Oxidation of L-Methionine by Poly (pyridyl) Iron (III) Complexes in Aqueous Solutions

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Summary: The kinetics of oxidation of L-methionine by poly(pyridyl) iron (III) complexes in aqueous media have been investigated. The reactions are first order each in the oxidant, reductant and hydrogen ion. The immediate products are the respective poly(pyridyl) iron (II) complexes and methionine sulphoxide. Each reaction is discussed in terms of the outer-sphere mechanism.

Introduction

Several studies on the interactions of poly (pyridyl) complexes of iron (III) and iron (II) with inorganic and organic reagents have been reported [1-8]. Many of these reactions are rationalised in terms of the outer-sphere mechanism, supported by Marcus-type dependence of rate on the driving force of the reaction. Occasionally, however, inner sphere pathways have been encountered [8].

On the other hand, a broad spectrum of reagents has been reacted with L-methionine in the hope that understanding of its function *in vivo* might be advanced. Recently, we have studied its reaction with anionic complexes [9-11] such as $HCrO_4-$, $CoW_{12}O_{40}^{5-}$ and $IrCl_6^{2-}$. The reactions with $HCrO_4^-$ and $AuCl_4^-$ are thought to proceed via sulpher-bonded inner sphere complexes [9-12] but simple electron transfer reminiscent of the outer-sphere mechanism is proposed for its reactions [10-11], with $CoW_{12}O_4^{5-}$ and $IrCl_6^{2-}$. We now address its interactions with cationic species, $Fe(phen)_3^{3+}$ and $Fe(bipy)_3^{3+}$ in the light of the points raised above.

Results and Discussion

In both cases, the reaction stoichiometry was found to be 1:1 ($Fe(LL)_3^{3+}$: methionine), thus the reaction may be represented by equation (1).

$Fe(LL)_3^{3+} + R^+SCH_3 + H_2O \longrightarrow Fe(LL)_3^{2+} + R(CH_3)SO + 2H^+$ (1).
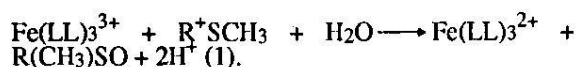
where R^+SCH_3 methionine, CH_3SCH_2 CH_2 $CH(NH_3^+)CO_2H$.

The formation of $Fe(LL)_3^{2+}$ was confirmed in each case by its characteristic absorption peak[3] (510 nm for $Fe(phen)_3^{2+}$ and 522 nm for $Fe(biphy)_3^{2+}$) while methionine sulphoxide was characterised as described earlier [9]. The observation of the latter product suggests that there is a direct attack by water on the sulphur with eventual transfer of an oxygen atom to sulphur to give the sulphoxide. This explanation appears to be plausible since the title reaction does not occur in the absence of water. (There is no reaction in dry MeOH or MeCN for example).

The kinetic results in Table 1 show that k_{obs} varies linearly with the concentration of L-methionine. This, as well as the strict linearity of pseudo-first order plots suggest that the reaction is first order in $Fe(LL)_3^{3+}$ and L-methionine as expressed in equation (2)

$-d[Fe(LL)_3^{3+}]/dt = k_o [Fe(LL)_3^{3+} [R^+SCH_3]$ (2)
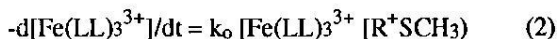
where $k_o = k_{obs}/[R^+SCH_3]$.

Table 1: Kinetic data for the variation of Methionine and Hydrogen ion concentrations in the Oxidation of Methionine by $Fe(phen)_3^{3+}$ and $Fe(bipy)_3^{3+}$ at 25°C.

$[H^+]$ (M)	$10^3[RSCH_3]$ (M) $^aFe(bipy)_3^{3+}$	10^4k_{obs} s^{-1}	$[H^+]$ (M)	$10^3[RSCH_3]$ (M) $^bFe(phen)_3^{3+}$	10^4K_{obs} (s^{-1})
0.25	2.00	0.42	0.05	2.00	0.19
0.25	4.00	0.81	0.05	4.00	0.37
0.25	6.00	1.23	0.05	6.00	0.56
0.25	8.00	1.60	0.05	8.00	0.74
0.25	10.00	2.00	20.05	10.00	0.92
0.25	12.00	2.44	0.05	12.00	1.10
0.25	14.00	2.82	0.05	16.00	1.48
0.25	16.00	3.21	0.05	20.00	1.83
0.50	8.00	3.30	0.10	8.00	1.45
0.75	8.00	4.90	0.20	8.00	2.76
1.00	8.00	6.51	0.30	8.00	4.18
1.25	8.00	8.23	0.40	8.00	5.60
1.50	8.00	9.81	0.50	8.00	6.96
1.75	8.00	11.37			
2.00	8.00	13.00			

Plots of k_o versus $[H^+]$ are all linear passing through the origin (Figure 1), suggesting that the overall rate law may be written as equation (3).

$-d [Fe(LL)_3^{3+}]/dt = k_3 [Fe(LL)_3^{3+} [RSCH_3) [H^+].$ (3)
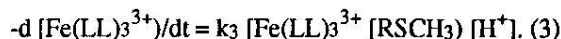
The values of k_3 obtained from plots of k_o versus $[H^+]$, together with the activation parameters for each reaction are presented in Table 2.

The dependence of $Fe(LL)_3^{3+}$ reactions on $[H^+]$ could be attributed to the protonation of the substrate prior to electron transfer. This view gains support from the observation that rate increases with ionic strength (Table 3) in keeping with positive Bronsted - Debye salt [14] expected for reactions between likely charged reactants.

Table 2: Values of the rate constant, k_3 at different temperatures and the Associated Activation Parameters.

Temp., °C	30	25 10^2k_3, $M^{-2} s^{-1}$	20	15
$Fe(phen)_3^{3+}$	2.12	1.73	1.42	1.06
$Fe(bipy)_3^{3+}$	9.77	8.44	6.49	4.89

$\Delta H\# (Fe(phen)_3^{3+} = 8.1 \pm 0.2$ K Jmol^{-1};
$\Delta H\# (Fe(bipy)_3^{3+} = 8.2 \pm 0.3$ K Jmol^{-1}
$\Delta S\# (Fe(phen)_3^{3+} = 277.0 \pm 2.0 JK^{-1}mol^{-1}$;
$\Delta S\# (Fe(bipy)_3^{3+} = -263.8 \pm 3.5$ J$K^{-1}mol^{-1}$

Table 3: Effect of Ionic strength on the reactions of methionine with $Fe(bipy)_3^{3+}$ and $Fe(bipy)_3^{3+}$ at 25°C.

I (M)	10^4k_{obs} (s^{-1}) $^aFe(bipy)_3^{3+}$	I (M)	10^4k_{obs} (s^{-1}) $^bFe(phen)_3^{3+}$
0.25	0.20	0.25	0.23
0.50	0.40	0.50	0.38
0.75	0.62	0.75	0.53
1.00	0.83	1.00	0.74
1.50	1.23	1.50	0.97
2.00	1.63	2.00	1.76

$^aFe(bipy)_3^{3+} = 2.0 \times 10^{-4}$M; Methionine $= 8.0 \times 10^{-3}$M; $[H^+] = 0.25$M
$^bFe(phen)_3^{3+} = 2.0 \times 10^{-5}$M; Methionine $= 8.0 \times 10^{-3}$M; $[H^+] = 0.05$M.

The equilibrium (4) has been considered for some poly(pyridyl) iron (III) reactions [5-7].

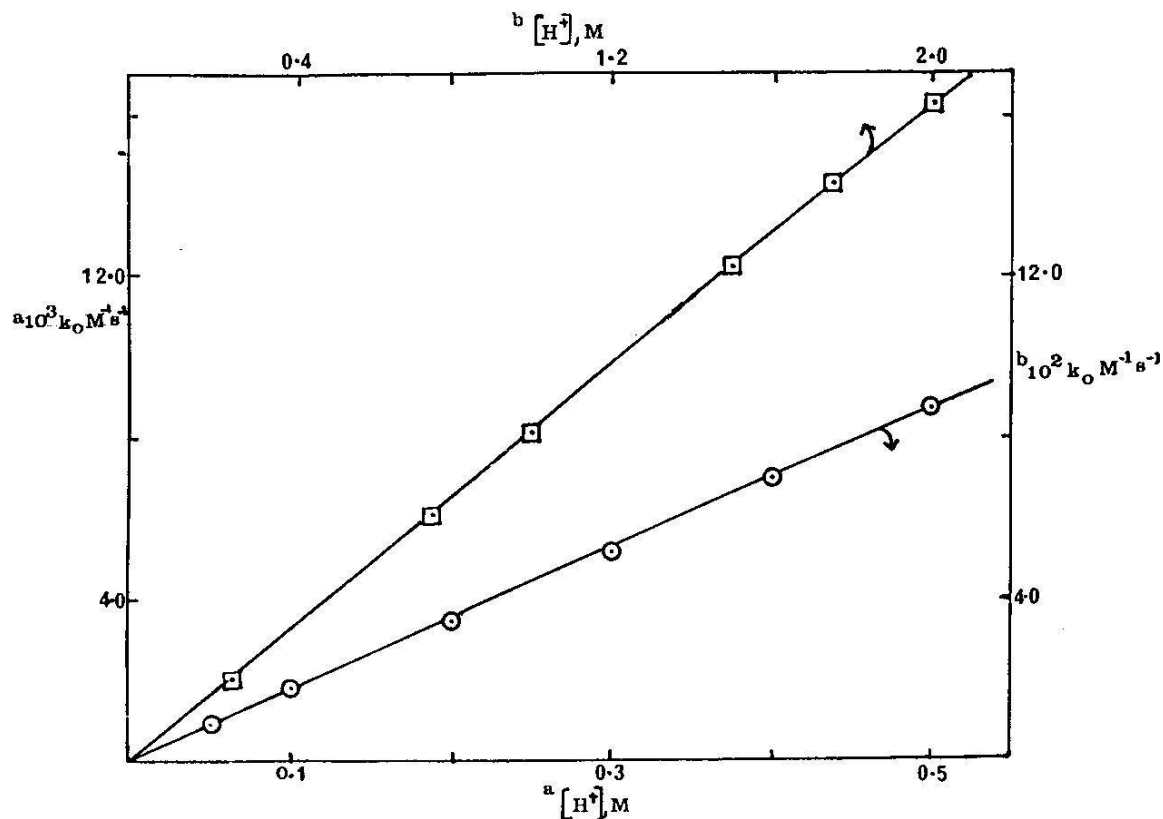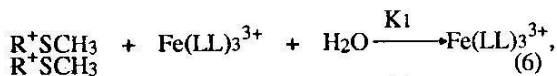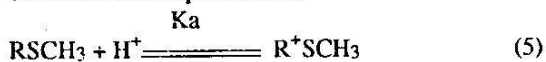$H^+ + Fe(LL)_3^{3+} \rightleftharpoons H Fe (LL)_3^{4+}$ (4)
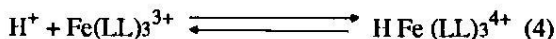
Fig.1: Dependence of k_o on $[H^+]$. $a = Fe(phen)_3^{3+}$ (⊙); $b = Fe(bipy)_3^{3+}$ (▣) $RSCH_3 = 8 \times 10^{-3}M$, $I = 1.0M$ (LiClO₄)

While the existence of some H $Fe(LL)_3^{4+}$ cannot be ruled out in the present study, its involvement in the rate determining step is not favoured because (a) reactions with protonated substrate would lead to a second order dependence on $[H^+]$, which was not observed and (b) reactions with the molecular form of the substrate cannot be used to explain our observed dependence of rate on ionic strength.

It therefore appears that the scheme below accounts for the empirical data.

$$RSCH_3 + H^+ \overset{Ka}{=\!=\!=\!=\!=} R^+SCH_3 \qquad (5)$$

$$R^+SCH_3 + Fe(LL)_3^{3+} + H_2O \overset{K_1}{-\!\!\!-\!\!\!-\!\!\!\longrightarrow} Fe(LL)_3^{3+}, \\ R^+SCH_3 \qquad\qquad\qquad\qquad\qquad (6)$$

$$R^+SCH_3, Fe(LL)_3^{3+} + H_2O \overset{k_2}{-\!\!\!-\!\!\!-\!\!\!\longrightarrow} Fe(LL)_3^{2+} \\ +R(CH_3S\!=\!O+2H^+ \qquad\qquad\qquad\qquad (7)$$

Thus the rate of loss of $Fe(LL)_3^{3+}$ is

$$-\,\frac{d\,[Fe(LL)_3^{3+}]}{dt} = \frac{KaK_1\,k_2\,[Fe(LL)_3^{3+})\,(RSCH_3)}{[H^+]/1 + Ka + KaK_1\,k_2\,[Fe(LL)_3^{3+}]\,[H^+]} \qquad (8)$$

Where $[RSCH_3] = [RSCH_3]T/1 + Ka[H^+] + KaK_1k_2(Fe(LL)_3^{3+}[H^+])$.

Provided $1 >> Ka$ $[H+] + Ka, K_1 K_2$ $[Fe(LL)_3^{3+}][H^+]$ equation (8) is identical to equation (3) with $k_3 = K_aK_1k_2$.

Reactions of L-Methionine with $HCrO_4^-$ and $AuCl_4^-$ are thought [9-12] to occur via formation of sulphur bonded inner sphere intermediates. However, poly(pyridyl) iron (III) complexes are usually regarded as substitution inert complexes [1-7]. Therefore, any interaction between the oxidants and the reductant should be weak.

In keeping with this:

(a)   spectrophotometric evidence for complexes with inner sphere character was lacking.

(b)   Michaelis - Menten plot of $1/k_{obs}$ versus 1/[methionine] was linear passing through the origin, indicating the absence of intermediates with significant formation constants, and

(c)   A plot of log k_3 versus E^o for methionine oxidation by $Fe(phen)_3^{3+}$, $Fe(bipy)_3^{3+}$, $CoW_{12}O_{40}^{5-}$ and $IrCl_6^{2-}$ (using data in Table 4) was reasonably linear (r = 0.98) with a least mean square slope of $-17.9 \, v^{-1}$. Provided the electron transfer step is the rate determining one, and outer sphere mechanism operates, Schuster [15] predicted a slope of $-16.9 \, v^{-1}$ at 25°C for such a line.

Table 4: Kinetic and Thermodynamic Parameters for the Oxidation of L-Methionine by $Fe(LL)_3^{3+}$, $CoW_{12}O_{40}^{5-}$ and $IrCl_6^{2-}$

Oxidant	E, V	Log k_3, $M^{-2}s^{-1}$	Ref
$Fe(phen)_3^{3+}$	1.06[a]	- 1.76	This work
$Fe(phen)_3^{3+}$	1.035[a]	- 1.09	This work
$CoW_{12}O_{40}^{5-}$	1.00b	- 0.795	10
$IrCl_6^{2-}$	0.957[a]	0.197	11

[a]From ref 3 [b] From ref 13.

It thus appears that the title reactions occur *via* the outer sphere mechanism. In this regard this is different [9,12] from the reactions of the substrate with $HCrO_4^-$ and $AuCl_4^-$ but similar [10,11] to those with $CoW_{12}O_{40}^{5-}$ and $IrCl_6^{2-}$.

Experimental

Reagents

$Fe(phen)_3$ $(ClO_4)_3$ and $Fe(bipy)_3(ClO_4)_3$ (hereafter designated $Fe(LL)_3^{3+}$ with LL = phen or bipy) were prepared as described by Ford-Smith and Sutin [4] and characterised by the method of Adedinsewo and Adegite [3]. All other chemicals were used as supplied.

Rate Measurements

Rate Kinetics were monitored under pseudo-first order conditions (L-methionone >10 $Fe(LL)_3^{3+}$) by following the decrese in obsorbance due to

$Fe(phen)_3^{3+}$ at λ= 600 and 620 nm respectively on a conventional spectrophotometer. Observed rate constants were obtained from pseudo-first-order plots, which were linear to greater than three half-lives. Dissolved oxygen did not show any effect on the rate and replicated runs agreed to ±3%. Perchloric acid was used for $[H^+]$ variation and ionic strength was maintained at 2.0M (unless otherwise indicated) using sodium perchlorate.

Polymerization studies

Polymerization studies performed as described earlier [13] did not yield the required polymers, suggesting that free radicals (if any) do not accumulate in these reactions.

Stoichiometry and Product Analysis

The Stoichiometries of the reactions were evaluated spectrophotometrically by measuring the absorbance of solutions containing fixed $Fe(LL_3^{3+}$ concentrations and varied (methionine) after the reactions had gone to completion. Methionine sulphoxide was found to be the organic product in each case as reported in an earlier communication [9].

Spectrophotometric studies

The visible spectra of $Fe(LL)_3^{3+}$ $(2x10^{-4}M)$, $[H^+]$ (0.25M) and L- methionine $(8.0x10^{-3}M)$ were recorded. There was no significant difference in the λ_{max} of $[Fe(LL)_3^{3+}$ alone and $Fe(LL)_3^{3+}$ mixed with $[H^+]$ and methionine probably suggesting absence of spectrophotometric evidence for the formation of inner sphere complexes.

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