of 424 nm to 411 nm, were omitted and the kinetics were analyzed for the slower second reaction i.e. degradation of porphyrin at 411 nm.
Figure 3.11 UV-Visible spectra showing the shift of the 424 nm peak to one at 411 nm for the AcOOH oxidation of F_{20}TPPFeCl. (Spectral scans were taken at 3 min. intervals with the Scan speed of 300 nm/min)
3.3.2 Effect of Varying [F20TPPFeCl]

The absorbance at 411 nm was measured to generate a linear log absorbance vs time plot from which the rate constants (slope= -kobs) were obtained. The pseudo-first-order rate constant values are presented for the effect of varying [F20TPPFeCl] in Table 3.8. A first-order dependence of the rate on [F20TPPFeCl] was observed from the straight line obtained (r = 0.995) by plotting log absorbance against time at fixed [AcOOH] (Figure 3.12). Linearity was not well maintained beyond the plotted limits of the iron porphyrin concentration.

3.3.3 Effect of Varying [AcOOH]

Oxidative degradation of F20TPPFeCl by AcOOH was investigated at several initial concentrations of the oxidant, keeping the concentration of F20TPPFeCl constant. The order with respect to the oxidant was found to be zero because the rate of the reaction was independent of change in concentration of the oxidant. The pseudo-first-order rate constant values for the effect of varying [AcOOH] are presented in Table 3.9.

3.3.4 Pathways for Intermediate-Species Formation

Independent of the nature of the oxidants looked into, the main debate concerns the structure of the high-valent metallo-oxo species generated by the reaction of the oxygen donor with iron porphyrins. In the particular case of oxidations catalyzed by iron porphyrins and promoted by alkyl or acyl peroxides (ROOH), two possible pathways have been envisaged for the
Table 3.8  Values of observed rate constant, $k_{\text{obs}}$ for the oxidation of $\text{F}_{20}\text{TPPFeCl}$ by AcOOH in acetonitrile at 25°C. Dependence of rate on $[\text{F}_{20}\text{TPPFeCl}]$

$[\text{AcOOH}] = 2.5 \times 10^{-3}$ mol dm$^{-3}$

<table>
<thead>
<tr>
<th>Entry</th>
<th>$[\text{F}_{20}\text{TPPFeCl}]$ ($\times 10^6$ mol dm$^{-3}$)</th>
<th>$k_{\text{obs}}$ ($\times 10^4$/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.7</td>
<td>1.0</td>
</tr>
<tr>
<td>2</td>
<td>9.4</td>
<td>0.9</td>
</tr>
<tr>
<td>3</td>
<td>14.1</td>
<td>0.4</td>
</tr>
<tr>
<td>4</td>
<td>18.8</td>
<td>0.3</td>
</tr>
<tr>
<td>5</td>
<td>21.15</td>
<td>0.2</td>
</tr>
</tbody>
</table>
Figure 3.12  Plot of log absorbance against time at fixed [AcOOH] for the oxidative destruction of F_{20}TPPFeCl in the absence of substrate.
Table 3.9  Values of observed rate constant, $k_{obs}$ for the oxidation of $\text{F}_{20}\text{TPPFeCl}$ by $\text{AcOOH}$ in acetonitrile at 25°C. Dependence of rate on $[\text{AcOOH}]$


\[
[F_{20}\text{TPPFeCl}] = 23.5 \times 10^{-6} \text{ mol dm}^{-3}
\]

<table>
<thead>
<tr>
<th>Entry</th>
<th>$[\text{AcOOH}]$ ($\times 10^3$ mol dm$^{-3}$)</th>
<th>$k_{obs}$ ($\times 10^4$/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>2.5</td>
<td>0.5</td>
</tr>
<tr>
<td>7</td>
<td>3.0</td>
<td>0.5</td>
</tr>
<tr>
<td>8</td>
<td>3.75</td>
<td>0.47</td>
</tr>
<tr>
<td>9</td>
<td>5.0</td>
<td>0.5</td>
</tr>
<tr>
<td>10</td>
<td>7.5</td>
<td>0.5</td>
</tr>
<tr>
<td>11</td>
<td>12.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>
formation of the metallo-oxo species: the heterolytic or the homolytic cleavage of the O-O bond in the (por)Fe-O-OR intermediate 1 (Scheme 3.6).

![Scheme 3.6]

### 3.3.5 General Factors Influencing the Reaction Outcome

The mechanism has been investigated in depth by Groves (1987 and 1988), Yamaguchi and Morishima (1992 and 1993), Traylor (1987 and 1989) and Ostavic, Arasasingham and Bruice (1991, 1992 and 1993) who independently recognized some general factors influencing the reaction outcome. These factors can be summarized as follows: (i) electron-donating substituents of acyl peroxides favor the homolytic cleavage and, *vice versa*, electron-withdrawing substituents increase the heterolytic pathway (Groves 1987 and 1988), (ii) the homolytic cleavage of 1 occurs under basic conditions or in the presence of an electron-donating group coordinated to the metal (Groves 1988), (iii) the heterolytic cleavage of 1 is favored by the presence of acid or by a general hydrogen bonding catalysis (Traylor 1987 and Yamaguchi 1992, (iv) from intermediate 1, homolysis produces an
oxoiron (IV) complex 2, while via heterolysis an oxoiron (V) complex (i.e. (por ‘+’)FeIV=O) 3 turns out to be the actual oxidizing species.

3.3.6 Intermediate Species in the Degradation of F20TPPFeCl by AcOOH

Despite a wealth of literature reports on high-valent oxidized intermediates (Groves 1981, Sugimoto 1988, Yamaguchi 1992, Iamamoto 1993, Nam 2000, Dey 2002), a definitive description of the UV-Visible changes associated with the formation of high-valent iron oxo porphyrin complexes is hard to find, particularly with respect to the Soret band. In this degradation of F20TPPFeCl by AcOOH, species 2 was not envisaged because, as said above, its formation is not permitted under acidic conditions. The presence of an oxoiron (V) species, instead of an oxoiron (IV), is defended by the literature data for heterolytic cleavage of the adduct ‘X’ under acidic catalysis (Groves 1987, Traylor 1989, Watanabe 1991, Machii 1995).

3.3.7 Mechanism and Rate Law

Independence of reaction rate on [AcOOH] strongly suggests that (i) the reaction under study occurs through the formation of an intermediate (complex ‘X’) which is the oxoiron (V) precursor; (ii) complex ‘X’ must be formed in a reversible stage because if ‘X’ had been generated through an irreversible stage, the rate of its formation would have a linear first order dependence on [AcOOH] (Banfi 1997). This adduct may be envisaged as a molecular complex between the porphyrin and the oxidant [(por)Fe … HOOAc] or as a peracetate iron salt [(por)Fe-OOAc]. Complexes of Fe- and Mn- porphyrins with AcOOH similar to the latter were proposed as a source of corresponding oxo-complexes (Groves 1983, 1984 and 1986, Machii 1995). Transformation of this by an irreversible step leads to (F20TPP ‘+)FeIV=O. The intermediate (F20TPP ‘+)FeIV=O then decomposes to
give a bleached product. According to these observations the mechanism of $(F_{20}TPP^{+})Fe^{IV}=O$ formation as well as its decomposition can be represented in Scheme 3.7.

$$
\text{F}_{20}\text{TPPFeCl} + \text{AcOOH} \xrightleftharpoons{k_1 \text{ fast}} k_2 \xrightarrow{\text{slow}} \left[ (F_{20}TPP^+)Fe^{IV}=O \right] + \text{AcOH}
$$

**Scheme 3.7**

Based on the above results, the rate law can be derived as:

$$
\text{Rate} = \frac{-d [F_{20}TPPFeCl]}{dt} = k_3 \left[ (F_{20}TPP^+)Fe^{IV}=O \right] \quad (3.4)
$$
3.4 A KINETIC STUDY OF IRON(III)PORPHYRIN MEDIATED BIOMIMETIC N-OXIDATION OF 2-CHLOROPYRIDINE BY AcOOH

The substrate, 2-chloropyridine was oxidized (N-oxidized) by this catalyst and oxidant and UV-Visible overlays showed loss of 2-chloropyridine peak at 280 nm (due to the loss of the chromophore on N-oxidation) in the presence of AcOOH in the medium of acetonitrile. A plot of absorbance vs time is shown in Figure 3.13 and similar plots were obtained for the same reaction at the various concentrations of catalyst, AcOOH and 2-chloropyridine as shown in Tables 3.10 to 3.12.

3.4.1 Effect of Varying [substrate]

Reaction orders have been determined by monitoring the disappearance of 2-chloropyridine at 280 nm in reactions catalyzed by F20TPPFeCl at the stage where the relationship between 2-chloropyridine conversions vs time was linear. We determined the dependence of the reaction rate on 2-chloropyridine, catalyst and oxidant at various concentrations. The reactions were studied at constant temperature (± 0.1 K). Rate constants, \( k_{\text{obs}} \), were evaluated from linear plots of log absorbance against time. Duplicate kinetic runs showed that the rate constants are reproducible to within ± 3 percent. Minimum of five determinations of \( k_{\text{obs}} \) were made for each system change. The reaction was followed at 25°C by varying the substrate concentration at constant [oxidant] and [catalyst]. For all reagent concentrations used, with respect to 2-chloropyridine the kinetic curves obeyed a zero order reaction law. The rate constant values are presented in Table 3.10.
Figure 3.13  Plot of absorbance vs time for the F\textsubscript{20}TPPFeCl-catalyzed oxidation of 2-chloropyridine in acetonitrile at 25\(^\circ\)C. (a) [2-chloropyridine] = 2.5\times 10^{-3} \text{ mol dm}^{-3}, [AcOOH]= 5.0 \times 10^{-3} \text{ mol dm}^{-3} and [F\textsubscript{20}TPPFeCl] = 14.1 \times 10^{-6} \text{ mol dm}^{-3} and (b) [2-chloropyridine] = 2.5 \times 10^{-3} \text{ mol dm}^{-3}, [AcOOH]= 5.0 \times 10^{-3} \text{ mol dm}^{-3} and [F\textsubscript{20}TPPFeCl]=18.8 \times 10^{-6} \text{ mol dm}^{-3}. The absorbance was recorded at 280 nm.
Table 3.10  Values of observed rate constant, $k_{obs}$ for the catalyzed oxidation and catalyst-degradation by AcOOH in acetonitrile at 25°C.

**Dependence of rate on [substrate]**

$[\text{AcOOH}] = 5.0 \times 10^{-3}\text{mol dm}^{-3}$  $[\text{F}_{20}\text{TPPFeCl}] = 9.4 \times 10^{-6}\text{mol dm}^{-3}$

<table>
<thead>
<tr>
<th>Entry</th>
<th>$[2\text{-chloropyridine}]$ ($\times 10^{3}\text{mol dm}^{-3}$)</th>
<th>$k_{obs}$ ($\times 10^{4}/\text{sec}$)</th>
<th>$^a k_{obs}$ ($\times 10^{4}/\text{sec}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>10.0</td>
<td>0.38</td>
<td>0.028</td>
</tr>
<tr>
<td>13</td>
<td>15.0</td>
<td>0.30</td>
<td>0.030</td>
</tr>
<tr>
<td>14</td>
<td>20.0</td>
<td>0.32</td>
<td>0.031</td>
</tr>
<tr>
<td>15</td>
<td>30.0</td>
<td>0.32</td>
<td>0.029</td>
</tr>
<tr>
<td>16</td>
<td>50.0</td>
<td>0.35</td>
<td>0.030</td>
</tr>
</tbody>
</table>

$^a$ $k_{obs}$ was obtained by following the decrease in absorbance at 411 nm during the course of the reaction.
Table 3.11  Values of observed rate constant, $k_{\text{obs}}$ for the catalyzed oxidation and catalyst-degradation by AcOOH in acetonitrile at 25ºC.

**Dependence of rate on [AcOOH]**

\[
[2\text{-chloropyridine}] = 2.5 \times 10^{-3} \text{ mol dm}^{-3} \quad \text{[F}_{20}\text{TPPFeCl}] = 9.4 \times 10^{-6} \text{ mol dm}^{-3}
\]

<table>
<thead>
<tr>
<th>Entry</th>
<th>[AcOOH] ($\times 10^3$ mol dm$^{-3}$)</th>
<th>$k_{\text{obs}}$ ($\times 10^4$/sec)</th>
<th>$^{a} k_{\text{obs}}$ ($\times 10^4$/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>25.0</td>
<td>0.34</td>
<td>0.039</td>
</tr>
<tr>
<td>18</td>
<td>27.5</td>
<td>0.38</td>
<td>0.041</td>
</tr>
<tr>
<td>19</td>
<td>30.0</td>
<td>0.36</td>
<td>0.040</td>
</tr>
<tr>
<td>20</td>
<td>34.0</td>
<td>0.35</td>
<td>0.040</td>
</tr>
<tr>
<td>21</td>
<td>38.0</td>
<td>0.35</td>
<td>0.042</td>
</tr>
<tr>
<td>22</td>
<td>42.5</td>
<td>0.34</td>
<td>0.040</td>
</tr>
</tbody>
</table>

$^{a}$ $k_{\text{obs}}$ was obtained by following the decrease in absorbance at 411 nm during the course of the reaction.
Table 3.12  Values of observed rate constant, $k_{obs}$ for the catalyzed oxidation and catalyst-degradation by AcOOH in acetonitrile at 25°C.

**Dependence of rate on [F$_{20}$TPPF$_{Cl}$]**

$[2$-chloropyridine$] = 2.5 \times 10^{-3}$ mol dm$^{-3}$  
$[\text{AcOOH}] = 5.0 \times 10^{-3}$ mol dm$^{-3}$

<table>
<thead>
<tr>
<th>Entry</th>
<th>[F$<em>{20}$TPPF$</em>{Cl}$] (×10$^6$ mol dm$^{-3}$)</th>
<th>$k_{obs}$ (×10$^4$/sec)</th>
<th>$^a k_{obs}$ (×10$^4$/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>4.7</td>
<td>0.17</td>
<td>0.085</td>
</tr>
<tr>
<td>24</td>
<td>14.1</td>
<td>0.51</td>
<td>0.032</td>
</tr>
<tr>
<td>25</td>
<td>18.8</td>
<td>0.70</td>
<td>0.025</td>
</tr>
<tr>
<td>26</td>
<td>21.15</td>
<td>0.78</td>
<td>0.023</td>
</tr>
<tr>
<td>27</td>
<td>24.0</td>
<td>0.87</td>
<td>0.018</td>
</tr>
</tbody>
</table>

$^a k_{obs}$ was obtained by following the decrease in absorbance at 411 nm during the course of the reaction.
3.4.2 Effect of Varying [oxidant]

Oxidation of 2-chloropyridine by AcOOH in the presence of F$_{20}$TPPFeCl as catalyst was investigated at several initial concentrations of the oxidant, keeping other variables such as concentrations of substrate and catalyst constant. The rate of the reaction was found to be independent of the initial concentration of the oxidant indicating zero order dependence of the rate on [oxidant]. The rate constant values are presented in Table 3.11.

3.4.3 Effect of Varying [catalyst]

At constant [substrate] and [oxidant], the reaction was carried out with five different concentrations of F$_{20}$TPPFeCl. The rate was found to increase steadily with increase in [F$_{20}$TPPFeCl]. The rate constant values are presented in Table 3.12. A linear plot of log $k_{obs}$ vs log [F$_{20}$TPPFeCl] with a slope of unity (Figure 3.14) was a clear indication of first order dependence of the rate of the reaction on [F$_{20}$TPPFeCl].

3.4.4 Nature of Intermediate Species

If the reaction proceeds through a radical pathway, a free radical inhibitor should quench the reaction. Benzoic acid (Serra 2004) and 2,6-di-tert-butyl-p-cresol (Guo 1999) have been employed to prove that the oxidation reactions catalyzed by metalloporphyrins involve radical pathway by their ability to quench substantially the reaction. In our work, benzoic acid, a radical inhibitor in the atmosphere of nitrogen was found to quench the reaction rate. By keeping the concentrations of 2-chloro pyridine, AcOOH and porphyrin constant, $2.5 \times 10^{-3}$, $5.0 \times 10^{-3}$, $21.15 \times 10^{-6}$ mol dm$^{-3}$ respectively and the concentration of benzoic acid, 1.0, 3.0, $5.0 \times 10^{-3}$ mol dm$^{-3}$, the rate constant values observed are 0.62, 0.49, $0.21 \times 10^{-4}$/ sec. Therefore the possibility of existence of (F$_{20}$TPP $^{+}$)Fe$^{IV}$=O is very clear.
Figure 3.14 Reaction order with respect to $F_{20}$TPPFeCl in the $F_{20}$TPPFeCl-catalyzed oxidation of 2-chloropyridine in acetonitrile at 25°C
3.4.5 Mechanism and Rate law

The kinetic results of this system of N-oxidation by AcOOH and \( \text{F}_2\text{TPPFeCl} \) allow us to conclude that the reactive intermediate involved in this system is \((\text{F}_2\text{TPP}^{+})\text{Fe}^{IV} = \text{O}\) and to give a rate law for the \( \text{F}_2\text{TPPFeCl} \) catalyzed N-oxidation of 2-chloro pyridine by AcOOH as

\[
\begin{align*}
\frac{-d\ [\text{2-chloropyridine}]}{dt} &= \frac{d\ [\text{2-Cl.py.N-oxide}]}{dt} & (3.5) \\
&= \frac{d\ [(\text{F}_2\text{TPP}^{+})\text{Fe}^{IV} = \text{O}]}{dt} & (3.6) \\
&= k_{\text{obs}}\ [\text{F}_2\text{TPPFeCl}] & (3.7)
\end{align*}
\]

Independence of reaction rate on 2-chloropyridine proves that \((\text{F}_2\text{TPP}^{+})\text{Fe}^{IV} = \text{O}\) formation occurs in an irreversible stage from intermediate ‘\( X' \). According to all the above observations, the mechanism of \((\text{F}_2\text{TPP}^{+})\text{Fe}^{IV} = \text{O}\) formation as well as 2-chloropyridine oxidation can be best represented in the over all Scheme 3.8.

![Scheme 3.8](image)

\text{Scheme 3.8}
In the case of $\text{F}_{20}\text{TPPFeCl}$ interaction with aryl peracids it was established that the transformation of its peroxo-complex to the corresponding oxene is catalyzed by acid (Groves 1988). Under the reaction conditions used for the kinetic study on the oxidation of 2-chloropyridine, we found that the rate of the oxidation catalyzed by $\text{F}_{20}\text{TPPFeCl}$ was independent of [AcOOH] in the range of the concentration shown in Table 3.11, the acid concentration being much greater than that of the catalyst. The results obtained in this work are very much similar to that of Banfi et al (1997) with Mn-porphyrin and the rate of $(\text{F}_{20}\text{TPP} \cdot \cdot \cdot)^{\text{Fe}^{\text{IV}}=\text{O}}$ formation (Scheme 3.8) can be calculated in the form of quasi-steady state approximation in accordance with Banfi.

$$\text{rate} = \frac{k_1 \times k_2 \times [\text{F}_{20}\text{TPPFeCl}] \times [\text{AcOOH}]}{(k_{-1} + k_2) \times \{1 + k_1 \times [\text{AcOOH}] / (k_{-1} + k_2)\}} \quad (3.8)$$

This is transformed to a rate equation of another form at high [AcOOH], which is identical to the experimental one (3.7).

$$\text{rate} = k_2 \times [\text{F}_{20}\text{TPPFeCl}] \quad (3.9)$$

### 3.4.6 Degradation of $\text{F}_{20}\text{TPPFeCl}$ in the Presence of Substrate

The disappearance of the Soret band of the metalloporphyrin at 411 nm was measured simultaneously along with the measurement of decrease in absorbance at 280 nm (for the loss of 2-chloropyridine) using photometric mode in the spectrophotometer. At different concentrations of substrate, oxidant and catalyst, the rate of the reaction was followed at 411 nm and the effect varying the concentrations of the reactants is given below.
3.4.6.1 **Effect of varying [substrate]**

At constant [oxidant] and [catalyst], the reaction was carried out with five different concentrations of [substrate]. Rate constants were found to be independent of [substrate]. Therefore the degradation reaction followed zero order with respect to substrate. The rate constant values are presented in Table 3.10.

3.4.6.2 **Effect of varying [oxidant]**

The reactions were carried out by varying the [oxidant] in each case while keeping constant all the other factors. The degradation reaction followed zero order with respect to oxidant also. The rate constant values are presented in Table 3.11.

3.4.6.3 **Effect of varying [catalyst]**

Oxidation of $\text{F}_{20}\text{TPPFeCl}$ by AcOOH was investigated at several initial concentrations of $\text{F}_{20}\text{TPPFeCl}$ keeping the other variable such as the concentration of substrate and oxidant constant. A consistency of the kinetic analysis of the catalyst destruction both in the presence and absence of substrate was seen. A plot of $\log$ (absorbance) vs time (Figure 3.15) gave a straight line ($r = 0.992$), which indicates that a first order dependence of the rate on $[\text{F}_{20}\text{TPPFeCl}]$. Pseudo first order rate constant values are given in Table 3.12.

3.4.6.4 **Mechanism of degradation of $\text{F}_{20}\text{TPPFeCl}$**

Independence of the rate of oxidative degradation on [AcOOH] shows that the catalyst-oxidation is not via direct interaction of the catalyst with the oxidant (path ‘c’ in Scheme 3.2.3). The intermolecular pathway for
Figure 3.15 Plot of log absorbance against time for the oxidative destruction of F$_{20}$TPPF eCl in the presence of substrate
the degradation (path ‘b’) is also ruled out since in our case, the rate of
catalyst destruction decreases with increase of [porphyrin]. The first order
dependence of the rate on only [porphyrin] strongly indicates that the
degradation takes place via intramolecular interaction of the active
intermediate iron-oxo species (Scheme 3.9).

\[
\begin{align*}
F_{20}TPPFeCl + AcOOH & \rightarrow F_{20}TPPFeV = O \\
& \text{active metallo-oxo intermediate} \\
& \text{Intramolecular degradation} \\
& \text{Bleached product}
\end{align*}
\]

Scheme 3.9

3.4.7 Substrate Oxidation vs Catalyst Degradation

From the kinetic analysis both in the presence and absence of
substrate, it is clear that there is a competition between the substrate
oxidation cycle, e.g. \(F_{20}TPPFeCl + AcOOH \rightarrow (F_{20}TPP^+)Fe^{IV} = O + 2-\text{cl},py\)
\(\rightarrow N\text{-oxide} + F_{20}TPPFeCl\) and catalyst degradation, e.g. \(F_{20}TPPFeCl + AcOOH \rightarrow \text{catalyst bleaching}\). Even with a substrate such as
2-chloro pyridine which left a little of unbleached catalyst by TLC analysis at
the reaction end, a degree of catalyst bleaching was found upon analysis of
the reaction by UV-Visible spectroscopy. The iron porphyrin complex was
readily destroyed in the absence of an oxygen acceptor and in the presence of
the oxygen acceptor, the destruction was there but little low due to the faster
oxygen transfer to the substrate than to the catalyst.
3.4.8 Overview of N-oxidation by AcOOH and F_{20}TPPFeCl

The mechanism of F_{20}TPPFeCl interaction with peroxy acetic acid in acetonitrile solution includes the reversible stage of molecular complex ‘X’ ‘catalyst …oxidant’ formation. Transformation of this by an irreversible step leads to (F_{20}TPP ^\cdot)^{Fe^{IV}}=O. The efficiency of F_{20}TPPFeCl as an N-oxidation catalyst is a reflection of several competition factors. We believe that the most important competition is that between F_{20}TPPFeCl → (F_{20}TPP ^\cdot)^{Fe^{IV}}=O + 2-cl.py → N-oxide + F_{20}TPPFeCl cycle versus catalyst degradation. Degradation of the catalyst follows intramolecular pathway. Clearly, a catalyst with a very fast oxidation cycle will be seen to be inefficient if it is rapidly degraded.
3.5 A KINETIC STUDY OF OXIDATIVE DEGRADATION OF F\textsubscript{20}TPPFeCl BY OXONE®

Conditions for the efficient use of the catalysts so far reported in the literature require particular specificities and the catalytic activity has been only shown, in the majority of the reported works, in the presence of selected species to act as axial ligand to the metal ion of the catalyst. But the study of oxidative degradation of the catalyst during the course of any reaction has been ignored. The efficiency of any catalyst is a mixed effect of ‘reactivity’ and ‘stability’. So it became essential to investigate the stability of the catalyst along with the catalytic activity for ascertaining the efficiency of the catalyst.

3.5.1 Stability of F\textsubscript{20}TPPFeCl in Acetonitrile and Water

Solvent system for this study was 80 percent water and 20 percent acetonitrile because of the problem of solubility of Oxone® in acetonitrile. First we studied the behavior of F\textsubscript{20}TPPFeCl (1.88 \times 10^{-4} \text{ mol dm}^{-3}) in water and acetonitrile with the above proportion by following UV-Visible spectroscopy (between 250 and 1100 nm). In this solvent system, a far greater stability was exhibited by F\textsubscript{20}TPPFeCl, which showed no degradation under the conditions studied in the kinetic runs below.

3.5.2 Oxidation of F\textsubscript{20}TPPFeCl by Oxone®

The destruction of F\textsubscript{20}TPPFeCl in the presence of Oxone® was studied first before studying the metallloporphyrin-catalyzed oxidation of sulfoxide. Study in the absence of substrate was made to verify the consistency of the behavior of catalyst and oxidant with and without substrate and to get supportive evidence for the mechanism of oxidation catalysis. Treatment of micromolar F\textsubscript{20}TPPFeCl with millimolar Oxone® in acetonitrile and water resulted in bleaching of the former as seen by the disappearance of the Soret band of the metallloporphyrin at 411 nm (Figure 3.16).
Figure 3.16  A plot of absorbance vs wave length showing disappearance of the Soret band of the metalloporphyrin at 411 nm
3.5.3 Shift of $\lambda_{\text{max}}$ of $\text{F}_{20}\text{TPPFeCl}$

On closer inspection, the bleaching was seen to be preceded by a rapid shift of the 424 nm peak to one at 411 nm over 2 minutes before slower bleaching (Figure 3.17). Here it is a reasonable assumption to treat this rapid initial shift as the first reaction of consecutive reactions in which $\text{F}_{20}\text{TPPFeCl}$ absorbing at 424 nm is converted to the one absorbing at 411 nm prior to the latter’s decomposition (Scheme 3.10). Attention was firstly focused on the slower second reaction.

![Scheme 3.10](image)

3.5.4 Effect of Varying [F$_{20}$TPPFeCl] in the Absence of Substrate

Oxidative degradation of $\text{F}_{20}\text{TPPFeCl}$ was investigated at several initial concentrations of $\text{F}_{20}\text{TPPFeCl}$, keeping the other variable such as [oxidant] constant. In each case of study, a plot of log [F$_{20}$TPPFeCl] vs time gave a straight line (Figure 3.18) indicating a first order dependence of the rate on [F$_{20}$TPPFeCl]. Linearity was not well maintained beyond the plotted limits of the iron porphyrin concentration. Values of the pseudo-first-order rate constants for this oxidation reaction are given in Table 3.13.

3.5.5 Effect of Varying [oxidant] in the Absence of Substrate

The reaction was investigated by varying the concentration of oxidant at fixed concentration of F$_{20}$TPPFeCl. The change in concentration of the oxidant did not alter the rate of the reaction. Therefore with respect to
Figure 3.17  UV-Visible spectra showing the shift of the 424 nm peak to one at 411 nm for the oxidation of $\text{F}_{20}\text{TPPFeCl}$ by Oxone$^\circ$. (Spectral scans were taken at 2 min. intervals with the Scan speed of 300 nm/min)
Figure 3.18 Plot of log absorbance against time for the oxidative destruction of F$_{20}$TPPFeCl in the absence of substrate

$R^2 = 0.9938$
Table 3.13  Values of observed rate constant, $k_{\text{obs}}$ for decrease in absorbance at $\lambda$=411nm for the oxidation of F$_{20}$TPPFeCl by Oxone® at 25°C.

Dependence of rate on [F$_{20}$TPPFeCl]

$[\text{oxidant}] = 2.5 \times 10^{-3}$ mol dm$^{-3}$

<table>
<thead>
<tr>
<th>Entry</th>
<th>[F$_{20}$TPPFeCl] ($\times 10^6$ mol dm$^{-3}$)</th>
<th>$k_{\text{obs}}$ ($\times 10^4$/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.7</td>
<td>1.0</td>
</tr>
<tr>
<td>2</td>
<td>9.4</td>
<td>0.91</td>
</tr>
<tr>
<td>3</td>
<td>14.1</td>
<td>1.01</td>
</tr>
<tr>
<td>4</td>
<td>18.8</td>
<td>1.0</td>
</tr>
<tr>
<td>5</td>
<td>21.15</td>
<td>1.0</td>
</tr>
</tbody>
</table>
oxidant the reaction followed zero order kinetics. Values of the pseudo-first-order rate constants for the effect of varying the concentration of the oxidant are given in Table 3.14.

3.5.6 **Nature of the Intermediate with $\lambda_{\text{max}} = 411$ nm**

Main debate in the metalloporphyrin chemistry concerns the type of the intermediate similar to that of the intermediate in this study formed with the $\lambda_{\text{max}}$ of 411 nm. Despite a wealth of literature reports on high-valent oxidized intermediates, the identification of such species is still difficult. The nature of the ‘oxidized intermediate’ has long been the subject of much debate in the field of metalloporphyrin oxidation reactions when formed from reaction with an oxidant such as Oxone$^\circledR$. Some favor an oxoferryl species (por)Fe$^{IV} = $O, biologically called as *compound II*, formed by the homolysis of the oxidant (Battioni 1988, Panicucci 1990, Gopinath 1991), the other an oxoperferryl species (por)Fe$^{V} = $O, more likely, (por$^{+}$)Fe$^{IV} = $O, biologically *compound I* (Traylor 1995), formed by heterolysis (Scheme 3.11).

![Scheme 3.11](image-url)
Table 3.14 Values of observed rate constant, $k_{\text{obs}}$ for decrease in absorbance at $\lambda=411\text{nm}$ for the oxidation of $\text{F}_{20}\text{TPPFeCl}$ by Oxone® at $25^\circ\text{C}$.

Dependence of rate on [Oxidant]

$$[\text{F}_{20}\text{TPPFeCl}] = 23.5 \times 10^{-6} \text{ mol dm}^{-3}$$

<table>
<thead>
<tr>
<th>Entry</th>
<th>[Oxidant]$\times10^3$ mol dm$^{-3}$</th>
<th>$k_{\text{obs}}\times10^4$/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>2.5</td>
<td>1.11</td>
</tr>
<tr>
<td>7</td>
<td>3.0</td>
<td>0.94</td>
</tr>
<tr>
<td>8</td>
<td>3.75</td>
<td>0.92</td>
</tr>
<tr>
<td>9</td>
<td>5.0</td>
<td>1.02</td>
</tr>
<tr>
<td>10</td>
<td>7.5</td>
<td>1.20</td>
</tr>
<tr>
<td>11</td>
<td>12.5</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Much evidence points to the key species in the degradation of metallocoporphyrin being the iron (IV) oxo radical cation porphyrin species, \((\text{por} \cdot ^{+})\text{Fe}^{\text{IV}=\text{O}}\). Traylor (1995) has presented convincing evidence for the heterolysis mechanism. A similar conclusion in favor of the intermediacy of \((\text{por} \cdot ^{+})\text{Fe}^{\text{IV}=\text{O}}\) has been reached by Artaud and Mansuy (1993) involving the same \(F_{20}\text{TPPFeCl}\). Also Oxone\textsuperscript{©} containing KHSO\(_5\) is a monopersulfate derivative with a non-symmetrical peroxodic oxygen-oxygen bond leading to a more favorable position for the heterolytic cleavage of this O-O bond (a step which is required for the formation of high-valent metal-oxo species) than other symmetrical peroxides such as \(K_2S_2O_8\) or even \(H_2O_2\). Therefore it is suggested that before slower bleaching of \(F_{20}\text{TPPFeCl}\), it is compound I, which is formed in the process of degradation.

### 3.5.7 Mechanism and Rate Law

Independent of reaction rate on \([\text{Oxone}^\text{©}]\) indicates strongly that (i) the reaction under study occurs through the formation of an intermediate complex prior to the formation of \((\text{por} \cdot ^{+})\text{Fe}^{\text{IV}=\text{O}}\), (ii) the intermediate complex must be formed in a reversible stage because the rate of its formation should have a linear dependence on \([\text{Oxone}^\text{©}]\) if this complex is generated through an irreversible stage. According to these observations the mechanism of \((\text{por} \cdot ^{+})\text{Fe}^{\text{IV}=\text{O}}\) formation as well as its decomposition can be represented by Scheme 3.12.

\[
\begin{align*}
\text{F}_{20}\text{TPPFeCl} + \text{Oxone}^\text{©} & \xrightleftharpoons[{k_{-1}}]{k_1} \text{intermediate complex} \\
\text{intermediate complex} & \xrightarrow{\text{fast} \ k_2} [(\text{por} \cdot ^{+})\text{Fe}^{\text{IV}=\text{O}}] \\
[(\text{por} \cdot ^{+})\text{Fe}^{\text{IV}=\text{O}}] & \xrightarrow{\text{slow} \ k_3} \text{bleached product}
\end{align*}
\]

**Scheme 3.12**
Based on the above results, the rate law for the oxidative degradation of the porphyrin is derived as:

$$\text{Rate} = \frac{-d [F_{20}TPPFeCl]}{dt} = k_3 [(\text{por}^{\cdot+})\text{Fe}^{IV}=O] \quad (3.10)$$
3.6 A KINETIC STUDY OF IRON(III)PORPHYRIN MEDIATED BIOMIMETIC S-OXIDATION OF SULFOXIDE BY OXONE®

The data reported in this study on the S-oxidation of 4,4'-diacetyldiaminodiphenylsulfoxide indicate that «Oxone®/Iron porphyrin » is an effective biomimetic system for catalytic oxygenations. The main features of the studies on the mechanism of these catalytic oxygenations are those expected for a Cytochrome P-450 model. In addition, the most important advantage of the « Oxone® / Iron porphyrin » is its extension to biological studies.

3.6.1 Oxidation of Sulfoxide

The oxygenation reaction has been performed in a system of buffered water / methanol§. Direct oxidation of water-soluble substrates by Oxone® has also been observed in aqueous methanol (Bloch 1985). Methanol was chosen as organic solvent because of the problem of solubility of the reactants in other solvents. The substrate sulfoxide was efficiently oxidized by this catalyst and oxidant and UV-Visible overlays showed loss of sulfoxide peak at 278 nm in the presence of Oxone® in the medium of water/methanol (80:20). Since Oxone® is soluble in buffered water solution, these metalloporphyrin-catalyzed oxidations can be extended to biochemical studies in physiological conditions. A plot of absorbance vs time is shown in Figure 3.19 and similar plots were obtained for the same reaction at the various concentrations of catalyst, Oxone® and sulfoxide.

§ In water/methanol (80:20), the porphyrin showed high stability in the absence of both oxidant and substrate. λ-max at 210 nm (for methanol) was monitored during the course of the reaction both in the presence and absence of substrate and it was found that there is no methanol loss due to oxidation by Oxone®.
Figure 3.19 A plot of absorbance vs time for $\text{F}_{20}\text{TPPFeCl}$ catalyzed oxidation of sulfoxide by Oxone®. The absorbance was recorded at 278 nm.
3.6.2 Effect of Varying [substrate]

Reaction orders have been determined by monitoring the disappearance of sulfoxide at 278 nm in reactions catalyzed by F$_{20}$TPPFeCl at the early stage of the oxidation where the relationship between sulfoxide conversions vs time was linear. We determined the dependence of the reaction rate on sulfoxide, catalyst and oxidant at various initial concentrations. Rate constants, $k_{\text{obs}}$, were evaluated from linear plots of log absorbance against time. Reaction order determinations were based on the measurements of initial rates at various substrate concentrations with the order being the slope of a plot, which was made between the logarithms of initial reaction rate vs the logarithm of the reactant concentration. The kinetic runs were made at different initial concentrations of substrate. The concentration of oxidant and catalyst were kept constant. It was observed that there is no change in the rate of the reaction by the variation of the concentration of the substrate. The reaction obeyed zero order kinetics with respect to the substrate. The rate constant values are presented in Table 3.15.

3.6.3 Effect of Varying [oxidant]

The reaction was studied at different initial concentrations of oxidant at 25°C, keeping the [substrate] and [catalyst] as constants. The rate constant values are presented in Table 3.16. The order with respect to oxidant was found to be zero because the rate of the reaction was not affected by changing the concentration of the oxidant in the range of the concentration shown in the table.
Table 3.15  Values of observed rate constant, $k_{obs}$ for the F$_{20}$TPPFeCl catalyzed oxidation of sulfoxide by Oxone® at 25°C. Dependence of rate on [Substrate]

\[
\text{[Oxone$^\oplus$]} = 5.0 \times 10^{-3} \text{ mol dm}^{-3} \quad \text{[F$_{20}$TPPFeCl]} = 23.5 \times 10^{-3} \text{ mol dm}^{-3}
\]

<table>
<thead>
<tr>
<th>Entry</th>
<th>[Sulfoxide] $(\times 10^3 \text{ mol dm}^{-3})$</th>
<th>$k_{obs}$ $(\times 10^4/\text{sec})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>2.0</td>
<td>2.05</td>
</tr>
<tr>
<td>13</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>14</td>
<td>4.0</td>
<td>3.1</td>
</tr>
<tr>
<td>15</td>
<td>6.0</td>
<td>2.91</td>
</tr>
<tr>
<td>16</td>
<td>8.0</td>
<td>2.90</td>
</tr>
</tbody>
</table>
Table 3.16  Values of observed rate constant, $k_{\text{obs}}$ for the $F_{20}$TPPFeCl catalyzed oxidation of sulfoxide by Oxone® at 25°C. Dependence of rate on [Oxidant]

[Substrate] = $5.0 \times 10^{-3}$ mol dm$^{-3}$  [F$_{20}$TPPFeCl] = $23.5 \times 10^{-3}$ mol dm$^{-3}$

<table>
<thead>
<tr>
<th>Entry</th>
<th>[Oxone®] ($\times 10^3$ mol dm$^{-3}$)</th>
<th>$k_{\text{obs}}$ (x10$^4$/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>51.0</td>
<td>12.11</td>
</tr>
<tr>
<td>18</td>
<td>58.0</td>
<td>12.30</td>
</tr>
<tr>
<td>19</td>
<td>62.0</td>
<td>11.48</td>
</tr>
<tr>
<td>20</td>
<td>66.0</td>
<td>11.20</td>
</tr>
<tr>
<td>21</td>
<td>76.0</td>
<td>12.04</td>
</tr>
</tbody>
</table>
3.6.4 Effect of Varying [catalyst]

At constant [substrate], [oxidant] and temperature, the reaction was carried out with five different concentrations of F$_{20}$TPPFeCl. Rate constants were found to increase as the concentration of F$_{20}$TPPFeCl increased. The order with respect to [F$_{20}$TPPFeCl] was found to be one as evidenced by the plot log $k_{\text{obs}}$ vs log [F$_{20}$TPPFeCl] with the slope of unity (Figure 3.20). The rate constant values are presented in Table 3.17.

3.6.5 Rate Equation and General Mechanism

With respect to F$_{20}$TPPFeCl, the order of the reaction was found to be one. In contrast the dependence on [sulfoxide] and [Oxone®] was zero order and overall we propose the rate equation as shown below:

\[
\frac{d \text{[sulfone]}}{dt} = -\frac{d \text{[sulfoxide]}}{dt} = k_{\text{obs}}[F_{20}\text{TPPFeCl}] \tag{3.11}
\]

The type of above rate equation is consistent with the mechanism of metalloporphyrin-catalyzed oxidation shown in Scheme 3.13, which involves slow rate-limiting formation of an oxidized intermediate from a porphyrin-oxidant complex, which then transfers oxygen to the substrate in a fast step.

![Scheme 3.13](image-url)
Figure 3.20  Reaction order with respect to F_{20}TPPFeCl in F_{20}TPPFeCl-
catalyzed oxidation of sulfoxide in acetonitrile at 25°C
Table 3.17  Values of observed rate constant, $k_{\text{obs}}$ for the F$_{20}$TPPFeCl catalyzed oxidation of sulfoxide by Oxone® at 25°C. Dependence of rate on [Catalyst]

[Substrate] = 5.0 × 10$^{-3}$ mol dm$^{-3}$  
[Oxidant] = 5.0 × 10$^{-3}$ mol dm$^{-3}$

<table>
<thead>
<tr>
<th>Entry</th>
<th>$[\text{F}_{20}\text{TPPFeCl}]$ (×10$^6$ mol dm$^{-3}$)</th>
<th>$k_{\text{obs}}$ (×10$^4$/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>4.7</td>
<td>1.84</td>
</tr>
<tr>
<td>23</td>
<td>9.4</td>
<td>4.00</td>
</tr>
<tr>
<td>24</td>
<td>14.1</td>
<td>6.32</td>
</tr>
<tr>
<td>25</td>
<td>18.8</td>
<td>8.27</td>
</tr>
<tr>
<td>26</td>
<td>21.15</td>
<td>9.22</td>
</tr>
</tbody>
</table>
3.6.6 Oxidized Intermediate

The general mechanism shown in Scheme 3.13 for metalloporphyrin-catalyzed oxidation is widely accepted. However, the nature of the ‘oxidized intermediate’ has been the subject of much debate when formed from reaction with oxidant such as Oxone®. If the reaction proceeds through a radical pathway, a free radical inhibitor should quench the reaction. In our work, benzoic acid, a radical inhibitor in the atmosphere of nitrogen was found to quench the reaction rate (data not shown).

In the light of all the above forgoing evidences from the study of oxidation reaction catalyzed by F_{20}TPPFeCl both in the presence and absence of substrate, a high-valent iron-oxo(V)porphyrin i.e. (por·+)Fe^{IV}=O is suggested as an intermediate in the oxidation of sulfoxide. Oxo derivatives of Fe and Mn (V) have been proposed to take part in oxidation processes and have been characterized in some cases by spectroscopy and even isolated (Chellamani 1995, Limburg 1999, Watanabe 2000, Meunier 2000, Dey 2002, Meyer 2005). A free sulfur-centered radical cation is not suggested here as an active intermediate in agreement with results of Baciocchi (1992 and 1994), because of the absence of any by-product arising from the cleavage of sulfide radical cations as potential intermediates (Battioni 1988, Traylor 1995).

3.6.7 Oxygen-Exchange

Most of the studies to determine the origin of the incorporated oxygen atom in the oxidation reactions catalyzed by metalloporphyrins have been performed in organic solvents or biphasic media with hydrophobic complexes. From these data it has been concluded that the oxygen atom originates from the primary oxidant, PhIO (Ortiz de Montellano 1995, Heimbrook 1987), LiOCl and KHSO_{5} (Meunier 1984). Although in the case
of iodosylbenzene, early experiments (Ortiz de Montellano 1995) suggested that high-valent iron-oxo complexes can exchange the coordinated oxygen atom with labeled water, a re-evaluation of $^{18}$O incorporation in metalfoporphyrin-mediated oxygenation reactions carried out in the presence of H$_2^{18}$O by Nam and Lee (1993 and 1997) indicated that the metal-oxo species does not quickly exchange its oxygen atom with water. The rate of such an exchange reaction is far below the rate of oxygen incorporation into the organic substrate. This higher efficiency in the capability of oxygen transfer in aqueous solutions is essentially due to the non-symmetrical peroxodic bond of the monopersulfate compared to the highly symmetric one of hydrogen peroxide more liable to homolytic cleavage.

In the case of oxygenations catalyzed by Cytochrome P-450, the source of the incorporated oxygen was molecular oxygen rather than water (Heimbrook 1987). Khenkin et al (1993) have proved that the oxygen exchange between high-valent metal oxo complex and water is slow relative to the rate of substrate oxidation. These data indicate that the oxygen transfer from the oxidant to the metalloporphyrin and then to the substrate is faster than any oxygen exchange between this oxidant and water molecules. The absence of oxygen exchange with water was previously reported in NaOCl-metalloporphyrin oxidations (Meunier 1984) and with hydrogen peroxide, alkyl hydro peroxide or ascorbic acid / O$_2$ as oxygen source in oxygenation of cis-stilbene catalyzed by iron-bleomycin (Heimbrook 1987).

The accumulated data on the influence of the porphyrin ligand on the relative reactivity of different substrates, the kinetics and the quantitative incorporation of one oxygen into the substrate strongly suggest that the catalytic S-oxidation is consistent with the direct transfer of an oxygen atom from a high-valent metal-oxo intermediate to the substrate. Therefore a mechanism involving direct oxygen transfer to sulfoxide in a process similar
to that for catalyzed epoxidation (Ostovic 1992, Traylor 1993) can be reasonably proposed (Scheme 3.14).

\[
\text{Por. M} \xrightarrow{\text{(O)}} \text{Por. M-OOR} \xrightarrow{} \text{Por. M=O} \xrightarrow{R_2SO} R_2SO_2
\]

Scheme 3.14

3.6.8 Destruction of \(F_{20}TPPFeCl\) in the Presence of Substrate

\(F_{20}TPPFeCl\) destruction was monitored at 411 nm during the course of the catalyzed oxidation of sulfoxide to sulfone by involving photometric mode in the spectrophotometer.

3.6.8.1 Effect of varying \([F_{20}TPPFeCl]\)

Varying the concentration of porphyrin and keeping the concentration of oxidant constant investigated the rate of the porphyrin destruction. When a plot of log absorbance against time was made, a straight line was obtained. Therefore the rate of porphyrin destruction was first order with respect to \(F_{20}TPPFeCl\). The pseudo first order rate constant values are presented in Table 3.18.

3.6.8.2 Effect of varying [oxidant]

Varying the concentration of oxidant and keeping the concentration of porphyrin constant investigated the rate of the porphyrin destruction. The rate was found to be independent of the oxidant concentration and hence zero order with respect to oxidant. The pseudo first order rate constant values are presented in Table 3.19.
Table 3.18  Values of observed rate constant, \( k_{\text{obs}} \) for decrease in absorbance at \( \lambda = 411\text{nm} \) for the oxidation of F\(_{20}\)TPPFeCl by Oxone\(^\circledast\) at 25\(^{\circ}\)C with the concentration of the substrate 5.0\times10^{-3} \text{ mol dm}^{-3}

Dependence of rate on [F\(_{20}\)TPPFeCl]

\[
[\text{Oxidant}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}
\]

<table>
<thead>
<tr>
<th>Entry</th>
<th>([\text{F}_{20}\text{TPPFeCl}] \times 10^6 \text{ mol dm}^{-3})</th>
<th>(k_{\text{obs}} \times 10^4/\text{sec})</th>
</tr>
</thead>
<tbody>
<tr>
<td>27</td>
<td>4.7</td>
<td>0.20</td>
</tr>
<tr>
<td>28</td>
<td>9.4</td>
<td>0.18</td>
</tr>
<tr>
<td>29</td>
<td>14.1</td>
<td>0.13</td>
</tr>
<tr>
<td>30</td>
<td>18.8</td>
<td>0.075</td>
</tr>
<tr>
<td>31</td>
<td>21.15</td>
<td>0.04</td>
</tr>
</tbody>
</table>
Table 3.19  
Values of observed rate constant, $k_{\text{obs}}$ for decrease in absorbance at $\lambda$=411nm for the oxidation of $\text{F}_{20}\text{TPPFeCl}$ by Oxone® at 25°C with the concentration of the substrate $5.0 \times 10^{-3}$ mol dm$^{-3}$

Dependence of rate on [Oxidant]

$[\text{F}_{20}\text{TPPFeCl}] = 23.5 \times 10^{-3}$ mol dm$^{-3}$

<table>
<thead>
<tr>
<th>Entry</th>
<th>[Oxone®] $\times 10^3$ mol dm$^{-3}$</th>
<th>$k_{\text{obs}} \times 10^4$/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>32</td>
<td>51.0</td>
<td>0.22</td>
</tr>
<tr>
<td>33</td>
<td>58.0</td>
<td>0.25</td>
</tr>
<tr>
<td>34</td>
<td>62.0</td>
<td>0.22</td>
</tr>
<tr>
<td>35</td>
<td>66.0</td>
<td>0.20</td>
</tr>
<tr>
<td>36</td>
<td>76.0</td>
<td>0.26</td>
</tr>
</tbody>
</table>
3.6.8.3  Mechanism of oxidative destruction of F$_{20}$TPPFeCl

From the kinetic analysis of destruction of F$_{20}$TPPFeCl, it is evident that the iron porphyrin is readily destroyed giving a yellow-brown non-assignable product in the absence of an oxygen acceptor and in its presence, the destruction is little low due to the fast oxygen transfer to the substrate than to the catalyst (Figures 3.21 and 3.22). Our results suggest clearly that among the various possible fates of the intermediate species, which is assumed to be the active form of the catalyst for sulfide and sulfoxide oxidation as for alkene epoxidation (Ostovic 1992 and Traylor 1993), route b of Scheme 3.15 is of comparable importance when the catalyst is even sterically hindered pentafluorophenyl substituted iron porphyrin.

![Scheme 3.15](image)

**Scheme 3.15**

3.6.9  Rate Law

Under the reaction conditions used for the kinetic study on sulfoxide oxidation we found that the rate of the oxidation catalyzed by F$_{20}$TPPFeCl was independent of [Oxone®] in the range of the concentration shown in Tables 3.16 and 3.19, the oxidant concentration being much greater than that of the catalyst. From Scheme 3.15, the rate of (por$^+$)$^\text{IV}$Fe$^\text{IV}$ formation can be calculated in the form of quasi-steady state approximation.
This is transformed to a rate equation of another form at high [Oxone\textsuperscript{\circledast}], which is identical to the experimental one (3.11).

\[
\text{rate} = k_2 [F_{20}TPPFeCl] \quad \text{(3.13)}
\]

3.6.10 Degradation Pathway

In the present system of S-oxidation of 4,4'-diacetyl diamino diphenyl sulfoxide in the presence of Oxone\textsuperscript{\circledast} and iron porphyrin catalyst, while the oxidation was promoted by the catalyst, its oxidative destruction also was taking place. The decrease in porphyrin destruction with increase in [porphyrin] rules out the possibility, unoxidized catalyst + oxidized intermediate $\rightarrow$ bleached catalyst. Kinetic independence of the degradation rate on [oxidant] rules out another possibility, oxidant + oxidized intermediate $\rightarrow$ bleached catalyst. The only way, by which the catalyst undergoes degradation in the current investigation is via intramolecular self-oxidation, oxidized intermediate + oxidized intermediate $\rightarrow$ bleached catalyst. Support in favor of this route comes from the first order dependence of rate on only [porphyrin] in porphyrin destruction, which is required for the intramolecular mechanism to be operative.

3.6.11 Overview of S-oxidation by Oxone\textsuperscript{\circledast} and F\textsubscript{20}TPPFeCl

The mechanism of reaction between F\textsubscript{20}TPPFeCl and Oxone\textsuperscript{\circledast} includes the formation of molecular complex, ‘catalyst ...oxidant’ in a reversible way. Transformation of this by an irreversible step leads to (por\textsuperscript{\textbullet\textsuperscript{+}})Fe\textsuperscript{IV}=O. The efficiency of F\textsubscript{20}TPPFeCl as an S-oxidation catalyst is a
Figure 3.21 Plot of absorbance vs time for (a) $F_{20}$TPPFeCl- catalyzed oxidation of sulfoxide and (b) porphyrin destruction in the presence of substrate. The absorbance was recorded at (a) 278 nm and (b) 411 nm.
Figure 3.22 Plot of absorbance vs time to show the first 20% of the reaction. (a) F$_{20}$TPPFeCl-catalyzed oxidation of sulfoxide and (b) porphyrin destruction in the presence of substrate. The absorbance was recorded at (a) 278 nm and (b) 411 nm.
reflection of several competition factors. So we again believe that the most important competition is that between $F_{20}TPPFeCl \rightarrow (por \cdot +)Fe^{IV} = O +$ sulfoxide $\rightarrow$ sulfone $+ F_{20}TPPFeCl$ cycle versus catalyst bleaching. The bleaching follows intramolecular self-oxidation pathway. The competition between these two factors may help to rationalize the often-contradictory comments on metalloporphyrin reactivity found in the literature.
3.7 A KINETIC STUDY OF OXIDATIVE DEGRADATION OF 
$F_{20}$TPPFeCl BY m-CPBA

There is a very limited number of works that has been devoted to 
study the stability of metalloporphyrin such as $F_{20}$TPPFeCl, that too in the 
presence of oxidant such as H$_2$O$_2$ (Serra 2004). The study on the stability of 
$F_{20}$TPPFeCl during the course of the oxidation reactions by m-CPBA is very 
rare. This work deals with the degradation of sterically hindered $F_{20}$TPPFeCl 
both in the presence and absence of a substrate. It gives more insight into the 
mechanism of the oxidation reactions catalyzed by metalloporphyrins when a 
study is made in detail on the interaction between the oxidant and catalyst in 
the absence of substrate.

3.7.1 Oxidation of $F_{20}$TPPFeCl by m-CPBA

We turned our attention to the oxidative destruction of $F_{20}$TPPFeCl 
in the presence of m-CPBA. When $F_{20}$TPPFeCl in micromolar amount was 
treated with m-CPBA in millimolar, bleaching of the former took place with 
the disappearance of the Soret band of the metalloporphyrin at 411 nm. On 
closer inspection, it was observed that the bleaching is preceded by a fast shift 
of the peak at 424 nm to one at 411 nm before slower bleaching. It can be 
assumed here that this rapid initial shift is one of the first consecutive 
reactions in which $F_{20}$TPPFeCl absorbing at 424 nm is converted to the one 
absorbing at 411 nm prior to the latter’s decomposition. We focused on the 
slower second reaction. The kinetics were analyzed after omitting the few 
seconds involving the rapid 424 to 411 nm shift to determine the reaction 
order.
3.7.2 **Effect of Varying [F_{20}TPPPFeCl]**

The oxidative destruction of F_{20}TPPPFeCl was investigated at several initial concentrations of F_{20}TPPPFeCl keeping the other variable such as [oxidant] constant. In each case, the plot of log [F_{20}TPPPFeCl] vs time (not shown) gave a straight line (r = 0.994), indicating a first order dependence of rate on [F_{20}TPPPFeCl]. The pseudo first order rate constants are given in Table 3.20.

3.7.3 **Effect of Varying [m-CPBA]**

The reaction was carried out by varying the [m-CPBA] in each case while keeping constant all the other factors. With respect to m-CPBA, the order of the reaction was found to be fractional as evidenced by the linear plot of log \(k_{obs}\) vs log [m-CPBA] with a slope of 0.56 (Figure 3.23). A plot of \(1/k_{obs}\) against \(1/[m-CPBA]\) is linear and does not pass through the origin (Figure 3.24) indicating that a complex is formed prior to the rate-limiting step. The rate constant values are presented in Table 3.21.

3.7.4 **Effect of Temperature**

The reaction was carried out at five different temperatures viz., 298, 303, 308, 313 and 318 K, keeping [F_{20}TPPPFeCl] and [m-CPBA] as constants. The \(k_{1.56}\) values are given in Table 3.22.

From the Eyring’s equation,

\[
\ln \left( \frac{k_2}{T} \right) = 23.7604 + \left( \frac{\Delta S^\#}{0.008318} \right) - \left( \frac{\Delta H^\#}{0.008318} \right) \frac{1}{T}
\]

---

\(^8\) While the effect of temperature could not be studied for the other systems, the reason being the instability of either oxidants or substrates in high temperatures, it was possible with the system using m-CPBA in the absence of substrate.
Table 3.20  Values of observed rate constant, $k_{\text{obs}}$ for decrease in absorbance at $\lambda=411$nm for the oxidation of $\text{F}_{20}\text{TPPFeCl}$ by m-CPBA at 25°C.

Dependence of rate on $[\text{F}_{20}\text{TPPFeCl}]$

$m$-CPBA = $2.5 \times 10^{-3}$ mol dm$^{-3}$

<table>
<thead>
<tr>
<th>Entry</th>
<th>$[\text{F}_{20}\text{TPPFeCl}]$ ($\times 10^6$ mol dm$^{-3}$)</th>
<th>$k_{\text{obs}}$ ($\times 10^4$/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.7</td>
<td>9.0</td>
</tr>
<tr>
<td>2</td>
<td>9.4</td>
<td>8.0</td>
</tr>
<tr>
<td>3</td>
<td>14.1</td>
<td>7.0</td>
</tr>
<tr>
<td>4</td>
<td>18.8</td>
<td>6.0</td>
</tr>
<tr>
<td>5</td>
<td>21.15</td>
<td>5.0</td>
</tr>
</tbody>
</table>
Figure 3.23  Reaction order with respect to m-CPBA in the oxidation of F_{20}TPPF\text{FeCl} by m-CPBA
Figure 3.24  Plot of $1/k_{obs}$ vs $1/[^m\text{-CPBA}]$ in the oxidation of $F_{20}\text{TPPFeCl}$ by $m$-CPBA
Table 3.21  Values of observed rate constant, $k_{obs}$ for decrease in absorbance at $\lambda=411\text{nm}$ for the oxidation of $F_{20}\text{TPPFeCl}$ by m-CPBA at 25°C.

Dependence of rate on [m-CPBA]

$$[F_{20}\text{TPPFeCl}] = 23.5 \times 10^{-6} \text{ mol dm}^{-3}$$

<table>
<thead>
<tr>
<th>Entry</th>
<th>[Oxidant] $\times 10^3$ mol dm$^{-3}$</th>
<th>$k_{obs} \times 10^4$/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>2.5</td>
<td>8.0</td>
</tr>
<tr>
<td>7</td>
<td>3.0</td>
<td>9.0</td>
</tr>
<tr>
<td>8</td>
<td>3.75</td>
<td>10.0</td>
</tr>
<tr>
<td>9</td>
<td>5.0</td>
<td>12.0</td>
</tr>
<tr>
<td>10</td>
<td>7.5</td>
<td>15.0</td>
</tr>
<tr>
<td>11</td>
<td>12.5</td>
<td>20.0</td>
</tr>
</tbody>
</table>
Table 3.22  Values of rate constants for decrease in absorbance at 
$\lambda$=411nm for the oxidation of F$_{20}$TPPFeCl by m-CPBA in 
acetonitrile at temperatures 298 to 318 K.

Dependence of rate on Temperature

[m-CPBA]=5.0 $\times$ 10$^{-3}$ mol dm$^{-3}$  [F$_{20}$TPPFeCl] =9.4$\times$10$^{-6}$ mol dm$^{-3}$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Temperature (K)</th>
<th>$k_{obs}$ $\times$ 10$^4$/ sec</th>
<th>$k_{1.56}$ $\times$ 10$^3$ 1$^{0.56}$ mol$^{0.56}$/ sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>298</td>
<td>2.0</td>
<td>3.88</td>
</tr>
<tr>
<td>13</td>
<td>303</td>
<td>3.0</td>
<td>5.83</td>
</tr>
<tr>
<td>14</td>
<td>308</td>
<td>4.7</td>
<td>9.14</td>
</tr>
<tr>
<td>15</td>
<td>313</td>
<td>7.0</td>
<td>13.61</td>
</tr>
<tr>
<td>16</td>
<td>318</td>
<td>9.1</td>
<td>17.69</td>
</tr>
</tbody>
</table>
$\Delta H^\#$ and $\Delta S^\#$ values were calculated from the slope and intercept of the plot, $\ln \left( \frac{k_{1.56}}{T} \right)$ vs $1/T$ respectively (Figure 3.25). Thus

$$\Delta H^\# = -\text{slope} \times 0.008318 \text{ k J mol}^{-1} \quad (3.14)$$

and

$$\Delta S^\# = (\text{intercept} - 23.7604) \times 8.318 \text{ J K}^{-1}\text{mol}^{-1} \quad (3.15)$$

From these equations, $\Delta H^\#$ and $\Delta S^\#$ values were calculated and found to be 57.95 kJmol$^{-1}$ and $-96.66$ JK$^{-1}$mol$^{-1}$ respectively.

### 3.7.5 Mechanism and Rate Law

Under the experimental conditions employed in the present study, $F_{20}\text{TPPFeCl}$ was oxidized by $m$-CPBA. The reaction showed first order dependence on $[F_{20}\text{TPPFeCl}]$ and fractional order dependence on $[m$-CPBA$. A linear plot of $1/k_{\text{obs}}$ vs $1/[m$-CPBA$]$ with a finite intercept suggests Michaelis-Menten type mechanism in which a complex is formed between iron porphyrin and oxidant prior to the rate-limiting step. Thus a generalized scheme for such oxidation reaction is represented in Scheme 3.16.

![Scheme 3.16](image-url)
Figure 3.25 A plot of $\ln \left( \frac{k_{1.56}}{T} \right)$ vs $1/T$ to arrive $\Delta H^\circ$ and $\Delta S^\circ$.
The mechanism (shown in Scheme 3.16) of bleaching of F$_{20}$TPPFeCl leads to the following rate law:

$$\text{rate} = \frac{-d[F_{20}\text{TPPFeCl}]}{dt} = k_{\text{obs}} [F_{20}\text{TPPFeCl at 411nm}] [\text{m-CPBA}]^{0.56}$$  \hspace{1cm} (3.16)

### 3.7.6 Intermediate Before Bleaching

Now the question arises as to the nature of the intermediate ($\lambda_{\text{max}} = 411$ nm) formed by homolytic cleavage or heterolytic cleavage (Scheme 3.17). Despite the identification of such species is still difficult, a wealth of literature reports on high-valent oxidized intermediates.

![Scheme 3.17](image)

**Scheme 3.17**

Much evidence points to the key species in the degradation of metalloporphyrin being the iron (IV) oxo radical cation porphyrin species, (F$_{20}$TPP $^+$) Fe IV=O. Traylor (1995) has presented convincing evidence for the heterolysis mechanism. Moreover m-CPBA has long been employed as a useful oxidant in generating a reactive intermediate, a high-valent iron (IV) oxo porphyrin cation radical (Groves 1981, Mandon 1992). Therefore it is *compound I* that is bleached in the presence of oxidant.
3.8 A KINETIC STUDY OF IRON(III)PORPHYRIN MEDIATED BIOMIMETIC EPOXIDATION BY m-CPBA

The epoxidation of the substrate isobutyl 3-butenoate took place efficiently by F$_{20}$TPPFeCl and UV-Visible overlays showed loss of isobutyl 3-butenoate peak at 270 nm in the presence m-CPBA in the medium of acetonitrile. The reaction was sluggish in the absence of catalyst. A plot of absorbance vs time is shown in Figure 3.26 and similar plots were obtained for the same reaction at the various concentrations of catalyst, m-CPBA and isobutyl 3-butenoate as shown in Tables 3.23 to 3.25. Reaction orders have been determined by monitoring the disappearance of isobutyl 3-butenoate in reactions catalyzed by F$_{20}$TPPFeCl at the early stage of the epoxidation reaction where the relationship between olefin conversions vs time was linear. We determined the dependence of the reaction rate on olefin, catalyst and oxidant at various initial concentrations. Reaction order determinations were made from the slope of a plot between logarithms of $k_{obs}$ at various concentrations of the reactant and the logarithm of the concentration of the reactant.

3.8.1 Effect of Varying [substrate]

At constant [oxidant] and [F$_{20}$TPPFeCl], the reaction was carried out with five different concentrations of substrate. Rate constants were found to be independent of [substrate] in all the cases and therefore with respect to substrate, the reaction followed zero order kinetics. The rate constant values are presented in Table 3.23.
Figure 3.26 Plot of absorbance vs time for the F<sub>20</sub>TPPFeCl-catalyzed oxidation of Isobutyl 3-butenoate by m-CPBA in acetonitrile at 25°C. [isobutyl 3-butenoate] = 10.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>, [m-CPBA] = 5.0 × 10<sup>-3</sup> mol dm<sup>-3</sup> and [F<sub>20</sub>TPPFeCl] = 23.5 × 10<sup>-6</sup> mol dm<sup>-3</sup>. The absorbance was recorded at 270 nm.
Table 3.23  Values of observed rate constant, $k_{obs}$ for the F$_{20}$TPPFeCl catalyzed oxidation of Isobutyl 3-butenolate by m-CPBA in acetonitrile at 25°C.

Dependence of rate on [Substrate]

$m$-CPBA $= 5.0 \times 10^{-3} \text{ mol dm}^{-3}$  
$[F_{20}\text{TPPFeCl}] = 23.5 \times 10^{-6} \text{ mol dm}^{-3}$

<table>
<thead>
<tr>
<th>Entry</th>
<th>[isobutyl 3-butenolate] $(\times 10^3 \text{ mol dm}^{-3})$</th>
<th>$k_{obs}$ $(\times 10^4$/sec$)$</th>
<th>$^a k_{obs}$ $(\times 10^4$/sec$)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>12.5</td>
<td>52.58</td>
<td>0.24</td>
</tr>
<tr>
<td>18</td>
<td>16.0</td>
<td>54.02</td>
<td>0.32</td>
</tr>
<tr>
<td>19</td>
<td>26.0</td>
<td>53.91</td>
<td>0.37</td>
</tr>
<tr>
<td>20</td>
<td>35.0</td>
<td>53.47</td>
<td>0.28</td>
</tr>
<tr>
<td>21</td>
<td>51.0</td>
<td>53.80</td>
<td>0.25</td>
</tr>
</tbody>
</table>

$^a$ $k_{obs}$ was obtained by following the decrease in absorbance at 411nm during the course of the reaction.
Table 3.24  Values of observed rate constant, $k_{obs}$ for the F$_{20}$TPPFeCl catalyzed oxidation of Isobutyl 3-butenolate by m-CPBA in acetonitrile at 25°C.

Dependence of rate on [Oxidant]

[Substrate] = 10.0 $\times$ 10$^{-3}$ mol dm$^{-3}$  
[F$_{20}$TPPFeCl] = 23.5 $\times$ 10$^{-6}$ mol dm$^{-3}$

<table>
<thead>
<tr>
<th>Entry</th>
<th>[m-CPBA] ($\times$10$^{3}$mol dm$^{-3}$)</th>
<th>$k_{obs}$ ($\times$10$^{4}$/sec)</th>
<th>$^{a}k_{obs}$ ($\times$10$^{4}$/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>2.5</td>
<td>47.86</td>
<td>0.35</td>
</tr>
<tr>
<td>23</td>
<td>3.0</td>
<td>54.02</td>
<td>0.38</td>
</tr>
<tr>
<td>24</td>
<td>3.75</td>
<td>69.0</td>
<td>0.43</td>
</tr>
<tr>
<td>25</td>
<td>5.0</td>
<td>84.42</td>
<td>0.52</td>
</tr>
<tr>
<td>26</td>
<td>7.5</td>
<td>112.24</td>
<td>0.65</td>
</tr>
<tr>
<td>27</td>
<td>12.5</td>
<td>149.56</td>
<td>0.78</td>
</tr>
</tbody>
</table>

$^{a}$ $k_{obs}$ was obtained by following the decrease in absorbance at 411nm during the course of the reaction.
### Table 3.25  Values of observed rate constant, $k_{\text{obs}}$ for the F$_{20}$TPPFeCl catalyzed oxidation of Isobutyl 3-butenoate by m-CPBA in acetonitrile at 25°C.

**Dependence of rate on [F$_{20}$TPPFeCl]**

[Substrate] = $10.0 \times 10^{-3}$ mol dm$^{-3}$  
[Oxidant] = $2.5 \times 10^{-3}$ mol dm$^{-3}$

<table>
<thead>
<tr>
<th>Entry</th>
<th>[F$_{20}$TPPFeCl] (×10$^6$ mol dm$^{-3}$)</th>
<th>$k_{\text{obs}}$ (×10$^4$/sec)</th>
<th>$^a k_{\text{obs}}$ (×10$^4$/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>28</td>
<td>4.7</td>
<td>12.03</td>
<td>0.30</td>
</tr>
<tr>
<td>29</td>
<td>9.4</td>
<td>25.21</td>
<td>0.16</td>
</tr>
<tr>
<td>30</td>
<td>14.1</td>
<td>35.94</td>
<td>0.10</td>
</tr>
<tr>
<td>31</td>
<td>18.8</td>
<td>49.11</td>
<td>0.08</td>
</tr>
<tr>
<td>32</td>
<td>21.15</td>
<td>52.19</td>
<td>0.07</td>
</tr>
</tbody>
</table>

$^a$ $k_{\text{obs}}$ was obtained by following the decrease in absorbance at 411 nm during the course of the reaction.
3.8.2 Effect of Varying [oxidant]

The reaction was investigated by varying the concentration of the oxidant at fixed concentrations of substrate and F\textsubscript{20}TPPFeCl. The order of the reaction with respect to oxidant was found to be fractional (Figure 3.27). Further, a plot of 1 / k\textsubscript{obs} vs 1 / [m-CPBA] gave a straight line with finite intercept (Figure 3.28) indicating that a complex is formed prior to the rate-limiting step. The rate constant values are presented in Table 3.24.

3.8.3 Effect of Varying [F\textsubscript{20}TPPFeCl]

The kinetic runs were made at different initial concentrations of [F\textsubscript{20}TPPFeCl]. The rate of the reaction increased with increase in F\textsubscript{20}TPPFeCl concentration (Table 3.25). A linear plot was obtained between log k\textsubscript{obs} and log [F\textsubscript{20}TPPFeCl] with a slope of unity (Figure 3.29) indicating that the order of the reaction with respect to catalyst is one.

3.8.4 Rate Law

With respect to F\textsubscript{20}TPPFeCl, the order of the reaction was found to be one, fractional with respect to oxidant and zero as expected with respect to substrate and a plot of 1/ k\textsubscript{obs} against 1/ [m-CPBA] is linear and does not pass through the origin indicating that a complex is formed prior to the rate-limiting step. The rate equation for this oxidation reaction is given as

\[
\frac{d \text{ [epoxide]}}{dt} = \frac{-d \text{ [isobutyl 3-butenoate]}}{dt}
\]  
(3.17)
\[ y = 0.7178x + 1.4076 \]
\[ R^2 = 0.9902 \]

Figure 3.27 Reaction order with respect to m-CPBA in \( F_{20}TPPFeCl \)-catalyzed oxidation of isobutyl 3- butenoate in acetonitrile at 25°C
Figure 3.28 Plot of $1/k_{obs}$ vs $1/[m\text{-CPBA}]$ in $F_{20}TPPFeCl$-catalyzed oxidation of Isobutyl 3-butenoate by m-CPBA in acetonitrile at 25°C
Figure 3.29  Reaction order with respect to F$_{20}$TPPFeCl in F$_{20}$TPPFeCl-catalyzed oxidation of isobutyl 3-butoenoate by m-CPBA in acetonitrile at 25°C
3.8.5 Mechanism

From the above findings, the mechanism of metalloporphyrin-catalyzed epoxidation is proposed in Scheme 3.18, which involves first a complex formation in a reversible way followed by slow rate-limiting conversion of the complex to an oxidized intermediate which then transfers oxygen to the isobutyl 3-butenoate substrate in a fast step.

![Scheme 3.18](image)

3.8.6 Intermediate Species

Oxoiron (V) species as intermediate in our case is proposed instead of an oxoiron (IV). This proposed intermediate is defended by the literature data for heterolytic cleavage of the complex under acidic catalysis (Groves 1987, Traylor 1989, Watanabe 1991, Yamaguchi 1993, Machii 1995). Also if the reaction proceeds through a radical pathway, a free radical inhibitor
should quench the rate of the reaction. 2, 6-di-tert-butyl-p-cresol (Guo 1999) and benzoic acid (Serra 2004) have been employed to prove that the oxidation reactions catalyzed by metalloporphyrins involve radical pathway by their ability to quench substantially the reaction. In our work, benzoic acid, a radical inhibitor in the atmosphere of nitrogen was found to quench the reaction rate (data not shown). Very recently Agarwala et al (2005) have proved the existence of the only intermediate, compound I in the system similar to ours containing the catalyst, $F_{20}$TPPFeCl, oxidant, m-CPBA and solvent, acetonitrile. Therefore it is suggested that the intermediate formed in the epoxidation of isobutyl 3-butenoate catalyzed by $F_{20}$TPPFeCl in the presence of m-CPBA is none other than compound I (Scheme 3.19), which could be further confirmed by the reaction in the absence of substrate. Because generation of the compound I species is usually rate determining, the determination of rate constant for reaction of alkene with compound I is generally not possible (Harden 1995).
Scheme 3.19
### 3.8.7 Overall Rate Equation

Application of the steady-state treatment to the mechanism shown in Scheme 3.19 leads to the rate equation (Laidler 1994),

\[
\text{rate} = \frac{k_2 k_3 [F_{20}TPPFeCl] [m-CPBA]}{k_2 + k_3} + \frac{k_1 k_3}{k_1} + [m-CPBA] + [\text{m-CPBA}]
\]

### 3.8.8 Degradation of the Catalyst in the Presence of Substrate

We believe that the oxidative destruction of the catalyst, a point often overlooked in such studies is significant here. Even with a substrate, a degree of catalyst bleaching was found upon analysis of the reaction by UV-Visible spectroscopy. The disappearance of the Soret band of the metalloporphyrin at 411 nm was measured simultaneously along with the measurement of decrease in absorbance at 270 nm for the loss of the substrate, isobutyl 3-butenoate. The rate constant values are presented in Tables 3.23 to 3.25. A first order dependence of the rate on $[F_{20}TPPFeCl]$ was observed by the linear plot of log $k_{obs}$ vs log $[F_{20}TPPFeCl]$ with a slope of unity (not shown). The order was found to be fractional (slope = 0.51) with respect to [m-CPBA] and zero with respect to [isobutyl 3-butenoate]. The kinetic analysis of the catalyst destruction in the presence and absence of substrate was consistent with the catalyzed oxidation of isobutyl 3-butenoate. The most striking finding in this study is that an increase in concentration of oxidant despite increasing the degradation of porphyrin increased the rate of epoxidation reaction also, which indicates that there is a competition between
the substrate and catalyst to accept oxygen from the oxidant. The oxygen transfer to the substrate to give the epoxide product is faster than to the porphyrin to give the bleached product.

3.8.8.1 Competition between catalyzed oxidation and catalyst-oxidation

According to all the above observations, it is clear that there is a competition between the substrate oxidation cycle, e.g. $\text{F}_{20}\text{TPPFeCl} + \text{m-CPBA} \rightarrow (\text{F}_{20}\text{TPP} \cdot ^+ \text{Fe IV=O} + \text{substrate} \rightarrow \text{epoxide product} + \text{F}_{20}\text{TPPFeCl}$ and catalyst degradation, e.g. $\text{F}_{20}\text{TPPFeCl} + \text{m-CPBA} \rightarrow \text{catalyst bleaching}$. Thus the mechanism of $\text{F}_{20}\text{TPPFe}^{\text{V}}=\text{O}$ formation, substrate oxidation and $(\text{F}_{20}\text{TPP} \cdot ^+ \text{Fe IV}=\text{O}$ degradation is best represented in the overall Scheme 3.20.

![Scheme 3.20](image)

3.8.8.2 Need for the study of degradation

Examination of the literature shows that there are several strategies commonly employed with the aim of reducing catalyst degradation during oxidation process. The first involves the use of electron-deficient substituents to the aryl groups of the commonly used meso-tetraaryl metalloporphyrins. It
has been suggested by Traylor et al (1995) that such substituents favor a two-electron reduction of the oxo-perferryl intermediate back to Fe$^{III}$, thus avoiding the one-electron reduction to the ferryl species, which is known to be susceptible to oxidative degradation. However, if ‘direct oxidation’ of the porphyrin ring of the resting catalyst is a general process, this offers an alternative explanation (at least in part) for reduced degradation with electron-withdrawing aryl substituents.

The second strategy uses bulky, often ortho, groups on the aryl group to reduce intermolecular catalyst interactions and so prevent oxidation of the resting catalyst by the oxo-perferryl intermediate. This strategy has been an established one since the mid-1980s (Traylor 1984). The third strategy is to ensure a very large excess of substrate (Traylor 1985), the idea being to ‘trap’ the oxo-perferryl species as efficiently as possible and prevent its destruction via intermolecular reaction with resting catalyst. However, again, if oxidative degradation is predominantly via direct oxidation of the resting catalyst, and the last two strategies are ineffective.

3.8.8.3 Route for the decomposition of F$_{20}$TPPFeCl by m-CPBA

In general the metalloporphyrin oxidative decomposition process is poorly understood. Banfi et al (1989) have noted the decomposition routes for oxidized metalloporphyrins: (i) oxidative decomposition of the porphyrin ring, (ii) formation of μ-oxo dimers and (iii) intramolecular self-oxidation. Decomposition by oxidation of the porphyrin ring are the least well characterized, but an important mode appears to involve reaction of the unoxidized metalloporphyrin with an oxidized form such as (por·$^+$)Fe IV=O. This route is precluded since the rate of the reaction decreases with increase of [F$_{20}$TPPFeCl] in our case. The use of metaltetraaryl porphyrins with ortho substituents to the aryl ring is a well-established tactic to reduce dimer formation (Traylor 1984). Furthermore, an intramolecular ‘self-oxidation’,
initiated for example by rearrangement of compound I to an iron porphyrin N-oxide (Leonord 1991), would depend on the concentration of the porphyrin only. Instead, the kinetic dependence of the decomposition of Compound I on [m-CPBA] indicates an oxidative decomposition of compound I, which probably involves oxidation of the porphyrin by m-CPBA. This is despite the presence of the strongly electron-withdrawing pentafluorophenyl meso-substituents.

3.8.9 Summary of the Study on Comparison with Epoxidation by H₂O₂

- The epoxidation reaction catalyzed by pentafluorophenyl iron (III) porphyrin follows two different mechanisms with these two oxidants, m-CPBA and H₂O₂.

- The intermediates involved in the epoxidation reactions are also different for m-CPBA and H₂O₂.

- The mechanism of oxidation reactions catalyzed by metallo porphyrin depends mainly on the interaction between oxidant and catalyst only.

- The reaction path in pentafluorophenyl iron (III) porphyrin catalyzed oxidations is decided by the nature of the oxidant.

- Porphyrin destruction does take place even with sterically hindered pentafluorophenyl iron (III) porphyrin.

- Destruction pathway is different for the two oxidants.

- The mode of destruction seems more or less similar for both m-CPBA and H₂O₂.
3.8.10 Overview of Epoxidation by m-CPBA and F$_{20}$TPPFeCl

The epoxidation of isobutyl 3-butenoate by m-CPBA catalyzed by F$_{20}$TPPFeCl follows Michaelis-Menten mechanism, which involves first a complex formation between oxidant and catalyst in a reversible way from which an intermediate, oxoperferryl species, (F$_{20}$TPP$^+$)Fe$^{IV}$=O is formed in a rate determining step. This species transfers oxygen atom in a fast step to the substrate to form the product. A degree of catalyst bleaching does take place in the presence of m-CPBA even with a halogenated metallo porphyrin such as F$_{20}$TPPFeCl. The intermediate (F$_{20}$TPP$^+$)Fe$^{IV}$=O decomposes via m-CPBA oxidation, probably of the porphyrin ring, to give a bleached product. This is true both in the presence and absence of the substrate. The epoxidation reaction catalyzed by pentafluorophenyl iron (III) porphyrin follows two different mechanisms with these two oxidants, m-CPBA and H$_2$O$_2$. 