Kinetics and mechanism of formation of tris(methyl 2-pyridyl ketoxime) complex of iron(II), its isomerisation, dissociation and oxidation to the iron(III) complex in solution

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Methyl 2-pyridyl ketoxime (LH) forms an orange-red coloured complex with Fe²⁺ in weakly acidic media (pH ~ 5) in the presence of hydroxylamine to prevent oxidation of Fe²⁺ to Fe³⁺. The optimum pH for the colour formation is ca. 3.2-4.6. This complex species I which is formed instantaneously has an absorbance maximum at 475 nm and it slowly changes to another species II having an absorbance maximum at 525 nm. Both the species have a composition Fe(LH)₃³⁺. However, the absorbance band of the species I is nearly symmetrical about the maximum position, while that of species II is distinctly unsymmetrical with a shoulder at ~ 500 nm. Obviously the species I has a cubic symmetry as expected for the 1,2,3(fac)-isomer, which is often referred to as the cis isomer for a complex of the type MA₂B₃ or M(AB₃) as is true for Fe(LH)₃³⁺ also since despite the fact that LH is a bidentate N,N donor, one of the ligating N is that of the pyridine ring while the other N belongs to the oximino (=NOH) group. Similarly the species II obviously has rhombic symmetry and hence is the 1,2,6(mer)-isomer of Fe(LH)₃³⁺, often referred to as the trans isomer².

Detailed kinetic studies on the formation of species I and its subsequent slow isomerization into the species II have been carried out and the results are reported in this paper. Also reported are the results of acid catalysed dissociation of the species II and its oxidation to the corresponding Fe(III) complex by perdisulphate in acidic media.

Materials and Methods
The ligand (LH) methyl 2-pyridyl ketoxime was prepared in pure state following literature method and its purity was checked by its melting point (120°C)¹. Iron(II) solution was prepared using Mohr’s salt, (NH₄)₂SO₄·FeSO₄·6H₂O (GR, E Merck). All other chemicals used were pure reagent grade or else purified by standard methods. Doubly distilled water was used in making the solutions.

Spectra of the complexes in solution were recorded using a Carl-Zeiss spectrophotometer (VSU-2P, Jena, Germany), pH measurements were made with a digital pH meter (Model 335, Systronics, India), fast kinetic runs were made using a stopped-flow spectrophotometer (SF-3A, Hi-Tech, England) coupled with a transient recorder (DL 905, Data Lab, England) and an oscilloscope (OS-1000A, Advance Instruments, England). The observed absorbance versus time trace as displayed on the oscilloscope was recorded using a XY-t chart recorder (PL-3, J J Lloyds, England). The observed rate constants (k obs) were evaluated from the data using a microprocessor supplied by the manufacturer (Hi-Tech, England) with the stopped-flow system. For k obs average value of at least three experiments was used in each case. The flow module of the SF-3A had arrangements for thermostating (±0.05°C) the reacting solutions and the observation cell. Rate measurements of the slower reacting systems were made by conventional spectrophotometry using a thermostated cell housing in the Carl-Zeiss VSU-2P spectrophotometer.

Results and Discussion
(a) Evaluation of protonation constant of the ligand LH.
The acid dissociation constant of the ligand (LH $K_a$ LH$^- + H^+$) has been reported earlier$^1$; at 28°C, $I=0.5$ mol dm$^{-3}$ (KCl) the $pK_a$ value of 9.97. The equilibrium constant for protonation of the ligand (LH $K_a$ LH$^- + H^+$) has been evaluated by conventional $pH$ potentiometric method$^3$. At 30°C, $I=0.1$ mol dm$^{-3}$ (NaClO$_4$) the log $K_{H}$ value is 5.8. A knowledge of the magnitude of this value was necessary to ascertain the nature of the predominant species in solution of the ligand (LH) in acidic media in the kinetic studies.

(b) Kinetic studies on the formation of the complex species I.

Kinetic studies on the formation of this complex from Fe$^{2+}$ and the ligand in solution were carried out spectrophotometrically (stopped-flow technique) at 475 nm in the $pH$ range of 3.8-4.5 using ligand concentration much in excess of the metal ion to maintain pseudo-first order conditions in the presence of a fair excess of hydroxylamine to prevent any possible oxidation of Fe$^{2+}$. The amount of hydroxylamine was held constant in all the experiments, but it was ascertained that its concentration has no effect on the rate of formation of the complex species I. The experimental results are in conformity with reaction Scheme 1.

\[
\begin{align*}
&\text{Fe}^{2+} + \text{LH}^2+ \rightarrow \text{Fe}^{2+} + \text{LH}^2+ + H^+ \\
&\text{Fe}^{2+} + \text{LH}^2+ \rightarrow \text{Fe}^{2+} + \text{LH}^2+ + H^+ \\
&\text{Fe}^{2+} + \text{LH}^2+ \rightarrow \text{Fe}^{2+} + \text{LH}^2+ + H^+
\end{align*}
\]

Scheme 1

The last step is likely to be fast as it involves transformation of high-spin Fe(LH)$_2$(H$_2$O)$_2$$^{2+}$ (CFSE = 4Dq) to low-spin Fe(LH)$_2$$^{2+}$ (CFSE = 24 Dq-2P). Since the $pK_a$ value of LH$^2+$ is 5.8 in the range of $pH$ (3.8-4.5) used in the experiments the ligand will be present predominantly as LH$^2+$ in solution. Scheme 1 leads to rate law (1) 

\[
[LH]^n/k_{obs} = [H^+]/[LH] + 1/k_r 
\]

A similar behaviour has been observed earlier$^4$ in the Fe$^{2+}$-dimethyl glyoxime system studied in 20% v/v ethanol + water medium. The values of $K_r$ and $k_r$ were evaluated using Eq. (1) at three different temperatures in the range of 35°-45°C graphically (see Fig. 1) and checked by least squares proce-

dure using Eq. (1). From the $k_r$ values at different temperatures the corresponding activation parameters $\Delta H^*$ and $\Delta S^*$ were evaluated using Eyring equation, and from $K_r$ values the corresponding $\Delta H$ and $\Delta S$ values using the relation

\[
-\log K = \Delta H/(5.6T) - \Delta S/4.6 
\]

All these values are given in Table 1.

(c) Kinetics of isomerisation of species I to species II.

This being a relatively slow process was followed by conventional spectrophotometry at 525 nm after forming the species I in situ. The results indicate that the rate of this isomerisation process is independent of $pH$ (in the range of $pH$ 3.8-4.5 in NaOAc + HOAc buffer) and excess concentration of the free ligand in the solution. (Fe(LH)$_2$$^{2+}$) = 2.5 $\times$ 10$^{-5}$ mol dm$^{-3}$, [LH] = (5.0-12.5) $\times$ 10$^{-4}$ mol dm$^{-3}$, [NH$_2$OH.HCl] = 5 $\times$ 10$^{-4}$ mol dm$^{-3}$. For this isomerisation process the observed rate constants at 50°, 55° and 60°C ($I=0.1$ mol dm$^{-3}$, NaClO$_4$ + NaOAc) are 0.043 $\pm$ 0.002, 0.066 $\pm$ 0.002 and 0.098 $\pm$ 0.005 s$^{-1}$ respectively.

Table 1—Values of $k_i$ and $K_r$ for formation of Fe(LH)$_2$$^{2+}$ in aqueous acetate buffer medium

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>$10^3 K_r$</th>
<th>$10^{-4} k_r$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>8.42 ± 0.25</td>
<td>0.52 ± 0.02</td>
</tr>
<tr>
<td>40</td>
<td>4.88 ± 0.10</td>
<td>1.00 ± 0.03</td>
</tr>
<tr>
<td>45</td>
<td>2.70 ± 0.01</td>
<td>2.00 ± 0.05</td>
</tr>
</tbody>
</table>

$\Delta H (kJ$ mol$^{-1}) = -86.6 \pm 0.5 (kJ$ mol$^{-1})$, $\Delta S (kJ$ mol$^{-1}) = 103.2 \pm 1.0$.
(\(\Delta H^e = 70.3 \pm 0.3 \, \text{kJ mol}^{-1}\), \(\Delta S^e = -55.5 \pm 1.5 \, \text{JK}^{-1} \cdot \text{mol}^{-1}\)). The isomerisation is an intramolecular transformation likely to proceed by a chelate ring opening process (one ended dissociation of a chelate ring)\(^3\) possibly at the oximino nitrogen (Fe-NOH bond); the significantly negative \(\Delta S^e\) is presumably due to electrostriction effect.

(d) Kinetics of acid assisted dissociation of the species II

For this investigation the tris complex species II, \(\text{Fe(LH)}_3^+\), was isolated as its perchlorate salt following the procedure reported earlier\(^1\) after keeping overnight at room temperature the complex species I formed in situ in solution to allow its complete isomerisation to species II. The aqueous solution of the isolated complex salt was found to be spectrally identical to that of species II formed in situ in solution. A solution of the complex ion (species II) in 0.01 mol dm\(^{-3}\) HClO\(_4\) immediately changes to a species having a maximum absorbance at \(\sim 490\) nm, while at a higher acid concentration (1-2 mol dm\(^{-3}\)) it readily forms another species having an absorbance maximum at \(\sim 465\) nm which gradually becomes colourless. Hence, dissociation of the complex proceeds in three steps presumably due to the transformations tris to bis to mono complexes and ultimately to \(\text{Fe}^{3+}\). The first step was followed conveniently at 0.002-0.009 mol dm\(^{-3}\) HClO\(_4\) at 525 nm, by stopped-flow spectrophotometry. The pseudo-first order rate constant for the dissociation showed dependence on \([H^+]\) as in Eq. (3)

\[
k_{\text{obs}} = k_0 + k_H[H^+]
\]

Using Eq. (3) \(k_0\) and \(k_H\) values were evaluated graphically and checked by least squares procedure, and from the \(k_0\) and \(k_H\) values the corresponding activation parameters, \(\Delta H^e\) and \(\Delta S^e\), and the results are given in Table 2. The \(k_0\) and corresponding \(\Delta H^e\) and \(\Delta S^e\) values are comparable to those for the spontaneous acid independent dissociation of \(\text{Fe(phen)}^2^+\) observed in acidic solution (at 25°C, \(k_0 = 2.67 \, \text{s}^{-1}\); \(\Delta H^e = 53.6\) kJ mol\(^{-1}\), \(\Delta S^e = -66.9\) JK\(^{-1}\)mol\(^{-1}\))\(^6\). The rates of dissociation for the second and third steps could not be followed conveniently since at higher acid concentrations where these occur the two steps overlap considerably.

(e) Kinetics and mechanism of oxidation of species II to the corresponding Fe(III) species by perdisulphate in aqueous solution

It has been reported earlier\(^1\) that the light yellow coloured Fe(III) complex formed with this ligand in acidic solution slowly gets reduced to the Fe(II) complex. But in the presence of perdisulphate the Fe(III) complex is stable in solution. Kinetics of oxidation of the Fe(II) complex species II to the corresponding Fe(III) complex by perdisulphate in weakly acidic aqueous solution has been studied by conventional spectrophotometry at 525 nm under pseudo-first order conditions (constant \(pH\) and excess of the oxidant). In the range of \(pH\) 4-5 the rate is independent of \(pH\) and the experimental results are consistent with Scheme 2, being similar to that proposed\(^7\) for similar oxidations of several Fe(III) complexes of 2,2'-bipyridine, 1,10-phenanthroline and their derivatives.

\[
\text{Fe(LH)}_3^+ + S_2O_8^2^- \rightarrow \text{Fe(LH)}_2^+ S_2O_8^2^{-} \\
1=k_{\text{ox}}
\]

\[
\text{Fe(LH)}_3^+ + (S_4O_6^2-) \rightarrow \text{Fe(LH)}_2^+ + S_4O_6^2^{-}
\]

Scheme 2

Using Eq. (4) values of \(k_{\text{ox}}\) and \(k_H\) were evaluated graphically and checked by least-squares procedure and from these \(k_{\text{ox}}\) values at three different temperatures the corresponding activation parameters \(\Delta H^e\) and \(\Delta S^e\) were evaluated using Eyring equation. \(\Delta H\) and \(\Delta S\) values corresponding to \(k_{\text{ox}}\) were also evaluated using the relation

\[
1/k_{\text{obs}} - 1/k_{\text{ox}} = 1/k_{\text{ox}}[S_2O_8^2-] + \ldots \ldots (4)
\]

Table 2—Values of \(k_0\) and \(k_H\) for acid assisted dissociation of \(\text{Fe(LH)}_3^+\) in aqueous solution

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>(k_0) (s(^{-1}))</th>
<th>(10^{-2} k_H) (dm(^3)mol(^{-1})s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>1.00 ± 0.02</td>
<td>3.2 ± 0.05</td>
</tr>
<tr>
<td>30</td>
<td>1.60 ± 0.05</td>
<td>3.8 ± 0.05</td>
</tr>
<tr>
<td>35</td>
<td>2.15 ± 0.05</td>
<td>5.0 ± 0.05</td>
</tr>
</tbody>
</table>

\[
\Delta H^e\] (kJ mol\(^{-1}\)) = 56.0 ± 0.3, \(\Delta S^e\) (JK\(^{-1}\)mol\(^{-1}\)) = -58.3 ± 1.0, -92.3 ± 1.5

Table 3—Oxidation of \(\text{Fe(LH)}_3^+\) by \(S_2O_8^2-\) in aqueous solution

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>(K_{\text{ox}}) (dm(^3)mol(^{-1}))</th>
<th>(10^3 k_{\text{ox}}) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>58.5 ± 0.2</td>
<td>4.17 ± 0.05</td>
</tr>
<tr>
<td>25</td>
<td>50.7 ± 0.2</td>
<td>5.71 ± 0.05</td>
</tr>
<tr>
<td>35</td>
<td>36.2 ± 0.2</td>
<td>11.76 ± 0.05</td>
</tr>
</tbody>
</table>

\[
\Delta H\] (kJ mol\(^{-1}\)) = -23.1 ± 0.1, \(\Delta H^e\) (kJ mol\(^{-1}\)) = 48.8 ± 0.2

\[
\Delta S\] (JK\(^{-1}\)mol\(^{-1}\)) = -44.9 ± 1.0, \(\Delta S^e\) (JK\(^{-1}\)mol\(^{-1}\)) = -125.4 ± 1.5
given in Eq. (2). All these values are given in Table 3. It is seen that the $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values are comparable to the corresponding values ($\Delta H^\ddagger$, 41.8 kJ mol$^{-1}$; $\Delta S^\ddagger$, $-111.7$ JK$^{-1}$mol$^{-1}$) for the oxidation of Fe(bipy)$_3^{2+}$ by S$_2$O$_5^-$ and the observations may be explained as in the case of similar other oxidations$^7$. Based on kinetic data the $K_{IP}$ value$^8$ for Ni(H$_2$O)$_6^{2+}$. MePO$_4^-$ is 41 dm$^3$mol$^{-1}$ at 25°C ($I=0$) while that$^7$ for Fe$^{2+}$,SO$_4^{-2}$ is 61 dm$^{-3}$ mol$^{-1}$. Hence, the observed $K_{ox}$ values are appropriate for those expected for an ion-pair formed between the cationic Fe(LH)$_3^{2+}$ and the anionic S$_2$O$_5^2^-$. However, no prediction can be made as to whether the electron transfer in the rate determining step is inner-sphere or outer-sphere in nature$^7$.

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References
6 Cf Ref 5, p 239.