Journal of Applied Sciences

ISSN 1812-5654

Journal of Applied Sciences 5 (4): 773-780, 2005
ISSN 1812-5654

Kinetics and Mechanism of the Oxidation of Dicyano-BIS-(2,2'-Bipyridine) Iron (II) Complex by Meta Periodate

Oladega O. Soriyan, Jide Ige, [1]A.O. Fadiran and O. Owoyomi
Department of Chemistry, Obafemi Awolowo University, Ile-Ife, Nigeria
[1]Department of Chemistry, University of Swaziland, P-Bag 4, Kawaluseni Swaziland

Abstract: The reaction of Dicyano-bis-(2,2′-bipyridine) Iron (II) Trihydrate with periodate shows 1.5 order overall; first order with respect to the complex and half-order with respect to IO^-_4. A detailed mechanism involving a series of one-electron transfer steps is proposed and shows agreement with experimental data. The kinetics and mechanism of the reaction exhibit significant solvent medium dependence. The reaction shows complexities resulting from the variety of species of both reactants present in solution. This is reflected in the ionic strength dependence studies. In acid and hydroxyl ion medium, the reaction strength dependence in neutral (distilled water) medium, indicative of the charges on the reacting species in the different media. Slopes of log k_r vs $I^{½}$ are less than unity in all cases. The rate law in acid medium is $\text{rate} = \left(a + b/\left[H^+\right]_T\right)\left[IO_4^-\right]_T^{½}\left[Fe(bipy)_2(CN)_2\right]_T$. The corresponding rate law in OH^- medium is $\text{rate} = \left(a' - b'\left[OH^-\right]\right)\left[IO_4^-\right]_T^{½}\left[Fe(bipy)_2(CN)_2\right]_T$. Observed inhibition by H^+ and OH^- is due to the less reactive $HFe(bipy)_2(CN)^+_2$ and $H_2Fe(bipy)_2(CN)^+_2$ species formed in H^+ medium and dimeric $H_2I_2O^{4-}_{10}$ in OH^- medium. IO^+_3 is suggested as one of the reactive periodate ions in acid medium. The reaction takes place through mixed inner and outer sphere mechanisms in acid and neutral medium. Electron transfer by the formation of an outer-sphere complex is the only possible reaction path in OH^- medium. Observed autocatalysis suggests the accumulation of reactive intermediate(s).

Key words: Oxidation, periodate, ion-pair, inhibition, ionic strength

INTRODUCTION

The many, sometimes complex, possible reaction pathways in periodate oxidations resulting from the various aquo species are probably responsible for the relatively little work done on the mechanism of its oxidation of inorganic metal complexes. Oxidation reactions involving periodate and organic reductants have been studied extensively[1-3] and have been found to have large variations in their rates with temperature and hydrogen ion activity. These variations can be explained by a more detailed knowledge of the species present in solution.

Meta-periodate is found by Crouthamel *et al.*[4] to exist in various degrees of hydration and protonation in solution as in the following equilibria:

$$H_4IO^-_{6(aq)} \rightleftharpoons IO^-_{4(aq)} + 2H_2O,\ K_D = 40 \quad (1)$$

$$H_5IO_{6(aq)} \rightleftharpoons H_4IO^-_{6(aq)} + H^+_{(aq)},\ K_2 = 5.1 \times 10^{-4} \quad (2)$$

$$H_4IO^-_{6(aq)} \rightleftharpoons H_3IO^{2-}_{6(aq)} + H^+_{(aq)},\ K_3 = 2.0 \times 10^{-7} \quad (3)$$

These equilibrium constants agree with the earlier reported values obtained from studies of dissociation of periodic acid[5]. At 25°C and in the absence of added acid, metaperiodate ion, IO^-_4, predominates forming at least 95% of the total periodate[6]. The ion dimerises[7] at pH>7.

$$2IO^-_4 + 2OH^- \rightleftharpoons H_2I_2O^{4-}_{10} \quad (4)$$

Hence in alkaline (i.e. OH^-) medium, competition for the reductant by meta-periodate and the dimeric form is to be expected. The extent of dimerisation and the relative reactivity of the dimer and meta-periodate species may be inferred from analysis of the kinetic data. At high

Corresponding Author: Oladega O. Soriyan, Department of Chemistry, Obafemi Awolowo University, Ile-Ife, Nigeria
E-mail: osoriyan@yahoo.com

temperatures and high pH the concentration of the dimer in solution becomes insignification because the dimeric species are thermally unstable with respect to the parent ion.

In the periodate oxidation of glycol[8] equilibrium equations 2 and 3 were applied. The reaction is OH^- and H^+ dependent and was postulated to go through an intermediate involving IO^-_4 and glycol adduct[9].

The existence of stable protonated species of $Fe(bipy)_2(CN)_2$ which exhibits di-basic character in strong concentrated mineral acid has been proposed[10,11] with the presence of three interconvertible species through the following equilibria

$$Fe(dipy)_2(CN)_2 \overset{H^+}{\rightleftharpoons} HFe(dipy)_2(CN)_2^+, K_5\ 3x10^3 \quad (5)$$

$$HFe(dipy)_2(CN)_2^+ \overset{H^+}{\rightleftharpoons} H_2Fe(dipy)_2(CN)_2^{2+} \quad (6)$$

The present study was motivated by the likely mechanistic consequence resulting from the strong solvent dependent characteristics of IO^-_4 and $Fe(bipy)_2(CN)_2$. The possible formation of a binuclear complex in which CN, donated by $Fe(bipy)_2(CN)_2$, acts as a bridging ligand between Fe (II) and IO^-_4 is also of interest.

MATERIALS AND METHODS

Materials: Analar grade sodium periodate, potassium cyanide, ferrous ammonium sulphate, sodium sulphate, sodium hydroxide and BDH laboratory reagent sulphuric acid were used. Dicyanobis-(2,2'-bipyridine)-Iron (II) trihydrate $[Fe(bipy)_2(CN)_2.3H_2O]$ was prepared from analar grade 2,2'-bipyridine according to the literature[10,11] and was characterised by its UV-Visible spectrum. The purity of the complex was ascertained by comparing the extinction coefficients of the UV and visible peaks with reported value[12,13]. The calculated extinction coefficients are less than the literature values by about 0.5%.

Kinetics: The measurement of kinetic data was established by following the change in absorbance of $Fe(bipy)_2(CN)_2$ at λ_{max} = 492 nm using SP500 series 2 UV-Visible Spectrophotometer equipped with a thermostable compartment. The reaction was run with periodate always in at least 20 fold excess and are prepared fresh since IO^-_4 ion on solvolysis decomposes slowly with production of ozone[14]. Sodium sulphate was used to make up the ionic strength which was fixed at 1.0 except in ionic strength dependent study. Low concentrations of sodium hydroxide were used because the less soluble dimeso-periodate $H_2I_2O^{4-}_{10}$, precipitaes at high $[OH^-]_T$. All reactions were monitored at constant temperature of 25°C.

Analysis of product shows No. I_2 was present and $Fe(bipy)_2(CN)^+_2$ was confirmed by $AgNO_3$ test. The presence of $Fe(bipy)_2(CN)^+_2$ was detected by its blue colour and its visible spectrum[10,11].

RESULTS

Plots of $\ln(A_t-A_\infty)$ vs t were linear to at least two half-lives. Auto-catalysis was observed beyond 80% reaction. Pseudo-first order rate constants (k_s) were obtained from the slopes of these plots. The reaction was studied in neutral (distilled water), acid and alkaline medium, using a 1:1 Fe (II) to periodate concentration ratio. In all such cases plots of $1/\ln(A_t-A_\infty)$ vs t were always linear, a confirmation that the reaction is 1.5 order overall. k_s was found to be proportional to $[IO^-_4]^{½}_T$ within the limits of experimental error. Specific reaction rate constants (k_r) were therefore calculated from k_s by dividing it by $[IO^-_4]^{½}_T$. k_r values so obtained were constant with minor variations (Table 1) for fixed values of $[H^+]_T$ and $[OH^-]_T$. The pseudo first order rate constant, k_s, was found to vary with Fe (II), as shown in Fig. 1.

$[IO^-_4]^{½}_T$ was fixed at 0.04 mol dm^{-3}. k_s decreases linearly with $[Fe(bipy)_2(CN)_2]_T$ in both neutral medium and at fixed acid concentration of 0.002 mol dm^{-3}. The decrease in k_s with increase in $[Fe(bipy)_2(CN)_2]_T$ is observed to be also valid in the periodate concentration range covered in Table 1.

The reaction is inhibited by acid at fixed Fe (II) complex concentration (3.093 x 10^{-3} mol dm^{-3}), in the acid range ≤ 0.040 mol dm^{-3} and periodate concentration range 0.0005-0.10 mol dm^{-3}. The plot of k_r vs $[H^+]^{-1}_T$ is linear (Fig. 2) and suggests a functional dependence of the

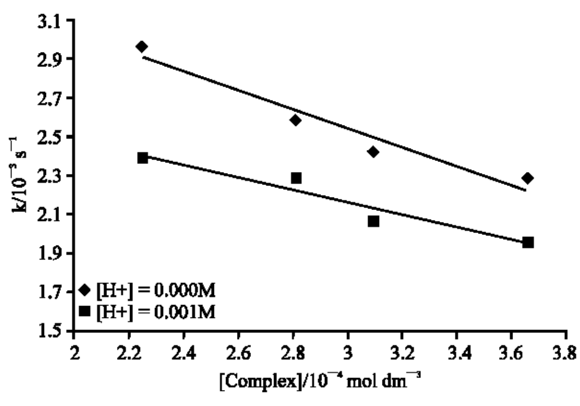


Fig. 1: Variation of k_s with $[complex]_T$ at fixed IO^-_4 concentration of 0.04 mol dm^{-3} T = 25°C

Table 1: Pseudo-first order rate constants (k_s) and specific reaction rate constants (k_r) at various $[IO^-_4]^{½}_T$. $[complex]_T$ is constant

$[IO^-_4]^{½}_T$ mol dm^{-3}	$[H^+]_T$ = 0.002 mol dm^{-3} $k_s/10^{-3}$ (s^{-1})	k_r mol$^{-½}$ dm$^{3/2}$s^{-1}	$[H^+]_T$ = 0.010 mol dm^{-3} $k_s/10^{-3}$ (s^{-1})	k_r mol$^{-½}$ dm$^{3/2}$s^{-1}	$[H^+]_T$ = 0.020 mol dm^{-3} $k_s/10^{-3}$ (s^{-1})	k_r mol$^{-½}$ dm$^{3/2}$s^{-1}
0.010	0.840	0.00840	0.722	0.00722	0.734	0.00734
0.020	1.042	0.00737	1.002	0.00709	1.005	0.00709
0.025	1.667	0.01054	1.140	0.00721	1.258	0.00796
0.030	1.841	0.01020	1.351	0.00783	1.383	0.00798
0.040	2.002	0.00930	1.548	0.00774	1.420	0.00710
0.050	2.204	0.00946	1.751	0.00783	1.505	0.00678
0.060	2.528	0.01000	1.793	0.00734	1.698	0.00693
0.080	3.013	0.01054	1.906	0.00667	1.854	0.00654
0.090	3.528	0.01176	-	-	-	-
0.100	-	-	-	-	1.969	0.00623

$[complex]_T = 3.093 \times 10^{-3} \times 10^{-3}$ mol dm^{-3}, T = 25°C

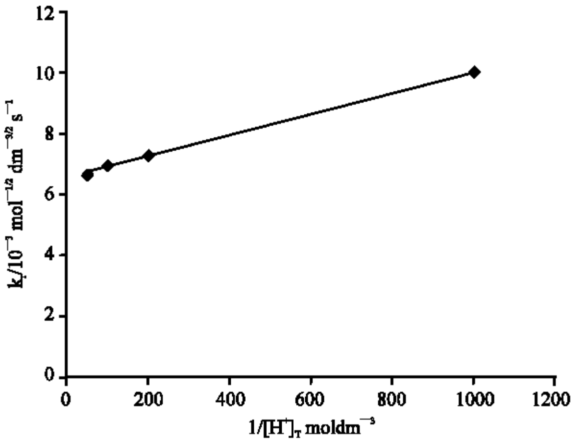


Fig. 2: Variation of k_r with $1/[H^+]_T$ T = 25°C $[complex]_T$ = 3.093×10^{-3} mol dm^{-3}

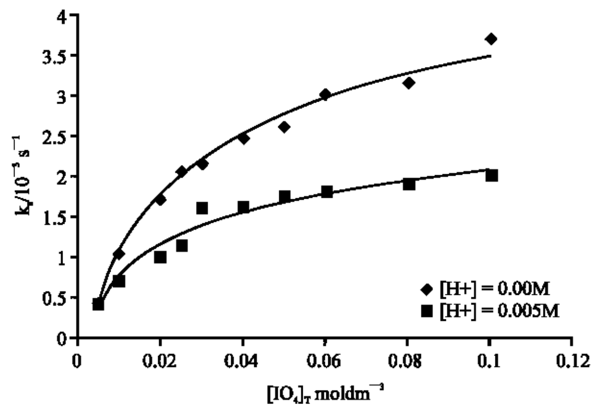


Fig. 4: A typical plot of k_s vs $[IO^-_4]^{½}_T$ at 25°C. $[complex]_T$ = 3.093×10^{-3} mol dm^{-3}

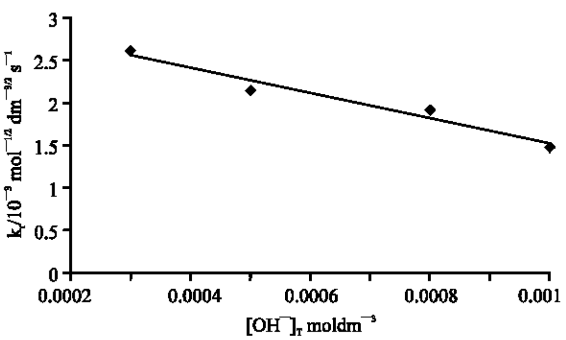


Fig. 3: Variation of k_r with $[OH^-]_T$ [complex] $_T$ = 1.827×10^{-3} mol dm^{-3}, $[IO^-_4]^{½}_T$ = 0.10 mol dm^{-3}, T = 25°C

$$k_r = a + b/[H^+]_T \qquad (7a)$$

where: $a = (6.55\pm0.25) \times 10^{-3}$ mol$^{-½}$dm$^{3/2}$s^{-1}
and $b = (3.45\pm0.20) \times 10^{-3}$ mol^{½}dm$^{-3/2}$s^{-1}

form; a represents k_r at infinite acid concentration when all the Fe (II) will be present as the protonated species. The results, in the same range of periodate concentration, for the variation of k_r with $[OH^-]_T$ are plotted in Fig. 3. Like H^+, OH^- inhibits the reaction but with a functional dependence of the form;

$$k_r = a'-b'[OH^-]_T \qquad (7a)$$

where $a' = (10.40\pm0.70) \times 10^{-3}$ mol$^{-½}$dm$^{3/2}$s^{-1}
and $b' = (0.72\pm0.02)$ mol$^{-3/2}$dm$^{9/2}$s^{-1}

For the data plotted in Fig. 3, the Fe (II) complex concentration was maintained constant at 1.827×10^{-5} mol dm^{-3}. For the study in alkaline media, OH^- in the range 3.0×10^{-4} mol dm^{-3} to 10.0×10^{4} mol dm^{-3} were used because of the lower solubility of the polymeric periodate (which is formed rapidly in alkaline medium) in water. At high $[OH^-]_T$ precipitates of the white crystalline polymeric periodate were observed.

Complete k_s-$[OH^-]_T$ profiles were obtained at fixed $[H^+]_T$ and in neutral (distilled water) medium. The k_s-$[IO^-_4]^{½}_T$ profiles shown in Fig. 4 are typical. The rest of the data is summarised in Table 1.

Ionic strength dependence studies were carried out in neutral, alkaline and acid medium which show a linear dependence of log k_r on $I^{½}$. The slopes are -0.09, 0.13 and 0.38 mol$^{-½}$dm$^{3/2}$, respectively. The positive slopes in alkaline and acid medium suggest reaction between similarly charged reactants though Fe (II) and metaperiodate carry opposite charges. For the experimental runs on ionic strength dependence periodate and Fe (II) concentration were fixed at 0.02 and 2.23 x 10^{-5} mol dm^{-3}, respectively. The low values (i.e <1.0) of the slopes suggest that the reaction is not simple and involves a variety of charged species. In all the studies, ionic strength was varied by the addition of Na_2SO_4. $[OH^-]_T$, $[H^+]_T$ were fixed at 3.0×10^{-3} and 2.0×10^{-3} mol dm^{-3}, respectively.

Equation 7 considered with the half-order and first order dependence of the rate of reaction on metaperiodate and the Fe (II), respectively, suggest the rate expression in Eq. 8.

$$\text{Rate} = \{a + b/[H^+]_T\}[[IO^-{}_4]^{½}{}_T[Fe(bipy)_2(CN)_2]_T \qquad (8)$$

MECHANISM AND DISCUSSION

To explain the above rate expression, we propose the following mechanism

$$H_4IO_6^- \;\; H^+ \xrightleftharpoons{1/k_2} H_5IO_6$$

$$IO_4^- \;\; 2H_2O \xrightleftharpoons{1/k_D} H_4IO_6^-$$

The three periodate species $IO^-{}_4$, $H_4IO_6^-$, H_5IO_6 present in solution can react with $Fe(bipy)_2(CN)_2$ and the protonated species $HFe(bipy)_2(CN)^+{}_2$ and $H_2Fe(bipy)_2(CN)^+{}_2$, formed in equilibria 5 and 6. The important reactions are

$$\begin{array}{l} HFe(bipy)_2(CN)_2^+ + H_5IO_6 \rightarrow \\ Fe(bipy)_2(CN)_2^+ + IO_3 + 3H_2O \end{array} \qquad (9)$$

$$\begin{array}{l} H_2Fe(bipy)_2(CN)_2^{2+} + H_4IO_6^- \rightarrow \\ Fe(bipy)_2(CN)_2^+ + IO_3 + 3H_2O \end{array} \qquad (10)$$

$$\begin{array}{l} Fe(bipy)_2(CN)_2 + IO_4^- + H_2O \rightarrow \\ Fe(bipy)_2(CN)_2^+ + IO_3 + 2OH^- \end{array} \qquad (11)$$

where, IO_3 is a reactive intermediate, which oxidises Fe (II) in another set of one-electron transfer steps involving two molecules of IO_3.

$$\begin{array}{l} Fe(bipy)_2(CN)_2^+ + 2IO_3 \rightarrow \\ Fe(bipy)_2(CN)_2^+ + H^+ + I_2O_6^- \end{array} \qquad (12)$$

$$\begin{array}{l} H_2Fe(bipy)_2(CN)_2^{2+} + 2IO_3 \rightarrow \\ Fe(bipy)_2(CN)_2^+ + 2H^+ + I_2O_6^- \end{array} \qquad (13)$$

$$\begin{array}{l} Fe(bipy)_2(CN)_2 + 2IO_3 \rightarrow \\ Fe(bipy)_2(CN)_2^+ + I_2O_6^- \end{array} \qquad (14)$$

$I_2O_6^-$ is a reactive intermediate which combines rapidly with the Fe (II) species to form the corresponding Fe (III) complex. One molecule of IO_3 can also react by direct one-electron transfer with the same complex species as in Eq. 15-17.

$$\begin{array}{l} HFe(bipy)_2(CN)_2^+ + IO_3 \rightarrow \\ Fe(bipy)_2(CN)_2^+ + HIO_3 \end{array} \qquad (15)$$

$$\begin{array}{l} H_2Fe(bipy)_2(CN)_2^{2+} + IO_3 \rightarrow \\ Fe(bipy)_2(CN)_2^+ + HIO_3 + H^+ \end{array} \qquad (16)$$

$$\begin{array}{l} Fe(bipy)_2(CN)_2 + IO_3 \rightarrow \\ Fe(bipy)_2(CN)_2^+ + IO_3^- \end{array} \qquad (17)$$

At steady state

$$IO_3 = \left[\frac{K_5\frac{1}{K_2}\frac{1}{K_D}K_9\left[H^+\right]^2 + K_5K_6\frac{1}{K_D}K_{10}\left[H^+\right]^2 + K_{11}}{K_5K_6K_{13}\left[H^+\right]^2 + K_5K_{12}\left[H^+\right] + K_{14}}\right] \left[IO_4^-\right]^{½} \qquad (18)$$

when

$$\left\{K_5K_6K_{13}\left[H^+\right]^2 + K_5K_{12}\left[H^+\right] + K_{14}\right\}\left[IO_3\right]^2 \gg \left\{K_5K_{15}\left[H^+\right] + K_5K_6K_{16}\left[H^+\right]^2 + K_{17}\right\}\left[IO_3\right] \qquad (19)$$

Assuming that Eq. 16 is the rate limiting step, the rate law for the reaction is

$$\text{Rate} = K_5K_6K_{16}\left[H^+\right]^2\left[IO_3\right]Fe(bipy)_2(CN)_2 \qquad (20)$$

$$\text{If } K_{13}K_5K_6\left[H^+\right]^2 \gg K_5K_{12}\left[H^+\right] + K_{14} \qquad (21)$$

and

$$\left[\left(K_6K_{10} + \frac{1}{K_2}K_9\right)^{½} + \frac{K_{11}^{½}}{\left[H^+\right]}\right]^2 \gg \frac{2K_{11}^{½}\left(K_6K_{10} + \frac{1}{K_2}K_9\right)^{½}}{\left[H^+\right]} \qquad (22)$$

Eq. 18 reduces to

$$[IO_3] = \left[\frac{\frac{1}{K_D}}{K_{13}K_6}\right]^{1/2} \left[\left(K_6K_{10} + \frac{1}{K_2}K_9\right)^{1/2} + \frac{K_{11}^{1/2}}{[H^+]}\right][IO_4^-]^{1/2} \quad (23)$$

and the rate law reduces to

Rate =

$$K_5K_{16}\left(\frac{1}{K_D}K_{13}\right)^{1/2}\left[\left(K_6K_{10} + \frac{1}{K_2}K_9\right)^{1/2} + \frac{K_{11}^{1/2}}{[H^+]_T}\right] \times [IO_4^-]_T^{1/2}[Fe(bipy)_2(CN)_2]_T \quad (24)$$

where, concentrations are expressed in terms of total initial concentrations subject to the constraints that

$$\frac{1}{K_D}\frac{1}{K_2}[H^+] \gg \frac{1}{K_D} + 1 \quad (25)$$

$$K_5[H^+] \gg K_5K_6[H^+]^2 + 1 \quad (26)$$

and $[H^+] = [H^+]_T$ at low $[IO^-_4]^{1/2}_T$ with

$$[H^+]_T \gg Fe(bipy)_2(CN)_2 \quad (27)$$

In arriving at our final rate law, we had to make many approximations. Equation 27 is valid within the conditions of the present experiment. Equation 26 is also valid since the mono-protonated Iron (II) complex is expected to be formed much more readily than the di-protonated species. Equation 25 is valid given the values of $1/K_2$, $1/K_D$; but this is only so at high $[H^+]^T$, greater than the acid concentrations covered in this report. The reverse approximation i.e. $\frac{1}{K_D} + 1 \gg \frac{1}{K_D}\frac{1}{K_2}[H^+]_T$ is valid at acid concentrations ≤ 0.002 mol dm^{-3}. Except at 0.002 mol dm^{-3} H^+; this is below the range of acid concentration covered. Given the complexity of the overall reaction, it is hoped that any error resulting from this approximation will have no serious quantitative effect. There is no way we can test the validity of Eq. 19 and 22. They appear reasonable in so far that they yield the desired rate law in Eq. 24. Equation 21 is valid provided K_{14} is negligibly small and $K_{12} \ll K_6[H^+]$.

It is obvious that Eq. 24 is the same as the experimentally obtained rate expression if

$$a = K_5K_{16}\left(\frac{1}{K_DK_6}\right)^{1/2}\left(K_6K_{10} + \frac{1}{K_2K_9}\right)^{1/2} \quad (28)$$

and

$$b = K_5K_{16}\left(\frac{1}{K_DK_6}\right)^{1/2}K_{11}^{1/2} \quad (29)$$

It should be noted however that there are other possible reaction pathways which will give a similar rate expression. Reactions 12-14 can take place by direct two-electron transfer; in which Fe changes its oxidation state from +2 to +4 as in equation 30 for example:

$$HFe(bipy)_2(CN)_2^+ + 2IO_3 \rightarrow Fe(bipy)_2(CN)_2^{2+} + HIO_3 + IO_3^- \quad (30)$$

The resulting complex, $Fe(bipy)_2(CN)^{2+}_2$ will be a highly oxidising intermediate which can undergo re-proportionation:

$$Fe(bipy)_2(CN)_2^{2+} + Fe(bipy)_2(CN)_2^+ \rightarrow 2Fe(bipy)_2(CN)_2^+ + H^+ \quad (31)$$

While it is true that direct two-electron transfer step has been proposed in some oxidation reactions involving oxyhalogens[15], it is obvious that such reactions are less feasible in the present system. This is inspite of the fact that the use of the above alternative scheme yields a similar rate law but with the less valid approximation that reactions 15-17 are slower than the corresponding direct two-electron transfer processes in Eq. 30.

Reaction between similarly charged species in acid medium, as suggested by ionic strength dependence is possible if IO^+_3 is one of the reacting periodate species. We postulate that IO^+_3 can be formed from the disproportionation of IO_3;

$$2IO_3 \rightleftharpoons IO_3^+ + IO_3^- \quad (32)$$

or from the reaction of H^+ and IO^-_4;

$$IO_4^- + 2H^+ \rightleftharpoons IO_3^+ + H_2O \quad (33)$$

While there is no evidence in the literature that this ion exists, $I(OH)^+_6$, protonated periodic acid, is proposed to be present in 10.0 M perchloric acid[16] i.e.

$$H_5IO_6 + H^+ \rightleftharpoons I(OH)_6^+ \qquad (34)$$

Since we are working in dilute sulphuric acid, reaction 34 is ruled out. Equation 32 is also ruled out since k_r does not show any dependence on IO^-_3 in all our experimental data. Inclusion of Eq. 33 in the reaction scheme such that the IO^+_3 formed can react as in

$$IO_3^+ + H_2Fe(bipy)_2(CN)_2^{2+} \rightarrow$$
$$Fe(bipy)_2(CN)_2^+ + IO_3 + 2H^+ \qquad (35)$$

$$IO_3^+ + HFe(bipy)_2(CN)_2^+ \rightarrow$$
$$Fe(bipy)_2(CN)_2^+ + IO_3 + H^+ \qquad (36)$$

$$IO_3^+ + Fe(bipy)_2(CN)_2 \rightarrow$$
$$Fe(bipy)_2(CN)_2^+ + IO_3 \qquad (37)$$

yielding

$$\text{Rate} = K_{14}K_6\left[\frac{K_{33}K_{35}}{K_{13}}\right]^{1/2}\left[1+\frac{1}{[H^+]_T}\left[\frac{K_{37}}{K_{35}K_5K_6}\right]^{1/2}\right]$$
$$[IO_4^-]_T^{1/2} \times [Fe(bipy)_2(CN)_2]_T \qquad (38)$$

if Eq. 14 is rate limiting.
Additional assumptions in deriving Eq. 38 are that

$$K_{33}[H^+]^2 >> 1 \qquad (39)$$

and

$$\left[[H^+] + \left[\frac{K_{37}}{K_{35}K_5K_6}\right]^{1/2}\right]^2 \gg$$
$$\frac{K_{36}[H^+]}{K_{35}K_6} - 2\left[\frac{K_{37}}{K_{35}K_5K_6}\right]^{1/2}[H^+] \qquad (40)$$

Equation 37 like Eq. 24 has the same form as the experimentally obtained rate expression Eq. 8, if

$$a = K_{14}K_6\left[\frac{K_{33}K_{35}}{K_{13}}\right]^{1/2} \qquad (41)$$

and

$$b = K_{14}\left[\frac{K_{33}K_{37}K_6}{K_{13}K_5}\right]^{1/2} \qquad (42)$$

The observed dependence of k_r on OH^- and the order of reaction with respect to IO^-_4 and $Fe(bipy)_2(CN)_2$ in OH^- medium suggest a rate expression of the form;

$$\text{Rate} = \{a'-b'[OH^-]_4\}[IO^-_4]^{1/2}_T[Fe(bipy)_2(CN)_2]_T$$

In alkaline medium, the dimeso-periodate $H_4I_2O_{10}^{4-}$ is more stable and may not be as reactive as the meta-periodate. Increasing $[OH^-]_T$ increases the concentration of these less reactive species and accounts for the inhibition by OH^-. This, coupled with the fact that the specific periodate and Fe (II) equilibria, in alkaline medium, are not as well known as those in acid medium, makes postulation of an actual mechanism in alkaline medium much more difficult.

In neutral medium the only periodate equilibria are 1 and 3. Protonation of $Fe(bipy)_2(CN)_2$ is slight and reactions 11, 14 and are significant with slight contributions from reactions 12 and 15. At steady state

$$[IO_3] = \left(\frac{K_{11}}{K_{14}}\right)^{1/2}[IO_4^-]^{1/2}$$

and

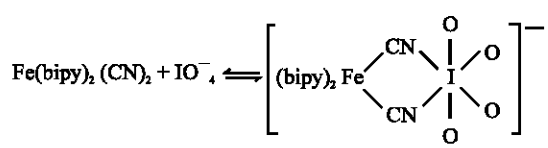
$$\text{Rate} = \left(\frac{K_{11}}{K_{14}}\right)^{1/2} K_{17}[IO_4^-]_T^{1/2}[Fe(bipy)_2(CN)_2]_T$$

Reactions like

$$HFe(bipy)_2(CN)_2^+ + H_4IO_6^- \rightarrow$$
$$Fe(bipy)_2(CN)_2^+ + 2H_2O + OH^-$$

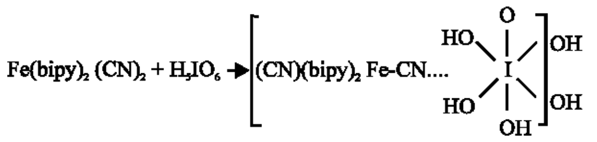
will account for the slight negative dependence of k_r on ionic strength.

We propose that the reaction goes by mixed inner and outer sphere mechanisms. A priori, the formation of an inner sphere complex such as I



(I)

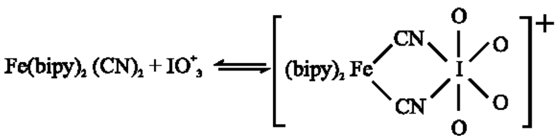
in which the coordination number of iodine is increased from 4 to 6 is feasible because CN is a pseudohalogen and is known to bond with halogen atoms like iodine[17]. This is similar to the proposed binuclear complexes of Birk and Weaver[12,13]. However, in acid and neutral medium the predominant periodate species are H_5IO_6 or $IOIO^+_3$ and $H_4IO^-_6$, respectively. Formation of a similar inner sphere complex (I) with H_5IO_6 and $H_4IO^-_6$, is impossible. Even when only one CN is donated as a bridging ligand with iodine not having a coordination number of 7, the inner-sphere complex (II),



(II)

formed is not energetically feasible.

With IO^+_3 the innersphere complex III is possible

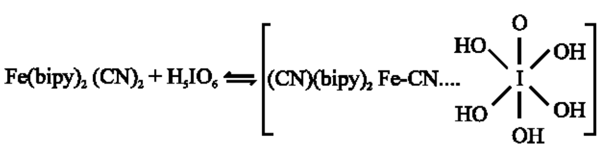


(III)

and contributes to the electron transfer process.

Formation of III will be catalysed by acid due to increase in $[IO^+_3]$ through equilibrium 36. However, observed inhibition by acid is due to the protonation of Fe (II). Formation of III using the protonated species of Fe (II) is inhibited due to coulombic repulsion between $HFe(bipy)_2(CN)_2/H_2Fe(bipy)_2^{2+}$ and IO^+_3. The proton is not on CN[8b], thus making the formation of III by protonated Fe (II) species possible.

Formation of outersphere complexes such as IV



(IV)

is equally likely. The three Fe (II) species can form complexes similar to IV with H_5IO_6 and $H_4IO^-_6$. It is however not clear how acid will affect the formation of IV but given the high proton affinity of the unprotonated Fe (II) in IV and the likely H-bonding between N and H, the $Fe(bipy)_2(CN)_2$-H_5IO_6 outer sphere complex will be most readily formed. This consideration coupled with the inertness of Fe (II) to substitution indicate that reaction by outersphere mechanism is also possible in acid medium.

Inner-sphere mechanism can also operate in neutral medium, where 95% of the periodate is present as IO^-_4 which enhances formation of I. However, $H_4IO^-_6$ formed from the solvation of IO^-_4 will react by outer sphere mechanism through formation of IV. A more detailed investigation is necessary to determine the extent to which each of these two modes of electron transfer contributes to the reaction in acid and neutral media.

Observed auto-catalysis in all the reactions is due to the accumulation of reactive intermediates. Observation of auto-catalysis is common in oxidations involving oxyhalogens[15]. In bromate oxidations for example, this is often due to the accumulation of Br_2. No I_2 was however, detected in the present work.

CONCLUSIONS

Overwhelming experimental evidence and the above discussion suggest that the reaction of IO^-_4 with $Fe(bipy)_2(CN)_2$ goes by outer sphere mechanism in alkaline medium with possibilities for mixed outer and inner-sphere mode of electron transfer in neutral and acid media. IO^+_3 or a positively charged periodate species exists in acid medium in addition to other species. The reaction exhibits interesting kinetics resulting from the strong solvent dependence of reactant species in solution.

REFERENCES

1. Buist, G.J. and C.A. Bunton, 1954. The mechanisim of oxidation of a-glycols by periodic acid. Part 1. Ethylene glycol. J. Chem. Soc., pp: 1406.
2. Buist, G.J., C.A. Bunton and J. Homas 1966. The mechanism of oxidation of a-glycols by periodic acid. Part VII. Geneneral acid base catalysis in the oxidation of pinacol and the reaction in alkaline solution. J. Chem. Soc., pp: (B) 1099.
3. Scott, J.E. and M.J. Tigwell and J. Biochem., 1978. Periodate oxidation and the shapes of glycosaminoglycuronans in solution. Biochem. J., 173: 103-114.
4. Crouthamol, C.E., A.M. Haves and D.S. Martin, 1951. Ionization and hydration equilibria of periodic acid. J. Am. Chem. Soc., 73: 82.
5. Crouthamel, C.E., H.V. Meek, D.S. Martin and C.V. Banks, 1949. Spectrophotometric studies of dilute aqueous periodiate solution. J. Am. Chem. Soc., 71: 3031.
6. Cotton, F.A. and G. Wilkinson, 1988. Advanced Inorganic Chemistry (A Comprehensive Text) Inter-Science Publishers, pp: 572-573.
7. Kross, R.M., H.M. Dogden and C.J. Nyman, 1968. Solubility product of Cesium metaperiodate and a nuclei magnetic resonance study of the orthoperiodate metaperiodate dehydration equilibrium. Inorg. Chem., 7: 446.
8. Price, C.C. and H. Kroll, 1938. The kinetics of the periodate oxidation of 1,2-glycols. J. Am. Chem. Soc., 60: 2726.

9. Duke, F.R., 1947. Theory and kinetics of specific oxidation II. The periodate-glycol reaction. J. Am. Chem. Soc., 69: 3054.
10. Schilt, A.A., 1960. Mixed ligand complexes of Iron (II) and (III) with cyanide and aromatic di-imines. J. Am. Chem. Soc., 82: 3000.
11. Schilt, A.A., 1960. Unusual Proton affinities of some mixed ligand Iron (II) complexes. J. Am. Chem. Soc., 82: 5779.
12. Birk, J.P., 1978. Kinetics of the hexachloroiridate (III) reduction of iodate ion. Inorg. Chem., 17: 1372-1374
13. Birk, J.P., 1969. Kinetics and mechanisms of the reduction of chromium (VI) by substitution-inert Iron (II) complexes in acidic aqueous solution. J. Am. Chem. Soc., 91: 3189.
14. Soji Amire and Jide Ige, 1985. Kinetics of the oxidation of tris (1,10-phenan throline) Iron (II) perchlorate by periodic acid. Nigerian J. Soc., 19: 138-144.
15. Jide Ige, J. Folorunso Ojo and O. Olubuyide, 1979. Kinetics and mechanism of the oxidation of tris (1-10-phenanthroline) Iron (II) by chlorine and bromine of the reduction of tris-(1-10phenanthroline) Iron (III) by iodide ions. Can. J. Chem., 57: 2065.
16. Dryhurst, G., 1970. Periodate Oxidation of Diol and Other Functional Groups. Oxford Pergamon Press, 3: 24-52.
17. Thyagarajan, B.S., 1968. Chemistry of Cyanogen Halides. Intra-Science Research Foundation, Santa Monica, Califonia, pp: 4-30.