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KINETICS OF PERIODATE OXIDATION OF *TRIS*-(4,4'-DIMETHYL-2,2'-BIPYRIDINE) IRON(II) IN ACID MEDIUM

E.T. Ayodele, A.A. Olajire* and S.O. Oladoye

Department of Pure and Applied Chemistry, Ladoke Akintola University of Technology,
P.M.B. 4000, Ogbomoso, Nigeria

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ABSTRACT. The kinetics and mechanism of periodate oxidation of the complex *tris*-(4,4'-dimethyl-2,2'-bipyridine) iron(II) in acid medium was investigated. The complex undergoes extensive protonation in acid medium. Both protonated and the unprotonated species undergo electron transfer reaction with the active periodate species such as IO_3^+ and $H_6IO_6^+$. The protonated species forms an ion pair with IO_3^- and thus suggests an outer-sphere mechanism for the reaction.

INTRODUCTION

Considerable work has been done on oxy-halogen ions of chlorine and bromine [1-3], but little is known of oxy-iodine systems particularly periodates. The scanty data on periodates may be attributed to the varied equilibria between meta, meso and para periodates [4, 5]. Also, except for previous work carried out by Amire and Ige [6], there is no available evidence in the literature of periodate oxidation of inorganic complexes. The periodates are both thermodynamically potent and kinetically facile oxidants. The oxidation potential is greatest in acid solution and can be progressively diminished by increasing the pH of the solution. The periodates are consistently used in structural analysis of organic compounds, particularly those with substituted hydroxyl or carbonyl groups. The pH dependence of the various periodate species in solution [4] offers quite interesting kinetic and mechanistic possibilities from the point of view of outer and inner sphere reaction pathways.

For the iron(II) complex, there is a lot of controversy as to whether the *bis*-dissociated iron(II) complex participates in the electron transfer process. The only available literature evidence is that of Sharkashiri and Gordon [7] and that of Ige and Soriyan [8] on oxidation of $Fe(phen)_3^{2+}$ by periodate.

In the present investigation, these kinetic and mechanistic possibilities are investingated. To help in the elucidation of the overall kinetics and mechanism of periodate oxidation of *tris*-(4,4'-dimethyl-2,2'-bipyridine) iron(II) complex in acid medium, the following investigation were carried out:

(i) rate dependence on ionic strength (μ) in acid medium using sodium sulphate (Na_2SO_4) to make up the ionic strength, and
(ii) parameters which affect the observed rate constant (k_{obs}) in acid medium at a fixed ionic strength.

To our knowledge, no detailed study of periodate oxidation of *tris*-(4,4'-dimethyl-2,2'-bipyridine) iron(II) in acid medium has been reported.

EXPERIMENTAL

Preparation of tris-(4,4'-dimethyl-2,2'-bipyridine) iron(II) perchlorate. The synthetic route used by Schilt and Taylor [9] for the synthesis of *tris*-(1,10-phenanthroline) iron(II) perchlorate was adapted for the preparation of *tris*-(4,4'-dimethyl-2,2'-bipyridine) iron(II) perchlorate. 0.245 g of sodium perchlorate (Analar, BDH) was added to a solution of 0.392 g ferrous ammonium sulphate hexahydrate $Fe(NH_4)_2(SO_4)_2.6H_2O$ (Analar, BDH) and 0.475 g 4,4'-dimethyl-2,2'-bipyridine (Analar, BDH) in 50 cm^3 hot water. The amorphous product obtained was recrystallized twice in hot water, and it gave dark red crystals which was vacuum dried for several days.

Characterization of the complex. The complex was characterized via its UV-visible spectrum. The spectrum was run on a Pye Unicam SP8 400 UV-Visible scanning spectrophotometer. The maximum wavelength of absorption (λ_{max}) in the visible region and the corresponding extinction coefficient, which are in excellent agreement with those from literature [10], are given in Table 1.

Table 1. Visible spectral data of *tris*-(4,4'-dimethyl-2,2'-bipyridine) iron(II) perchlorate.

Observed values		Literature values	
λ_{max} (nm)	ε_{max} ($dm^3\ mol^{-1}\ cm^{-1}$)	λ_{max} (nm)	ε_{max} ($dm^3\ mol^{-1}\ cm^{-1}$)
530	8468	529	8470

Kinetics measurements. The reaction was followed by monitoring the rate of change in absorbance with time at the wavelength of maximum absorption (λ_{max} 530 nm) for *tris*-(4,4'-dimethyl-2,2'-bipyridine) iron(II). The reactions were carried out under pseudo first order conditions with the meta-periodate always in at least 10-fold excess of the complex. Pseudo first-order rate constants were obtained from the slopes of the plot of log (A_t - A_∞) against time. The plots were always linear to at least 75% reaction.

RESULTS AND DISCUSSION

The dependence of the observed rate constant (k_{obs}) on the ionic strength (μ) was studied by varying the ionic strength in acid medium (H_2SO_4) using sodium sulphate (Na_2SO_4) to make up the ionic strength, and the $[IO_4^-]$ and $[Fe(Me_2bipy)_3^{2+}]$ were fixed at 4.72×10^{-4} and 2.36×10^{-5} mol dm^{-3}, respectively. The results obtained are summarized in Table 2. The plot of $\log_{10}k_{obs}$ versus $(\mu^{1/2})/(\mu^{1/2} + 1)$ (Figure 1) is linear with a positive slope of 0.68. The positive slope obtained shows that the reacting species carry the same type of charge. The likely reacting species are $IO_3^+/H_6IO_6^+$ and $Fe(Me_2bipy)_3^{2+}$. The IO_3^+ is derived from the protonation of the iodate ion (IO_4^-) in acid solution (equation 1). Also, IO_3 is formed as an intermediate from the deprotonation of $HFe(Me_2bipy)_3^{3+}$ by H_5IO_6 (equation 2) and the reaction of $H_6IO_6^+$ with $Fe(Me_2bipy)_3^{2+}$ (equation 3).

$$2H^+ + IO_4^- \longrightarrow IO_3^+ + H_2O \tag{1}$$

$$HFe(Me_2bipy)_3^{2+} + H_5IO_6 \longrightarrow Fe(Me_2bipy)_3^{3+} + IO_3 + 3H_2O \tag{2}$$

$$Fe(Me_2bipy)_3^{2+} + H_6IO_6^+ \longrightarrow Fe(Me_2bipy)_3^{3+} + IO_3 + 3H_2O \tag{3}$$

The IO_3 intermediate generated in equations (2) and (3) can undergo disproportionation reaction yielding IO_3^+ as shown in equation (4).

$$2IO_3 \longrightarrow IO_3^+ + IO_3^- \tag{4}$$

Similarly $H_6IO_6^+$ is formed by the protonation of H_5IO_6 as depicted in equation (5) below:

$$H_5IO_6 + H^+ \rightleftharpoons H_6IO_6^+ \tag{5}$$

The slope obtained from Figure 1 (i.e. 0.68) is less than the expected value of 2.0 due to contributions from other reaction pathways like equations (2) and (6).

$$Fe(Me_2bipy)_3^{2+} + IO_3 \longrightarrow Fe(Me_2bipy)_3^{3+} + IO_3^- \tag{6}$$

Table 2. Dependence of k_{obs} on ionic strength in acid medium (H_2SO_4).

μ (mol dm^{-3})	$k_{obs}/10^{-3}$ (s^{-1})	$\log_{10}k_{obs}$	$(\mu^{1/2})/(\mu^{1/2} + 1)$
0.001	1.47	-2.83	0.031
0.005	1.71	-2.77	0.066
0.009	1.74	-2.76	0.088
0.013	1.83	-2.74	0.102
0.017	1.77	-2.75	0.115
0.029	1.88	-2.72	0.145
0.050	2.05	-2.69	0.183
0.100	2.14	-2.67	0.240
0.300	2.40	-2.62	0.355
0.500	2.80	-2.55	0.415
0.700	3.08	-2.51	0.456
0.900	3.20	-2.49	0.487

$[H^+] = 1.00 \times 10^{-4}$ mol dm^{-3}; $[IO_4^-] = 4.72 \times 10^{-4}$ mol dm^{-3}; $[Fe(Me_2bipy)_3^{2+}] = 2.36 \times 10^{-5}$ mol dm^{-3}; T = 25 °C.

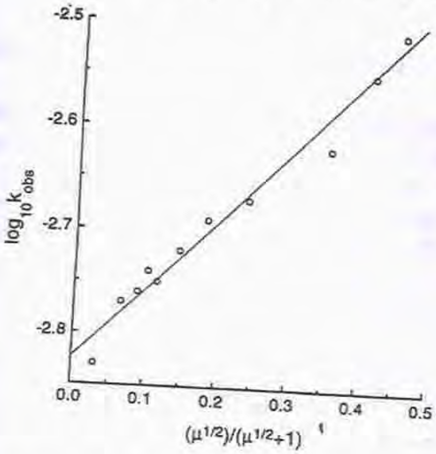

Figure 1. Plot of $\log_{10}k_{obs}$ *vs* $(\mu^{1/2})/(\mu^{1/2} + 1)$ in acid medium using Na_2SO_4 to make up the ionic strength at 25 °C.

Table 3 shows the dependence of k_{obs} on periodate ion concentration in acid medium at a fixed ionic strength of 1.00 mol dm^{-3}. The acid concentration (i.e. [H^+], from H_2SO_4) was kept constant at 1.00 x 10^{-3} mol dm^{-3}. The plot of k_{obs} versus [IO_4^-] is non-linear (Figure 2), but the plot of $\log_{10} k_{obs}$ versus $\log_{10}$ [IO_4^-] (Figure 3) in the [IO_4^-] range 0.5 x 10^{-4} ≤ ([IO_4^-], mol dm^{-3}) ≤ 5.0 x 10^{-4} is linear with a positive slope of 0.20. Similarly, the plot of 1/k_{obs} versus 1/[IO_4^-] is linear (Figure 4) in the [IO_4^-] range of 0.5 x 10^{-4} mol dm^{-3} to 3.5 x 10^{-4} mol dm^{-3} with a slope of 0.22 and an intercept of 5.7. Aqueous solutions of periodate ions were reported to undergo various equilibria in acid medium [3, 4, 11]. From these equilibria studies, the ions IO_3^+ and $H_6IO_6^+$ are the only predominant species that can react to any significant extent.

Table 3. Dependence of k_{obs} on periodate ion concentration in acid medium.

[IO_4^-] (mol dm^{-3})	$k_{obs}/10^{-4}$ (s^{-1})	$\log_{10}k_{obs}$	$\log_{10}$[IO_4^-]	$(1/k_{obs})/10^3$	(1/[IO_4^-])/10^3 (mol dm^{-3})
0.5	1.06	-3.97	-4.30	9.43	20.0
1.0	1.27	-3.90	-4.00	7.87	10.0
1.5	1.36	-3.87	-3.82	7.35	6.7
2.0	1.51	-3.82	-3.70	6.62	5.0
2.5	1.52	-3.82	-3.60	6.57	4.0
3.0	1.59	-3.80	-3.52	6.29	3.3
4.0	1.65	-3.78	-3.40	6.06	2.5
5.0	1.71	-3.77	-3.30	5.85	2.0
6.0	1.69	-3.77	-3.22	-	-
7.0	1.80	-3.74	-3.15	-	-
8.0	1.84	-3.73	-3.10	-	-
10.0	1.90	-3.72	-3.00	-	-
12.0	1.88	-3.73	-2.92	-	-
14.0	1.90	-3.72	-2.85	-	-
16.0	1.90	-3.72	-2.80	-	-

[H^+] = 1.0 x 10^{-3} mol dm^{-3}; [$Fe(Me_2bipy)_3^{2+}$] = 2.36 x 10^{-5} mol dm^{-3}; μ = 1.00 mol dm^{-3}; T = 25 °C.

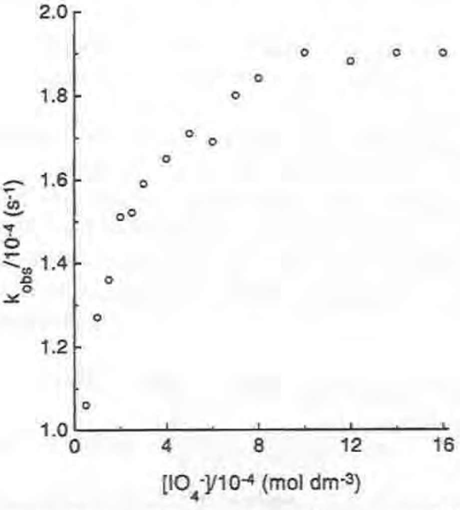

Figure 2. Plot of k_{obs} *vs* [IO_4^-] in acid medium at μ = 1.00 mol dm^{-3} and T = 25 °C.

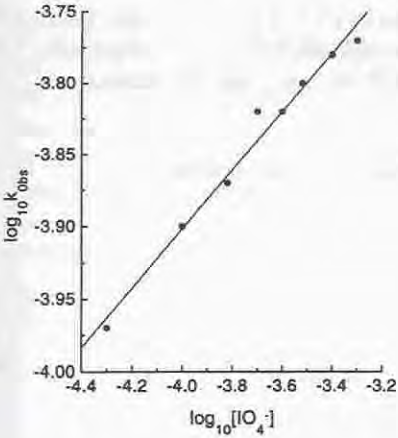

Figure 3. Plot of $\log_{10}k_{obs}$ *vs* $\log_{10}[IO_4^-]$ in acid medium at $\mu = 1.00$ mol dm^{-3} and T = 25 °C.

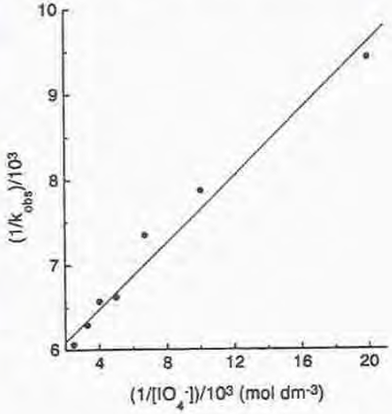

Figure 4. Plot of $1/k_{obs}$ *vs* $1/[IO_4^-]$ in acid medium at $\mu = 1.00$ mol dm^{-3} and T = 25 °C.

The dependence of k_{obs} on the complex concentration was studied by varying the complex concentration from 0.59×10^{-5} mol dm^{-3} to 5.90×10^{-5} mol dm^{-3}, a ten-fold variation. The acid and periodate ion concentrations were fixed at 5.0×10^{-4} mol dm^{-3} and 1.0×10^{-4} mol dm^{-3}, respectively. The results obtained at $\mu = 0.50$ mol dm^{-3} are given in Table 4. As shown in Table 4, k_{obs} is independent of the concentration of the iron(II) complex.

At fixed values of μ (0.50 mol dm^{-3}), iron(II) complex concentration (2.36×10^{-5} mol dm^{-3}) and periodate ion concentration (1.0×10^{-4} mol dm^{-3}), k_{obs} was determined as a function of acid concentration in the range $0.20 \times 10^{-3} \leq ([H^+]$, mol dm$^{-3}) \leq 8.0 \times 10^{-3}$. The results obtained are given in Table 5. The plot of $\log_{10} k_{obs}$ versus $\log_{10} [H^+]$ (Figure 5) is linear with a slope of 0.75. The observed acid dependence of k_{obs} suggests protonation of the periodate ion prior to reaction; and has the rate law of the form:

$$k_{obs} = k_o[H^+]^n \tag{7}$$

where n is positive and less than 1. The low value of n (i.e. n = 0.75) is characteristic of reactions in which prior protonation of one of the species takes place [12]. The paraperiodic acid (H_5IO_6) and iodate ion (IO_4^-) are capable of protonation to form $H_6IO_6^+$ and IO_3^+, respectively, as shown in equations (1) and (5) [13].

Table 4. Dependence of k_{obs} on the complex concentration in acid medium.

$[Fe(Me_2bipy)_3^{2+}]/10^{-5}$ (mol dm^{-3})	$k_{obs}/10^{-3}$ (s^{-1})
0.59	6.15
1.18	5.63
2.36	5.48
3.54	5.63
4.72	5.67
5.90	5.65

$[IO_4^-] = 1.0 \times 10^{-4}$ mol dm^{-3}; $[H^+] = 5.0 \times 10^{-4}$ mol dm^{-3}; $\mu = 0.5$ mol dm^{-3}; T = 25 °C.

Table 5. Dependence of k_{obs} on acid concentration.

$[H^+]/10^{-3}$ (mol dm^{-3})	$k_{obs}/10^{-2}$ (s^{-1})	$\log_{10}k_{obs}$	$\log_{10}[H^+]$
0.2	0.15	-2.82	-3.70
0.5	0.37	-2.43	-3.30
1.0	0.57	-2.24	-3.00
2.0	0.97	-2.01	-2.70
3.0	1.27	-1.90	-2.52
4.0	1.49	-1.83	-2.40
8.0	1.81	-1.59	-2.10

$[IO_4^-] = 1.0 \times 10^{-4}$ mol dm^{-3}; $[Fe(Me_2bipy)_3^{2+}] = 2.36 \times 10^{-5}$ mol dm^{-3}; $\mu = 0.5$ mol dm^{-3}; T = 25 °C.

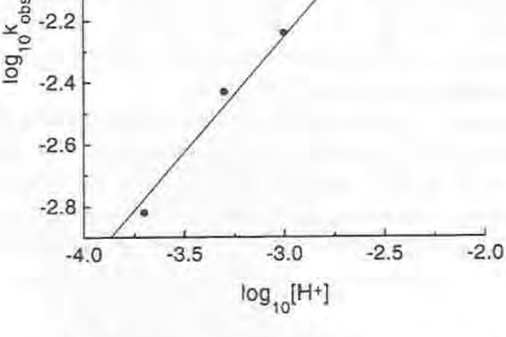

Figure 5. Plot of $\log_{10}k_{obs}$ *vs* $\log_{10}[H^+]$ at $\mu = 1.00$ mol dm^{-3} and T = 25 °C.

In 2.0×10^{-3} mol dm^{-3} H^+ (from H_2SO_4) and at iron(II) complex concetnration of 8.26×10^{-5} mol dm^{-3} and periodate ion concentration of 1.0×10^{-4} mol dm^{-3} the temperature dependence of k_{obs} was studied in the range $20 \leq (T, °C) \leq 40$. The results are given Table 6; and plotted as ln(k/T) versus 1/T (Figure 6). The graph is linear with a slope of -1.175×10^3 K^{-1} and an intercept of -6.52. From the slope and intercept, the activation parameters $\Delta H^{\#}$ and $\Delta S^{\#}$ were calculated and found to be 10 kJ mol^{-1} and -252 J mol^{-1}K^{-1}, respectively, and these values are about the same for $\Delta H^{\#}$ and $\Delta S^{\#}$ obtained for the periodate oxidation of *tris*-(1,10-phenanthroline) iron(II) [6].

Table 6. Dependence of k_{obs} on temperature in acid medium.

T (K)	$k_{obs}/10^{-3}$ (s^{-1})	ln(k/T)	$(1/T)/10^{-3}$ (K^{-1})
293	7.59	-10.56	3.41
298	8.67	-10.44	3.36
303	9.29	-10.39	3.30
308	10.10	-10.33	3.25
313	10.53	-10.29	3.19

$[H^+] = 2.0 \times 10^{-3}$ mol dm^{-3}; $[IO_4^-] = 1.0 \times 10^{-4}$ mol dm^{-3}; $[Fe(Me_2bipy)_3^{2+}] = 8.26 \times 10^{-5}$ mol dm^{-3}; $\mu = 0.10$ mol dm^{-3}.

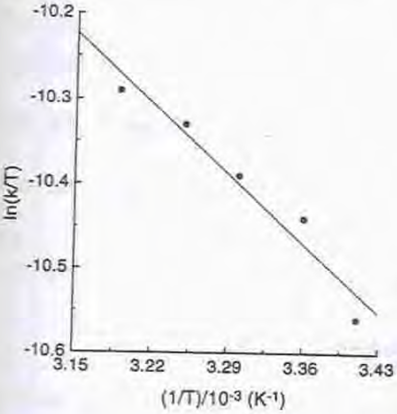

Figure 6. Plot of ln(k/T) against 1/T in acid medium.

The dissociation of the complex in acid medium was studied in the acid concentration range $1.0 \times 10^{-3} \leq ([H^+]$, mol dm$^{-3}) \leq 20.0 \times 10^{-3}$. The complex concentration was fixed at 2.36×10^{-5} mol dm^{-3}. The results are presented in Table 7.

Table 7. Dissociation of the complex in acid medium.

$[H^+]/10^{-3}$ (mol dm^{-3})	$K_d/10^{-3}$ (s^{-1})
1.0	2.58
5.0	3.75
10.0	4.62
15.0	5.08
20.0	5.80

$[Fe(Me_2bipy)_3^{2+}] = 2.36 \times 10^{-5}$ mol dm^{-3}; $\mu = 1.00$ mol dm^{-3}; T = 25 °C.

The complex $Fe(Me_2bipy)_3^{2+}$ dissociates to some extent in acid medium (Table 7). The scheme suggested for the dissociation [14] is according to the following equations.

$$Fe(Me_2bipy)_3^{2+} \rightleftharpoons Fe(Me_2bipy)_2^{2+} + Me_2bipy \qquad (8)$$

$$Fe(Me_2bipy)_2^{2+} \rightleftharpoons Fe(Me_2bipy)^{2+} + Me_2bipy \qquad (9)$$

$$Fe(Me_2bipy)^{2+} \rightleftharpoons Fe^{2+} + Me_2bipy \qquad (10)$$

We therefore propose the following reactions

$$Fe(Me_2bipy)_2^{2+} + IO_3^+ \longrightarrow Fe(Me_2bipy)_2^{3+} + IO_3 \qquad (11)$$

$$Fe(Me_2bipy)_2^{2+} + H_6IO_6^+ \longrightarrow Fe(Me_2bipy)_2^{3+} + IO_3 + 3H_2O \qquad (12)$$

$$Fe(Me_2bipy)^{2+} + IO_3^+ \longrightarrow Fe(Me_2bipy)^{3+} + IO_3 \qquad (13)$$

$$Fe(Me_2bipy)^{2+} + H_6IO_6^+ \longrightarrow Fe(Me_2bipy)^{3+} + IO_3 + 3H_2O \qquad (14)$$

where $Fe(Me_2bipy)_2^{2+}$ and $Fe(Me_2bipy)^{2+}$ are the dissociation products of $Fe(Me_2bipy)_3^{2+}$ in equations (8) and (9).

However, measured k_{obs} values were independent of $[Fe(Me_2bipy)_2^{2+}]$ (Table 4). This confirms that equations 11-14 are not important in the oxidation process.

For the undissociated *tris*-(4,4'-dimethyl-2,2'-bipyridine) iron(II) complex, the proposed reaction scheme is,

$$Fe(Me_2bipy)_3^{2+} + IO_3^+ \longrightarrow Fe(Me_2bipy)_3^{3+} + IO_3 \qquad (15)$$

$$Fe(Me_2bipy)_3^{2+} + H_6IO_6^+ \longrightarrow Fe(Me_2bipy)_3^{3+} + IO_3 + 3H_2O \qquad (16)$$

as suggested from the ionic strength dependence on the k_{obs} (Table 2). In acid medium, the complex can also be protonated [15] as shown in the following equation [10].

$$Fe(Me_2bipy)_3^{2+} + H^+ \rightleftharpoons HFe(Me_2bipy)_3^{3+} \qquad (17)$$

The protonated species may then undergo the following reaction.

$$HFe(Me_2bipy)_3^{3+} + H_5IO_6^+ \longrightarrow Fe(Me_2bipy)_3^{3+} + IO_3 + H_2O \qquad (18)$$

A reaction order of 0.2 with respect to $[IO_4^-]$ obtained (Figure 3) suggests that the reaction proceeds via a complex mechanism. This observation is not strange since fractional order as low as 0.16 with respect to similar oxyiodine species has been reported elsewhere [16].

Similarily, in acid medium an ion pair formation resulting from the reaction of the iron(II) complex with protonated periodate ion may be possible as shown in equation (19).

$$\begin{tikzcd} \mathrm{Fe(Me_2bipy)_3^{2+}} + \mathrm{H_6IO_6^{+}} \arrow[r, shift left, "K_{ip}"] & {[\mathrm{Fe(Me_2bipy)_3.H_6IO_6}]^{3+}} \arrow[l, shift left, "\text{fast}"] \arrow[d, "\text{slow}"', "k_2"] \\ & \mathrm{Fe(Me_2bipy)_3^{3+}} + \mathrm{IO_3} + 3\mathrm{H_2O} \end{tikzcd} \tag{19}$$

Although, this is limited by coulombic repulsion, the ready protonation of the iron(II) complex may make the formation of the ion pair possible.

The rate law suggested by equation (19) is

$$\frac{-d[Fe(Me_2bipy)_3^{2+}]}{dt} = \frac{K_2K_{ip}[Fe(Me_2bipy)_3^{2+}][H_6IO_6^{+}]}{1+K_{ip}[H_6IO_6]} \tag{20}$$

This can be explained by the common mechanism [7], where K_{ip} is the equilibrium constant for the ion pair formation.

The observed pseudo first order rate constant k_{obs} is given by

$$k_{obs} = \frac{K_2K_{ip}[H_6IO_6^{+}]}{1+K_{ip}[H_6IO_6^{+}]} \tag{21}$$

A plot of $1/k_{obs}$ *vs* $1/[H_6IO_6^{+}]$ should be linear since rearranging the above expression (equation 21) for k_{obs}, yields:

$$\frac{1}{k_{obs}} = \frac{1}{K_{ip}K_2[H_6IO_6^{+}]} + \frac{1}{K_2} \tag{22}$$

The ion pair formation here suggests that the reaction proceeds through an outer sphere mechanism.

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The authors are grateful to Professor Jide Ige for his useful suggestions.

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$$\begin{tikzcd}[column sep=large] \mathrm{Fe(Me_2bipy)_3}^{2+} + \mathrm{H_6IO_6}^{+} \arrow[r, shift left, "K_{ip}"] & \mathrm{[Fe(Me_2bipy)_3.H_6IO_6]}^{3+} \arrow[l, shift left, "\text{fast}"] \arrow[d, "\text{slow}"', "k_2"] \\ & \mathrm{Fe(Me_2bipy)_3}^{3+} + \mathrm{IO_3} + 3\mathrm{H_2O} \end{tikzcd} \tag{19}$$

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