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Oxidation of hypophosporus acid by poly(pyridine)iron(III) complexes

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ABSTRACT

The kinetics of the titled reaction in aqueous solution of perchloric acid was monitored spectrophotomerically at ionic strength of I = 2.0M ($NaClO_4$). The reaction obeys the rate law: Rate = 2k $[Fe(LL)_3^{3+}][H_3PO_2]$ where k = 1.83×10^{-4} $dm^3 mol^{-1}s^{-1}$ and 1.13×10^{-4} $dm^3 mol^{-1}s^{-1}$ at 25.0 $\pm$0.1°C for the reaction with LL = 1,10-phenanthroline and 2,2'-bipyridine respectively. $[H^+]$ varied in the range 0.6 – 2.0 M had no effect on the rate. Plausible reaction steps have been suggested.

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INTRODUCTION

Most redox reaction of iron (III) complexes [1-7] are thought to occur through the outersphere activated complex [5]. Marcus predicts that when this mechanism is operating a dependence of the reaction rate on the change in free energy involved is expected and a plot of log k (k is the electron transfer rate constant) against the standard redox potential couple E° would be linear with a slope of ca. 8 [5]. This theory had been expressed and modified in a variety of ways over the years [8]; though the conjecture of outersphere path using the theory is not outright, since some possible innersphere reaction have also shown obeyance to the theory [9-10].

Innersphere 1:1 complex formation is thought to precede the act of electron transfer in a number of hypophosphorus acid (also refer to as oxyacid) oxidation with metal ion oxidants [11-14]. However, some report have been made where the mechanism is possibly outersphere [15-19] and in some cases Marcus theory had been used further to suggest the operation of such a mechanism [18].

Except for a few reported cases [6,7,18], literature reveals that the operation of this theory had not been tested for redox reaction of metal ion oxidant and inorganic acid reductant that exist mostly as unionised in aqueous solution. The objective of the titled reaction is thus to provide more information on the kinetics and mechanism of the two reactants, and to further test the applicability of the Marcus theory to such systems.

MATERIALS AND METHODS

The iron (III) complexes were prepared and characterised by the method of Ford and Sutin [1]. Sodium hypophosphite was recrystallised for distilled water. Perchloric acid used to investigate the effect of hydrogen ion on the rate of reaction. Sodium perchlorate was used for maintaining a constant ionic strength for each run. All other reagents were used without further purification. Hypophosphorus acid has a dissociation constant of 10^{-2} M at 25°C and will be present mostly in unionised form in a fairly strong acid medium [11].

Stoichiometry

The stoichiometry of each of these reactions was determined by spectrophotometric titration. For each of the oxidant, the absorbances of solutions containing various concentrations of the oxyacid in the range $2.0 \times 10^{-5} – 2.0 \times 10^{-3}$ M and a constant oxidant concentration of 2.0×10^{-4} $mol^{-1}dm^{-3}$ at $[H^+]$ = 0.6 $mol^{-1}dm^{-3}$, I = 2.0 $mol^{-1}dm^{-3}$ ($NaClO_4$), T = 25.0°C were measured at 600 and 620 nm respectively for $Fe(phen)_3^{+3}$ and $Fe(bpy)_3^{+3}$ after the reaction had gone to completion. The stoichiometries of these reactions were then evaluated from plots of absorbances versus [oxidant]/[reductant].

Spectroscopic Studies

The comparison of the spectra of the iron (III) complexes in the acid range 0.6-2.0 M and separately that of the reaction mixture in the same acid range between 500 – 700 nm were made. There were no clear spectral shifts from the λ_{max} at 600 and 620 nm for

$Fe(phen)_3^{3+}$ and $Fe(bpy)_3^{3+}$ respectively. This suggests the unlikelyhood of precursor complex formation prior to the electron transfer step.

Kinetics

The reactions were run under pseudo-first order condition by employing a large excess of the oxyacid over the oxidant concentration and monitoring spectrophotometrically the gradual decrease in absorbance of $Fe(phen)_3^{3+}$ and $Fe(bpy)_3^{3+}$ at 600 nm and 620 nm respectively. The ionic strength was maintained at 2.0 $mol^{-1}dm^{-3}$ with $NaClO_4$ at T = 25 ±0.1°C.

RESULTS AND DISCUSSION

Results from stoichiometric studies show the mole ratio of 2:1 in favour of the oxidant, and when this is combined with results from the product analysis, the overall reaction can be represented as in equation 1.

$$2Fe(LL)_3^{3+} + H_3PO_2 + H_2O \rightarrow 2Fe(LL)_3^{2+} + H_3PO_3 + 2H^+ \quad ..(1)$$

Spectral analysis shows an absorption maximum at 510 and 520 nm respectively after the reaction had been completed for $Fe(phen)_3^{2+}$ and $Fe(bpy)_3^{2+}$. Phosphorous acid was confirmed as the product of the oxidation of hypophosphorous acid by the addition of saturated ammonium molybdate solution to the reaction mixture ; the absence of any precipitate of ammonium phosphomolybdate indicate the absence of phosphate ion and thus the presence of phosphorous acid.

Hypophosphorous acid is reported to be a better and faster reducing agent than phosphorous acid [20], hence the reverse reaction of equation 1 is not likely to occur especially with the large excess of the reductant used.

With the concentration of the reductant in at least a hundred fold excess over those of the oxidants, pseudo-first order plot were linear to at least 70% of the reaction. This suggest that the reaction is first order in the oxidants; the invariance of $k_3/(H_3PO_2)$ (where k_1 is the pseudo-first order rate constant) over the concentration range studied for the reductant also shows the reaction to be first order with respect to H_3PO_2 (Table 1). At constant $[H^+]$, the rate law will be:

$$\frac{-d[Fe(LL)_3^{3+}]}{dt} = 2k_2[Fe(LL)_3^{3+}][H_3PO_2] \quad …..(2)$$

where k_2 is the second order constant and has the value 1.83×10^{-4} $dm^3\ mol^{-1}\ s^{-1}$ and 1.13×10^{-4} $dm^3\ mol^{-1}\ s^{-1}$ respectively for $Fe(phen)_3^{2+}$ and $Fe(bpy)_3^{2+}$ at 25.0 ±0.1°C.

Acid and ionic strength independence

The second order rate constants for the oxidation of hypophosphorous acid was independent of acid and ionic strength in the range 0.6 – 2.0 M (Table 1). This suggests that none of the reactants is significantly protonated under our reaction condition and that the reaction is between a predominantly charged and uncharged reactant. The constancy of the electronic spectra of the oxidants in the acid concentration range studied further suggests non-protonation.

Hypophosphorous acid has a dissociation constant of 10^{-2} M at 25°C and ionises according to the equilibrium,

$$H_3PO_2 \rightleftharpoons H_2PO_2^- + H^+ \quad ….(3)$$

The acid will mostly be in the unionised form in a fairly strong acid medium. There are reports of the existence of the oxyacid in two tautomeric forms in aqueous solution, an unreactive and a reactive form, and that the acid catalyses the tautomerisation of the unreactive to the reactive, followed by the reaction of the reactive form with the oxidizing agent [12, 21].

The acid independent path observed in this work indicates negligible ionisation or that the two suggested forms of the oxyacid have similar kinetic behaviour in the reaction medium. Mishra and Ben-Zvic reported a similar observation [11, 20].

Effect of change in dielectric constant

The second order rate constant k_2 increases with decrease in the dielectric constant of the reaction medium (Table 2) and a plot of log k_2 against 1/D gave straight lines with positive slopes as expected for a reaction between a charged and an uncharged reaction [22], thus further corroborating our earlier assertion.

Michaelis Menten plot

Evidence from kinetics and/or spectrophotometry have been used to suggest an initial 1:1 complexation with innersphere character in hypophosphorous acid oxidation by metal ion oxidants [11-14]. The possibility of forming such a complex was assessed by using the modified Michaelis-Menten equation [23]; a plot of $1/k_{obs}$ against $1/[H_3PO_2]$ gave straight lines through the origin for each of the reaction (Fig. 1). This result further support the absence of any spectral shift of the reaction mixture from the maximum at 600nm and

Table 1: Second order rate constants for the oxidation of H_3PO_2 by $Fe(LL)_3^{3+}$ [2.0×10^{-4} mol dm^{-3}] at T = 25.0 $\pm$0.1°C

H_3PO_2, mol dm^{-3}	$[H^+]$ mol dm^{-3}	I, mol dm^{-3}	10^4, k_2 (dm^3 mol^{-1} s^{-1})	
			Fe $(phen)_3^{3+}$	Fe $(bpy)_3^{3+}$
0.10	0.6	2.0	1.83	1.13
0.20	0.6	2.0	1.84	1.13
0.25	0.6	2.0	1.84	1.13
0.50	0.6	2.0	1.84	1.12
0.75	0.6	2.0	1.82	1.12
1.0	0.6	2.0	1.82	1.13
0.1	0.6	2.0	1.82	1.13
0.1	0.85	2.0	1.84	1.11
0.1	1.15	2.0	1.80	1.15
0.1	1.45	2.0	1.82	1.10
0.1	1.75	2.0	1.80	1.11
0.1	2.0	2.0	1.82	1.11
0.1	0.6	0.6	1.82	1.12
0.1	0.6	0.85	1.80	1.11
0.1	0.6	1.15	1.84	1.13
0.1	0.6	1.45	1.82	1.13
0.1	0.6	1.75	1.85	1.14
0.1	0.6	2.0	1.84	1.13

Table 2: Effect of change in dielectric constant of the reaction medium on the second order rate constants of k_2 of $Fe(phen)_3^{3+}$, $Fe(bpy)_3^{3+}$ with concentration = 2.0×10^{-4} mol dm^{-3} and $[H_3PO_2]$ = 0.10 mol dm^{-3}, $[H^+]$ = 0.6 mol dm^{-3}; I = 2.0 mol dm^{-3} ($NaClO_4$), T = 25°C

C_2H_5OH (%)	10^2 1/D	10^4 k_2, (dm^3 mol^{-1} s^{-1})	
		$Fe(phen)_3^{3+}$	$Fe(bpy)_3^{3+}$
0	1.27	1.83	1.13
5	1.32	5.90	4.10
10	1.37	6.10	4.30
15	1.42	6.40	4.50
20	1.48	6.80	4.90
25	1.54	7.0	5.10
30	1.61	7.30	5.50

Table 3: Dependence of k_2 on the driving force E° for the reactions of some oxidants with H_3PO_2

Oxidant	10^4 k_2, (dm^3 mol^{-1} s^{-1})	E°, (oxidant, V)	Reference
$Fe(bpy)_3^{3+}$	1.13	0.97	This work
$Co^{III}W$	3.50	1.0	17
$Fe(phen)_3^{3+}$	1.83	1.06	This work
Au(III)	1.37	1.20	14

620nm for $Fe(phen)_3^{2+}$ and $Fe(bpy)_3^{2+}$ respectively. Thus any pre-equilibrium constant for the formation of any intermediate would be small.

Mechanism of the reaction

$$Fe(LL)_3^{3+} + H_3PO_2 \overset{K_4}{\rightleftharpoons} [Fe(LL)_3^{3+} \cdot H_3PO_2] \ldots(4)$$

$$[Fe(LL)_3^{3+} \cdot H_3PO_2] \xrightarrow{k_3} Fe(LL)_3^{2+} + H_2\dot{P}O_2 + H^+ \ldots(5)$$

$$Fe(LL)_3^{3+} + H_2\dot{P}O_2 + H_2O \xrightarrow{k_4} Fe(LL)_3^{2+} + H_3PO_3 + H^+ \ldots.(6)$$

On the basis of the above findings, scheme 1 below is proposed.

Scheme 1

In the above scheme an outersphere precursor complex forms followed by a rate determining electron transfer step. The precursor complex is necessarily outersphere since $Fe(LL)_3^{3+}$ is substitution inert as evident from the spectral identification of the product as $Fe(LL)_3^{2+}$.

If equation (5) above is rate determining and the outersphere activated complex is obtained from (4), the rate law of the reaction will be,

$\text{Rate} = K_4k_3\,[Fe(LL)_3^{3+}]\,[H_3PO_2]$ …..(7)

Equation (7) is the same as equation (2) with $2k_2 = K_4k_3$

H_2PO_2 radical is a well-established intermediate in hypophosphorous acid oxidation [18], however, result from polymerisation test in the present work is not appreciable. This does not preclude however, the above non-complimentary mechanism is from operating, especially when one considers the nature of the reacting species under our reaction condition, the stoichiometry and result from product analysis. The bulk of the redox reaction of $Fe(LL)_3^{3+}$ shows it to be a monoelectron acceptor in non-complementary redox reaction [1-7]. Thus it is possible that the lifetime of the free radical is too short for it to react with acrylonitrile to give appreciable polymerization product. Complementary mechanism is often conceded to whenever an inclusive polymerization test is observed in such redox reactions [10-14,1]. However, the monovalent complex $Fe(LL)_3^{+}$ has not been reported as a participant in redox reaction of $Fe(LL)_3^{3+}$.

$$2Fe(LL)_3^{3+} + H_3PO_2 \overset{K_5}{\rightleftharpoons} [Fe(LL)_3^{3+}, H_3PO_2, Fe(LL)_3^{3+}] \ldots.(8)$$

$$[Fe(LL)_3^{3+}, H_3PO_2, Fe(LL)_3^{3+}] \xrightarrow{k_b} 2Fe(LL)_3^{2+} + H_2PO_2^{+} + H^+ \ldots.(9)$$

$$H_2PO_2^{+} + H_2O \longrightarrow H_3PO_2 + H^+ \ldots.(10)$$

In the light of the above discussion, scheme 2 has been proposed.

Scheme 2

The scheme entails the trapping of a reductant between two oxidants to form an outersphere activated complex, followed by a rate determining release of two electrons to the metal centres. The rate of reaction of the hypophosphorous acid with $Fe(LL)_3^{3+}$ in this work is slow. This may thus be attributed to the thermodynamically unfavourable release of two electrons to the metal centres. The specie $H_2PO_2^{+}$ has been postulated before [20]. If step (9) is rate determining, then,

$\text{Rate} = k_5[Fe(LL)_3^{3+}, H_3PO_2, Fe(LL)_3^{3+}]$….(11)

Substituting into equation (11) from equation (8) gives the rate law,

$\text{Rate} = 2k_5k_8\,[Fe(LL)_3^{3+}]\,[H_3PO_2]$

Where $2k_2 = 2K_5k_6$

In the oxidation of hypophosphorous acid by metal ion oxidant, complex rate laws have been reported for reactions that possess innersphere character [11-14] and simple rate laws as obtained in the present work for those that are possibly outersphere [15-19]. Using our results and those obtained from other likely outersphere paths (Table 3), a plot of log k_2 against the standard redox potential couple of the oxidants gave straight line with slope of 8.0 V^{-1} when the method of least square analysis was employed (Fig. 2).

The good fit with the Marcus theory suggest that scheme 1 is plausibly operative and that the first electron transfer step is the rate determining. Additional evidence that may support the that the titled reaction occur by outersphere mechanism are (i) simple rate (ii) product analysis showing $Fe(LL)_3^{2+}$ as the reduced product of the oxidant. Shakashiri and Gordon [24] have used such result as a support for substitution inertness (iii) absence of kinetic or spectral evidence for the formation of intermediate complex. Similar results had been obtained earlier [6,7] where outersphere was suggested.

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