Kinetics and Mechanisms of Oxidations by Metal Ions. X.[1) Oxidation of Phosphinic and Phenylphosphinic Acids by Tris(polypyridyl)iron(III) Complexes

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A kinetic study on the oxidation of phosphinic(hypophosphorous) and phenylphosphinic acids by trispolypyridyliron(III) complexes using excess of either phosphinic or phenylphosphinic acid has been made in perchloric acid. The pseudo first-order rate constant k_{obs}, with respect to iron(III) complex, is independent of $[H^+]$. The results indicated that phenylphosphinic acid is more reactive than phosphinic acid towards any given iron(III) complex. The formation of an intermediate complex is indicated by the kinetics and supported by the spectrophotometry of the reaction mixture. The differences in the observed thermodynamic parameters of this intermediate complex, probably an outer-sphere complex, and those predicted by the Fuoss equation are discussed. It is suggested that the 'inactive' form of either of the acid is reactive towards the iron(III) complexes. It is also shown that the rate of disproportionation of the intermediate complex is not affected by the form of phosphinic or phenylphosphinic acid entering into the complex formation. The values of β_2 and k_1, the equilibrium constant for the formation of the oxidant-substrate complex and the rate limiting constant for its disproportionation respectively, are reported together with respective thermodynamic and activation parameters.

Efforts continue to identify the tautomeric form of oxoacids of phosphorous in their oxidation by metal or metal-complex ions. It had been shown that permanganate[2) and vanadium(V)[3) oxidations of phosphonic (phosphorous) acid involved the 'inactive' form $HP(O)(OH)_2$. However, Ce(IV) in nitric acid[4) oxidized the 'active' $HP(OH)_2$ form of phosphinic acid. The acid dependence in vanadium(V) oxidation of phenylphosphinic acid[5) indicated simultaneous oxidation of 'active' $C_6H_5P(OH)_2$ form by VO_2^+(aq.) (acid independent path) and 'inactive' $C_6H_5PH(O)(OH)$ form by $V(OH)_3^{2+}$ (aq.) (acid dependent path).

A survey of literature indicated that tris(polypyridyl)iron(III) complexes have not been used as oxidants for the oxoacids of phosphorus although it has been extensively used for the oxidations of both inorganic[6) and organic[7) substrates. Yet another reason for undertaking this study was to test the applicability of the Fuoss and Eigen equation[8) which has been applied successfully to several reactions proceeding through the formation of outer-sphere complex.[9) It might be added that an outer-sphere complex was expected in the present case because the tris(polypyridyl)iron(III) complexes are considered substitution inert.

The results indicated that the 'inactive' form of phosphinic and phenylphosphinic acid is the reactive species and the complex formed between tris(polypyridyl)iron(III) and phosphinic acid does not strictly conform to the outer-sphere complex as predicted by the Fuoss-Eigen equation.[8)

Experimental

Reagents. Phosphinic and phenylphosphinic acids (Fluka) were used as received. The stock solutions were standardized by cerimetry.[10) Sodium perchlorate was prepared by the neutralization of a known weight of sodium carbonate (BDH, AnalaR) by standard perchloric acid (E. Merck, GR). The neutralized solution was boiled to remove any dissolved carbon dioxide and made to volume. It was used to adjust the ionic strength. Lithium perchlorate was received from G. F. Smith and used as such. The stock solution of perchloric acid was standardized against a standard alkali. 1,10-Phenanthroline (E. Merck) and 2,2′-bipyridine (BDH) were used as received. Sodium thiosulfate (BDH, AnalaR) was standardized iodometrically against a standard solution of dichromate (BDH, AnalaR) using starch as the indicator. Twice distilled water, once distilled from an all glass still in presence of alkaline permanganate, was used for the preparation of solutions.

Preparation of $[FeL_3]^{3+}$ Complexes. Iron(III) complexes of 1,10-phenanthroline (phen) and 2,2′-bipyridine (bpy), FeL_3^{3+}, were prepared by the interaction of iron(II) sulfate and respective ligand in 1:3 ratio. In fact, the ligand was taken in slight excess to ensure complete complexation of Fe(II). The iron(II) complexes were then oxidized by lead dioxide.[11,12) The blue solution of iron(III) complex was filtered through a sintered G4 crucible and the perchlorate salt was precipitated by the addition of minimum quantity of 70% perchloric acid. The solid so obtained was recrystallized from aqueous perchlorate solution.

The standard stock solution of the respective complex was prepared in perchloric acid (10 mol dm^{-3}) by weight and stored in the refrigerator. Although such stock solutions are stated to be stable for at least three months at room temperatures in the dark,[13) the solutions older than 48 hours were discarded. The spectral characteristics of FeL_3^{2+} and FeL_3^{3+} solutions matched well with those reported in the literature.[14)

Stoichiometry. A number of reaction mixtures having different FeL_3^{3+} concentrations and known excess of phosphinic acid were prepared in different $[H^+]$. On complete reduction of the iron(III) complex, the amount of phosphonic acid produced was determined as described below.[15)

The reaction mixtures were suitably diluted or neutralized to bring down the concentration of perchloric acid to less than 0.1 mol dm^{-3}. A 50 ml of the solution was added to a known solution of iodine in phosphate buffer, and the pH 7.3 was adjusted. After about one hour the solutions in iodine flasks were acidified with 6 mol dm^{-3} acetic acid and immediately titrated for the liberated iodine with a standard thiosulfate solution to a starch-iodine end point. The results of several such estimations indicated that $\Delta[H_3PO_2]/\Delta[FeL_3^{3+}]=0.51\pm0.04$. Hence the stoichiometric equation for the reaction is expressed by Eq. 1.

$$2FeL_3^{3+}+H_3PO_2+H_2O \rightarrow 2FeL_3^{2+}+H_3PO_3+2H^+ \quad (1)$$

Rate Measurements. The rate was measured under pseudo first-order conditions ($[RH_2PO_2]\geq10[FeL_3^{3+}]$, where R=$C_6H_5$ for phenylphosphinic acid and R=H for phosphinic acid). The reagents, FeL_3^{3+} and phosphinic/phenylphosphinic acid with required concentrations of sodium perchlorate and perchloric acid, were taken separately. These were allowed to attain the thermal equilibrium in a thermostated water bath maintained at the desired temperature with a possible variation of ±0.1 °C. The reaction was initiated by the quick mixing of the desired volumes of FeL_3^{3+} and phosphinic/phenylphosphinic acid solutions.

The kinetics was followed by measuring the absorbance of $Fe(phen)_3^{2+}$ at 510 nm and that of $Fe(bpy)_3^{2+}$ at 520 nm on a Beckman DU-2 spectrophotometer. The quartz cell, 1 cm pathlength, was immediately returned to the cell compartment after the transfer of the reaction mixture. The absorbance of the FeL_3^{2+} complex was quickly measured thereafter.

The slow hydrolysis of $Fe(phen)_3^{2+}$ to free Fe^{2+}(aq.) and 1,10-phenanthroline[16) does not affect the measurements of A_∞ in reactions where the rate of oxidant loss is much faster. It is for this reason that reactions on stopped-flow time scale could be studied for several half lives of the reactions. However, in reactions where the rate of oxidant loss is either of comparable magnitude or slower than the rate of hydrolysis of FeL_3^{2+} there arises a problem both in following the reaction even upto the first half-life and measuring A_∞ because the hydrolyzed product Fe^{2+}, reacting rapidly,[17) vitiates both the kinetics and A_∞. Hence for the measurement of A_∞, the reaction mixture was reduced with a pinch of solid iron(II) sulfate[18) and the absorbance (A_∞) of the resulting solution was immediately recorded.

Since the $t_{1/2}(=0.691/k_{obs})$ with $[H_3PO_2]=0.1$ and $[H^+]=1.0$ mol dm^{-3} at 35 °C approximated to about 4 hours, the rate measurements had to be restricted to the initial 35—40% of the reaction. The plots of $\ln(A_\infty-A_t)$ against time for the mentioned range were linear; where A_∞ and A_t are the absorbance at infinite time and time 't'. The gradient of the linear plots ($=k_{obs}$) was estimated using a computer program based on the method of least squares.

Test for Free Radical. The formation of a free radical during the progress of the reaction was indicated by the polymerization of acrylonitrile added to the reaction mixtures degassed with nitrogen. The individual solutions of FeL_3^{3+} and phosphinic or phenylphosphinic acid, similarly degassed, did not initiate the polymerization of the acrylonitrile monomer.

Spectrophotometry. The visible (450—750 nm) spectra of FeL_3^{3+} and reaction mixtures having FeL_3^{3+} and RH_2PO_2 in the ratios of 1 : 1 and 1 : 10 were recorded on a Shimadzu 240 UV-vis Graphicord spectrophotometer at room temperature (27 °C). The spectra shown in Figs. 1 and 2 are for $Fe(bpy)_3^{3+}$ (8.0×10^{-4} mol dm^{-3}) and phosphinic and phenylphosphinic acids in 2.5 mol dm^{-3} perchloric acid respectively. It is worth noting that absorbance increased with increasing concentrations of oxoacid of phosphorous and a pronounced hump developed near 530 nm for 1 : 10 mixture. The spectra is indicative of the formation of a complex, probably an outer-sphere complex.

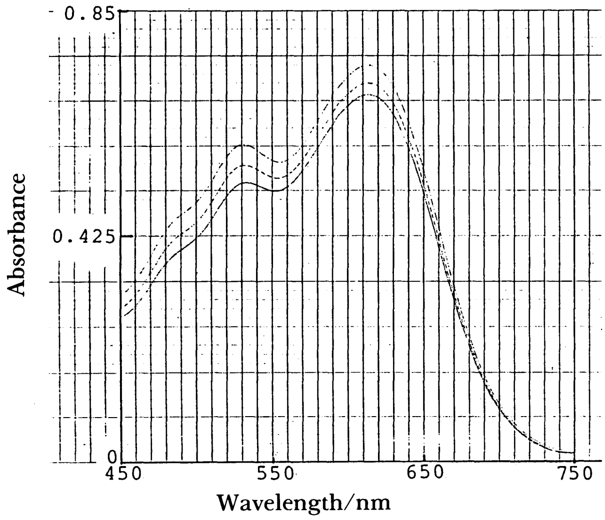

Fig. 1. Visible spectra of the mixtures of $Fe(bpy)_3^{3+}$ and H_3PO_2 at 27 °C in the ratio 1 : 0(——), 1 : 1 (----), and 1 : 10 (—•—) where $[Fe(bpy)_3^{3+}]=8.0\times10^{-4}$ mol dm^{-3}, and $[H^+]=2.5$ mol dm^{-3}.

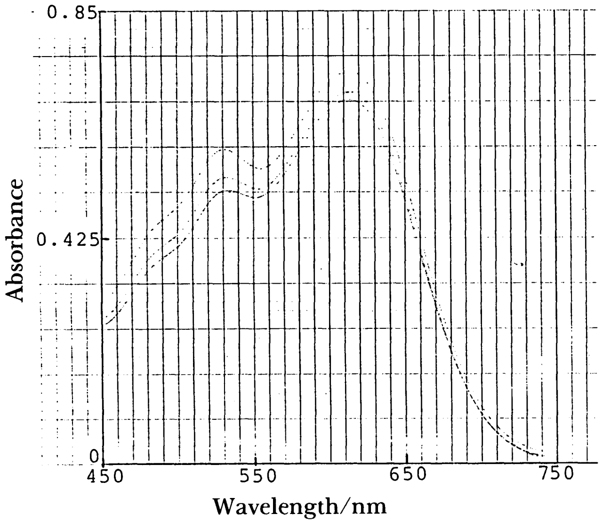

Fig. 2. Visible spectra of $Fe(bpy)_3^{3+}$ and $C_6H_5H_2PO_2$ at 27 °C in the ratio 1 : 0 (——), 1 : 1 (----), and 1 : 10 (—•—) where $10^4[Fe(bpy)_3^{3+}]=8.0$ and $[H^+]=2.5$ mol dm^{-3}.

Results

Dependence on FeL_3^{3+}. The first order reduction of FeL_3^{3+} is confirmed by the invariance of k_{obs} over a ten-fold variation in the initial $[FeL_3^{3+}]$. The results for the oxidation of phenyl phosphinic acid are in

Table 1. Dependence of $k_{obs}(s^{-1})$ on the Initial $[FeL_3^{3+}]$ at 25 °C.

$10^3[C_6H_5H_2PO_2]=3.0$, $[H^+]=0.5$, and $I=1.0$ mol dm^{-3}

$10^5[Fe(phen)_3^{3+}]$	10^5k_{obs}	$10^5[Fe(bpy)_3^{3+}]$	10^5k_{obs}
1.26	10.1	1.46	8.67
5.05	10.0	5.87	8.61
7.58	10.2	8.75	8.77
10.1	9.92	11.7	8.66
12.6	10.1	14.6	8.70

Table 1. The slightly higher k_{obs} value for $Fe(phen)_3^{3+}$ oxidation compared to the value for $Fe(bpy)_3^{3+}$ oxidation is consistent with the higher redox potential of $Fe(phen)_3^{3+}$.

Dependence on [1,10-phenanthroline]. These experiments are designed to know whether the complex between FeL_3^{3+} and oxoacid of phosphorous is formed in accordance with the equilibrium (2). The formation of the complex was indicated by the spectrophotometric studies of the reaction mixtures described earlier.

$$FeL_3^{3+}+nH_3PO_2 \rightleftarrows FeL_{(3-n)}(H_3PO_2)_n^{3+}+nL \qquad (2)$$

where n has a maximum value of 1 as indicated by the order of the reaction with respect to phosphinic acid.

A retardation in k_{obs} was expected if $FeL_{(3-n)}(H_3PO_2)_n^{3+}$ is reduced to the products in the rate limiting step. The fact that k_{obs} is independent over more than twelve-fold variation in [1,10-phenanthroline], Table 2, the probability of the formation of an inner-sphere complex is excluded from the purview of any mechanism to be proposed for the reaction.

Dependence on $[Fe(phen)_3^{2+}]$. The rates were measured in terms of disappearance of $Fe(phen)_3^{3+}$ at 360 nm ($\varepsilon_{Fe(phen)_3^{3+}}=5500$ and $\varepsilon_{Fe(phen)_3^{2+}}=1000$ dm^3 mol^{-1}cm^{-1})[19] and then in terms of appearance of $Fe(phen)_3^{2+}$ at 510 nm ($\varepsilon_{Fe(phen)_3^{2+}}=11000$,[20] and $\varepsilon_{Fe(phen)_3^{3+}}=300$ dm^3 mol^{-1}.[21] The values $10^5k_{obs}=5.27$ and 5.37 s^{-1}, obtained at two wavelengths respectively are in agreement with the value $10^5k_{obs}=4.8$ s^{-1} obtained at $[H_3PO_2]=0.10$ mol dm^{-3} in the absence of $Fe(phen)_3^{2+}$ under identical experimental conditions ($10^5[Fe(phen)_3^{3+}]=6.32$, $10^5[Fe(phen)_3^{2+}]=3.16$, $[H_3PO_2]=0.11$, $[H^+]=0.5$ and $I=1.0$ mol dm^{-3} at 36 °C). Hence, reaction (3) or any such other equilibrium has no mechanistic significance.

$$[FeL_3 \cdots H_3PO_2]^{3+} \rightleftarrows FeL_3^{2+}+H_3PO_2^+ \qquad (3)$$

Dependence on $[H_3PO_2]$. In this study it was noted that k_{obs} did not increase proportionately with $[H_3PO_2]$. The plot between k_{obs} and $[H_3PO_2]$, Fig. 3, is nonlinear. However, the plots between k_{obs}^{-1} and $[H_3PO_2]^{-1}$ are linear with an intercept on the rate ordinate. The results of the temperature dependence study are in Table 3.

Table 2. Dependence of k_{obs} (s^{-1}) on the Initial [1,10-phenathroline] at 30 °C.

$10^5[Fe(phen)_3^{3+}]=6.32$, $[H^+]=0.5$, $[H_3PO_2]=0.1$, and $I=1.0$ mol dm^{-3}

10^5[phen]/mol dm^{-3}	0.5	1.0	2.0	4.0	6.32
10^5 k_{obs}/s^{-1}	3.45	3.47	3.44	3.46	3.48

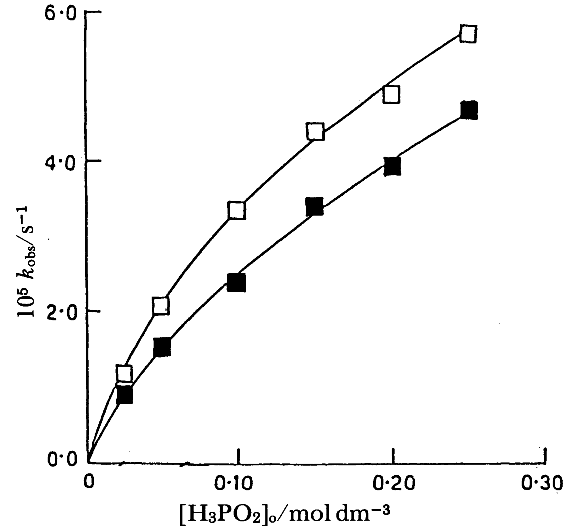

Fig. 3. Plot between $k_{obs}(s^{-1})$ and $[H_3PO_2]$ at 30 °C with $10^4[Fe(phen)_3^{3+}]=0.632$ and $[H^+]=0.5$ and $I=1.0$ mol dm^{-3} (□) and with $10^4[Fe(bpy)_3^{3+}]=0.729$ and $[H^+]=0.5$ and $I=1$ mol dm^{-3} at 30 °C (■).

Dependence on $[H^+]$. The results of the rate measurement at different $[HClO_4]$ between 0.3—3.0 mol dm^{-3} at constant ionic strength are in Table 4.

Table 3. Dependence of k_{obs} on the Initial $[H_3PO_2]$ in the Oxidation by $Fe(phen)_3^{3+}$ at Different Temperatures.

$20^5[Fe(phen)_3^{3+}]=6.32$, $[H^+]=0.5$, and $I=1.0$ mol dm^{-3}

$[H_3PO_2]$ Temp/°C	0.025	0.05	0.1 $10k_{obs}$/s^{-1}	0.15	0.20	0.25
30	1.23	2.14	3.46	4.40	5.00	5.50
36	1.47	2.80	4.80	6.60	7.84	9.74
40.5	1.80	3.46	6.42	8.95	10.7	13.4
44.5	2.52	4.95	8.80	13.0	17.4	21.7
50	3.42	6.90	11.9	18.6	27.0	32.7

Table 4. Dependence of k_{obs} on the Initial $[H^+]$ at Constant Ionic Strength at 36 °C.

(a) $10^5[Fe(phen)_3^{3+}]=6.32$, $[H_3PO_2]=0.1$, and $I=3.0$ mol dm^{-3}
(b) $10^5[Fe(bpy)_3^{3+}]=7.30$, $[H_3PO_2]=0.09$, and $I=3.0$ mol dm^{-3}

$[H^+]$/mol dm^{-3}	10^5k_{obs}/s^{-1}		$[H^+]$/mol dm^{-3}	10^5k_{obs}/s^{-1}	
	(a)	(b)		(a)	(b)
0.314(0.313)	4.86	3.39	1.703	4.80	3.40
0.509(0.508)	4.88	3.46	2.002	4.80	3.40
0.707(0.706)	4.84	3.40	2.202	4.90	3.35
1.005(1.004)	4.88	3.30	2.502	4.86	3.46
1.304(1.303)	4.80	3.35	3.002	4.94	3.42

Figures in the parentheses are $[H^+]$ calculated for $[H_3PO_2]=0.09$ mol dm^{-3}.

Table 5. Dependence of k_{obs} on the Ionic Strength at 25 °C.

$10^5[Fe(phen)_3^{3+}]=6.32$, $10^3[C_6H_5H_2PO_2]=2.0$, and $[H^+]=0.1$ mol dm^{-3}

$[MClO_4]$/mol dm^{-3}	0.0	0.1	0.3	0.5	0.7	1.0
I/mol dm^{-3}	0.1	0.2	0.4	0.6	0.8	1.1
	············		$10^5k_{obs}/s^{-1}$		············	
M=Na	11.7	11.0	10.3	9.85	9.43	9.12
M=Li	11.8	10.2	9.93	9.45	9.05	

The concentration shown under $[H^+]$ in the table is the sum of $[H^+]$ from perchloric acid and dissociation of phosphinic acid. A K_a value=0.051, extrapolated from the data of Espenson and Binau[22e] is used to calculate the dissociated $[H^+]$ from phosphinic acid. The conclusion of the study is that k_{obs} is independent of $[H^+]$.

Medium Effects. Redox and substitution reactions are affected by the medium effects[23,24] where uncertainties in hydrogen ion effects may be related to differences in the activity coefficients of the counter ions (Na^+ or Li^+) used as perchlorate salts for adjusting the ionic strength to a constant value while varying the $[H^+]$. These effects are usually absent for intramolecular redox reactions.[25] Indeed the presence of medium effects is confirmed by the fact that k_{obs} values corresponding to Li^+ are consistently lower than the values obtained for the corresponding Na^+. The results are in Table 5.

Effect of Ionic Strength. The results, Table 5, indicate that k_{obs} decreased with increasing ionic strength. The plot of logarithmic value of k_{obs} against $I^{1/2}/(1+I^{1/2})-0.05I$ is linear with the slope value=-0.48 for Na^+ and -0.53 for Li^+ which is much less than the theoretical value expected for the reaction between charged ions involved in the reaction. This discrepancy could be due to the presence of more than one equilibrium before the rate determining step.

Empirical Rate Law. All the above results are summarized by the empirical rate law given in Eq. 4.

$$\frac{-d[FeL_3^{3+}]}{dt}=\frac{d[FeL_3^{2+}]}{dt}=\frac{a[RH_2PO_2]_o[FeL_3^{3+}]_o}{1+b[RH_2PO_2]_o} \tag{4}$$

where a and b are empirical constants and subscript "o" denotes the analytical concentration used.

Discussion

Since the rate of the reaction is independent of $[H^+]$, there is a possibility that two equilibria, which are affected by the H^+ in the opposite directions, are present so that the net effect of H^+ is not noticed. The two such equilibria are considered in Eqs. 5 and 6. The consideration of the equilibrium (5) is influenced by the fact that in the tris (1,10-phenanthroline)iron(III) oxidation of ascorbic acid,[19,26] the pK_{1a} of which is much higher[19,25,26] than that of phosphinic acid[22] and phenylphosphinic acid,[27] both undissociated ascorbic acid and hydrogen ascorbate ion are considered reactive. The equilibrium (6) has been considered in several studies.[19,20,28,29] The concentration of the complex $[FeL_3\cdots RH_2PO_2]^{3+}$, formed through the equilibria (7) and (8), remains stationary under any given $[H^+]$ which explains no effect of H^+on the observed rate of the reaction. The mechanism involving reactions (5)—(10) is considered below.

$$RH_2PO_2 \overset{K_a}{\rightleftarrows} RHPO_2^- + H^+ \tag{5}$$

$$H^+ + FeL_3^{3+} \overset{K_c}{\rightleftarrows} HFeL_3^{4+} \tag{6}$$

$$HFeL_3^{4+} + RHPO_2^- \overset{\beta_1}{\rightleftarrows} [FeL_3\cdots RH_2PO_2]^{3+} \tag{7}$$

$$FeL^{3+} + RH_2PO_2 \overset{\beta_2}{\rightleftarrows} [FeL_3\cdots RH_2PO_2]^{3+} \tag{8}$$

$$[FeL_3\cdots RH_2PO_2]^{3+} \xrightarrow{k_1} RHPO_2^{\cdot} + FeL_3^{2+} + H^+ \tag{9}$$

$$RHPO_2^{\cdot} + H_2O + FeL_3^{3+} \xrightarrow{\text{fast}} RH_2PO_3 + FeL_3^{2+} + H^+ \tag{10}$$

It is thus seen that the formation of the complex $[FeL_3\cdots RH_2PO_2]^{3+}$ in equilibrium (7) involved equilibrium (5) and equilibrium (6) whereas it is also formed through equilibrium (8) alone. The exact path of its formation cannot be stated unambiguously because $\beta_2=\beta_1K_aK_c$. The consideration of the above reactions leads to the rate law in Eq. 11.

$$k_{obs}=\frac{2k_1\beta_2[RH_2PO_2]_o}{(1+K_a[H^+]^{-1})(1+K_c[H^+])+\beta_2[RH_2PO_2]_o} \tag{11}$$

Although the rate law in Eq. 11 is not independent of $[H^+]$, yet with the appropriate assumption that $1+\beta_2[RH_2PO_2]_o \gg K_a[H^+]^{-1}+K_c[H^+]+K_aK_c$ because the values of K_a and K_c are much less than 1; the Eq. 11 is thus reduced to Eq. 12 which is independent of $[H^+]$. The Eq. 12 is identical to the empirical rate law in Eq. 4 where $a=2k_1\beta_2$ and $b=\beta_2$.

$$k_{obs}=\frac{2k_1\beta_2[RH_2PO_2]_o}{1+\beta_2[RH_2PO_2]_o} \tag{12}$$

The Eq. 12 holds in the sense that plots of k_{obs}^{-1} against $[RH_2PO_2]_o^{-1}$, Fig. 4, are linear at all temperatures. From the gradient and intercept of such plots, the values of β_2 and k_1 are derived and are given in Tables 6 and 7 respectively.

Alternate Mechanism. A simple and straight forward mechanism providing a rate law independent of $[H^+]$ could also be described by the reactions (8)—(10). The consideration of these reactions leads to the deduction of the rate law given in Eq. 12. There is no way to differentiate between the mechanisms described by reactions (5)—(10) and the one described by the reactions (8)—(10).

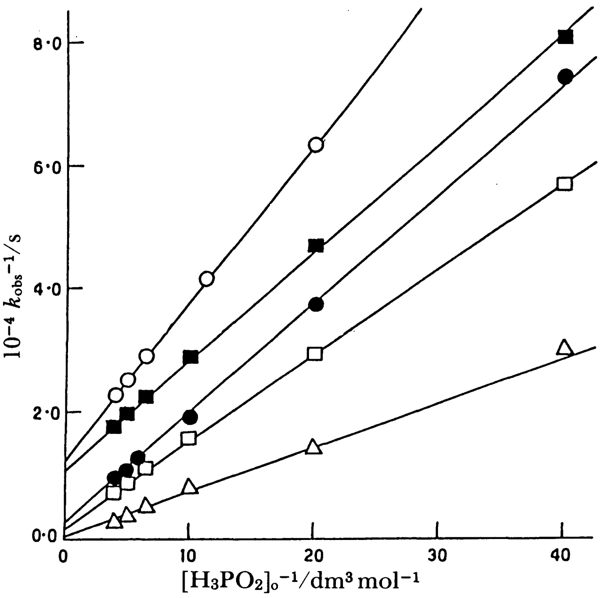

Fig. 4. Plot between k_{obs}^{-1} and $[H_3PO_2]^{-1}$ at different temperatures for the oxidations affected by $Fe(phen)_3^{3+}$ at 30 °C (■), 40.5°C (□), and 50 °C (△) and for the oxidations by $Fe(bpy)_3^{3+}$ at 30 °C (○) and 40.5 °C (●).

Table 6. Values of β_2 for H_3PO_2 at Different Temperatures and the Thermodynamic Parameters

Temp/°C	25^{a)}	30	36	40.5	44.5	50
Ligand			β/dm^3 mol^{-1}			
phen	11.6	6.4	2.8	1.7	1.1	0.6
bpy	7.1	4.4	3.0	1.1	0.9	0.8

a) Extrapolated value.
$\Delta H°$(phen)=−90±10 kJ mol^{-1}, $\Delta H°$(bpy)=−75±10 kJ mol^{-1}, $\Delta S°$(phen)=−290±40 J K^{-1} mol^{-1}, $\Delta S°$(bpy)=−245±30 J K^{-1} mol^{-1}.

Table 7. Values of the Rate Limiting Constant k_1(s^{-1}) at Different Temperatures and Activation Parameters

Temp/°C	30	36	40.5	44.5	50
Ligand			10^5k_1(s^{-1})		
phen	4.46	11.2	21.1	42.5	128
bpy	4.23	8.06	26.0	42.5	85.5

$\Delta H^{\ne}$(phen)=121±5 kJ mol^{-1}, $\Delta H^{\ne}$(bpy)=125±6 kJ mol^{-1}, $\Delta S^{\ne}$(phen)=70±10 J K^{-1} mol^{-1}, $\Delta S^{\ne}$(bpy)=84±12 J K^{-1} mol^{-1}.

The dissociation of ferriin is a first-order reaction[30] in [H$^+$]. Hence in the absence of any dependence of rate on H$^+$, it is apparent that the dissociation of ferriin is not a part of the mechanism. That there is no dissociation of ferriin is further supported by the results on the effect of variation of 1,10-phenanthroline on the observed rate.

Fuoss equation[8] has been favored as tool to differentiate between an outer-sphere and inner-sphere complex. The Fuoss equation is given in Eq. 13.

$$K_o=\frac{4\pi N_A \mathbf{a}^3}{3000}\exp\left(\frac{-z_1z_2e^2}{\mathbf{a}DkT}+\frac{z_1z_2e^2\mathbf{k}}{DkT(1+\mathbf{ka})}\right) \tag{13}$$

where N_A is Avogadro's number, $\mathbf{a}$=the centre to centre separation of the ions at closest approach, e=electronic charge, z_1 and z_2 are the charges on the ions with appropriate sign, D is the dielectric constant, k=Boltzmann's constant, and $\mathbf{k}$ the Debye-Hückel parameter.

The approach is based on the theoretical calculation of the association constant and the associated thermodynamic parameters and then these are compared with the experimentally obtained data.

The values of K_o were calculated at different temperatures by considering r=7 Å[16] for $Fe(phen)_3^{3+}$ and 3 Å for phosphinic acid (calculated by the relation $4\pi r^3/3=M/n_Ad$ where M is the molecular weight and d is the density) and $\mathbf{a}$=10 Å and using the value of D at different temperatures.[31] These are given in Table 8 wherein are also reported the calculated thermodynamic parameters. The value of K_o, 4.86 dm^3 mol^{-1}, at 25 °C is somewhat less than the value of β_2 extrapolated to the same temperature. The other differences are (i) K_o increased with the temperature whereas β_2 decreased and (ii) the values of the enthalpy and entropy are positive for K_o whereas these parameters have negative values for β_2. We at this point are not sure whether this is an exception to the applicability of the Fuoss equation or whether the complex formed is an inner-sphere complex. The possibility of the formation of an inner-sphere complex such as proposed in the oxidation of I$^-$ by hexacyanoferrate(III) ion[32] cannot be over ruled. The assignment of an inner-sphere or outer-sphere mechanism to a redox reaction is often difficult.[33]

'Active' vs. 'Inactive' Form. The presence of H$^+$ in the reaction system requires the consideration of the equilibrium (14). This equilibrium is attractive in the sense that it is independent of [H$^+$] though the conversion of 'inactive' form to 'active' form is catalyzed by H$^+$. The active form is thought to be produced as an intermediate in the exchange of phosphorus bonded hydrogen in phosphinic acid with tritium[34] or deuterium.[35] The value of the equilibrium constant is of the order of 10^{-12}.[36]

$$H^++H_2P(O)OH \overset{K}{\rightleftarrows} H_2P(OH)(OH^+) \rightarrow H:P(OH)_2+H^+ \tag{14}$$

Table 8. Values of Outer-Sphere Association K_o, Calculated for $Fe(phen)_3^{3+}\cdots H_3PO_2$ from the Fuoss Equation

Temp/°C	25	30	35	40	45
K_o/dm^3 mol^{-1}	4.86	4.91	4.96	5.01	5.07

$\Delta H°$=1.65 kJ mol^{-1}, $\Delta S°$=18 J K^{-1} mol^{-1}.

The following reactions (15)—(17) duplicate the reactions (8)—(10) and are supposed to have the 'inactive' form as the reactive entity.

$$\underset{\text{(inactive)}}{FeL_3^{3+}+H_2P(O)(OH)} \overset{\beta}{\rightleftarrows} [FeL_3\cdots H_2P(O)(OH)]^{3+} \qquad (15)$$

$$[FeL_3\cdots H_2P(O)(OH)]^{3+} \xrightarrow{k} H_2PO_2^{\bullet} + H^+ + FeL_3^{2+} \qquad (16)$$

$$FeL_3^{3+}+H_2O+H_2PO_2^{\bullet} \xrightarrow{\text{fast}} H_3PO_3+FeL_3^{2+}+H^+ \qquad (17)$$

The consideration of the reactions (14)—(17) and the fact that $1 \gg K$ leads to the rate law in Eq. 18 which is similar to the rate law in Eq. 12.

$$\frac{d[FeL_3^{2+}]}{dt} = \frac{2k\beta[FeL_3^{3+}][H_3PO_2]_o}{1+\beta[H_3PO_2]_o} \qquad (18)$$

However, if the 'active' form $H:P(OH)_2$ is reactive then the respective reactions are in Eqs. 14 and 19—21. The rate law based on these reactions, and acknowledging the fact that $1 \gg K$, will have the form given in Eq. 22.

$$FeL_3^{3+}+H:P(OH)_2 \overset{\beta_a}{\rightleftarrows} [FeL_3\cdots H:P(OH)_2]^{3+} \qquad (19)$$

$$[FeL_3\cdots H:P(OH)_2]^{3+} \xrightarrow{k_a} :P(OH)_2+H^++FeL_3^{2+} \qquad (20)$$

$$FeL_3^{3+}+H_2O+:P(OH)_2 \xrightarrow{\text{fast}} HP(O)(OH)_2+H^++FeL_3^{2+} \qquad (21)$$

$$\frac{d[FeL_3^{2+}]}{dt} = \frac{2k_a\beta_aK[FeL_3^{3+}][H_3PO_2]_o}{1+\beta_aK[H_3PO_2]_o} \qquad (22)$$

Thus in the plots between k_{obs}^{-1} and $[H_3PO_2]_o^{-1}$, Fig. 4, the slope and intercept are equivalent to those given in Eq. 23.

$$\text{Slope}=(2k_a\beta_aK)^{-1};\ \text{intercept}=1/2k_a,\quad \text{and intercept/slope}=K\beta_a \qquad (23)$$

It is thus seen that $k=k_a$ which means that the rate limiting constant for the disproportionation of the complex is not affected by the reactive form of phosphonic acid. However, $\beta=K\beta_a$ so that $\beta_a=\beta/K=10^{12}\beta$ (or $\beta_2=6.4\times10^{12}$ dm^3 mol^{-1} at 30 °C). Considering that FeL_3^{3+} is inert to substitution this high value of β_a is certainly inadmissible. Hence it is concluded that 'active' form is not the reactive entity thus leaving the 'inactive' form to be the reactive species.

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