The Redox Reaction between Di-µ-Oxo-Tetrakis (2, 2'- bipyridine) – Dimanganese (III, IV) Perchlorate and 1, 3-Dihydroxybenzene in Hydrochloric Acid

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Abstract: The redox reaction between di-µ-oxo-tetrakis (2, 2'- bipyridine) – dimanganese (III, IV) perchlorate $[(bipy)_2 Mn^{III} O_2 Mn^{IV} (bipy)_2]^{3+}$ and 1,3-dihydroxybenzene (H_2Q) in hydrochloric acid was investigated using spectroscopic technique. The stoichiometry of the reaction was 2:3 for $[(bipy)_2 Mn^{III} O_2 Mn^{IV} (bipy)_2]^{3+}$: H_2Q. The rate of reaction was first order with respect to both species while the overall rate of reaction was second order. Investigation of the effect of ionic strength on the reaction gave evident for non-dependence of the rate of reaction on change in dielectric constant, D, of the medium. The rate of the reaction increased with increase in the concentration of the acid and was found to be unaffected by the addition of added (Ni^{2+}, NO_3^- and $HCOO^-$) ions. There was no gel-formation in the course of the reaction and Michaelis-Menten's type plot gave a straight line starting from the origin.

Keywords: *Redox reaction, 1,3-dihydroxybenzene, di-µ-oxo-tetrakis (2, 2'- bipyridine) – dimanganese (III, IV) perchlorate.*

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1.0   Introduction

1,3- dihydroxybenzene (H_2Q) is known for its bactericidal, fungicidal and anti-itching properies (Loginova *et al.,* 2012). It is also useful in rubber adhesives, plastics, synthetic resins, synthetic fibers, dyes, preservatives etc (Schmiedel and Decker, 2012). It also plays the role of promoting the regeneration of horny at low concentration. 1,3-dihydroxybenzene has structural component that is capable of inhibiting N-terminal domain of heat shock protein 90, which is a drug target for anti-cancer treatments (Sidera and Patsavoudi, 2004).However, exposure of humans to 1,3- dihydroxybenzene have been reported to be associated with drinking water consumption and inhalation. 1, 3- dihydroxybenzene may be present in ground water at trace to low levels especially in areas where aquifers flow through rocks that are rich in organic material (Lynch *et al.,* 2020). 1,3-dihysroxybenzene is a very toxic compound when inhaled or consumed. It can cause skin itching, irritation of the nose, throat and lung as well as skin rashes, shortness of breath, interfering with normal supply of oxygen to the blood and other toxic impact (Eddy and Udoh, 2006). Consequently, owing to their toxicity, measures needed to remove them from water are receiving research attention. One of the most effective method of removing contaminants from aqueous solution is adsorption unto suitable surfaces (Ekop and Eddy, 2009; Odoemelam and Eddy, 2009). However, because 1, 3-dihydroxybenzene is often presence in trace concentration, adsorption process may not be very effective in removing them from aqueous solution. Several studies indicated that oxidation process is an effective method of removing this molecule from solution.

Iyun (1999) studies the kinetic and mechanism of oxidation of 1, 3, dihyroxybenzene by trioxoiodate (V) ion in aqueous perchloric under pseudo-first order conditions and remarked that the oxidation of phenols by metal complexes leading to the production of quinones has generated great interest and that most studies on this oxidation is focused on the I, 2- and 1, 4-dihydroxybenzenes because of their biological and pharmaceutical significances. 1, 3-dihyoxybenzene has been isolated in roasted barley,

cane molasses, coffee, beer and wine. They are useful as flavouring agent and as metabolites (Innocenti *et al*., 2006a, b). McBride (1989) studied the kinetic of oxidation of dihydroxybenzenes (DHB) to quinones in acetate-buffered suspensions of synthetic hirnessite using Mn dissolution to monitor the progress of the reaction. Free Mn^{2+}in the aqueous phase was continuously monitored by electron spin resonance, while ultraviolet-visible (UV-VIS) spectroscopy was utilized to quantify dihydroxybenzene and quinone concentrations. The results obtained indicated that the initial Mn dissolution was very rapid due to a surface reaction this was succeeded by slow release of Mn accompanied by more complete oxidation of the phenols which suggested that the process is limited by the rate of dissolution of the solid. Ngamchuea *et al*. (2020) studied the oxidation of 1, 3-dihydrobenzene using cyclic voltammetry method and found that the molecules undergoes a $1H^+$ 1 electron oxidation at pH < pKa1 and a 1 electron oxidation at pH > pKa2 to form radicals. The radicals then readily react to form dimers/polymers deposited on the electrode surface.

Di-μ-oxo-tetrakis (2, 2'- bipyridine)- dimanganese (III, IV) perchlorate which can be written as $[(bipy)_2 Mn^{III} O_2 Mn^{IV} (bipy)_2]^{3+}$ has various possible applications and useful participation in numerous biological systems containing manganese complex. During photosynthesis, there is a manganese complex which is made up of one calcium and four manganese atoms that serves as a model for the splitting of water molecule through absorption of photon (Vinyard *et al.,* 2014). It is responsible for the oxidation of water to oxygen in plants, algae and cyanobacteria. Therefore, it is important that the redox reactions between di-μ-oxo-tetrakis (2, 2'- bipyridine) – dimanganese (III, IV) perchlorate and 1, 3-dihydroxybenzene in hydrochloric acid be investigated.

2.0   Materials and Methods

Spectrumlab 752s UV/visible spectrophotometer, hydrochloric acid (HCl), sodium chloride (NaCl) nickel nitrate ($Ni(NO_3)_2$), sodium formate (HCOONa), sodium nitrate ($NaNO_3$) and distilled water were used. All reagents were analar grade.

Synthesis and characterization of di-μ-oxo-tetrakis (2, 2'- bipyridine) – dimanganese (III, IV) perchlorate was carried out by the addition of 4.3 g of $Mn(CH_3COO)_2$.. $4H_2O$ in 60 ml of distilled water

followed by addition of 9.46 g of 2, 2' bipyridine that was prepared in 30 ml of acetone, 8 ml of 1 mol dm^{-3} acetate buffer (pH 4.5) was added to the solution and the pH adjusted was to 4.5. The solution was allowed to cool to 0 °C in an ice bath. Potassium permanganate (1.18 g dissolved in 50 ml of water) was added drop wise with stirring and the resulting solution was filtered followed by addition of concentrated $NaClO_4$ to precipitate the product to a paste. The product was washed with a mixture of ethanol and diethyl ether solutions. The complex formed was re-crystallized at room temperature and filtered. The filtrate was re-crystalized through slow addition of a concentrated solution of $NaClO_4$ and stirring. The solution was cooled and filtered to obtain the product. The re-crystallized product was allowed to dry in a desiccator to a constant weight (Nafjapour and Moghaddam (2012). Uv/Visible spectrum of the synthesized compound, $[(bipy)_2 Mn^{III} O_2 Mn^{IV} (bipy)_2]^{3+}$ was recorded at $\lambda_{max} = 683$ nm.

The stoichiometry of the reaction was determined spectrophotometrically by keeping the concentration of $[(bipy)_2 Mn^{III} O_2 Mn^{IV} (bipy)_2]^{3+}$ constant at 5.0×10^{-5}mol dm^{-3} while that of H_2Q was varied between $(1.0 – 10.0) \times 10^{-5}$ mol dm^{-3} at $[H^+] = 1 \times 10^{-4}$ mol dm^{-3}, μ= 1.0 mol dm^{-3}, T = 30 ± 1 °C at λ_{max} = 683 nm until a constant absorbance value was obtained. The absorbance at infinity (A_∞) was plotted against the mole ratio and the point of inflection on the curve of the absorbance versus mole ratio plot corresponds to the stoichiometry of the reaction.

The kinetic study was performed under pseudo-first order conditions with the concentration of H_2Q at least 24-folds excess over that of $[(bipy)_2 Mn^{III} O_2 Mn^{IV} (bipy)_2]^{3+}$ at T = 30 ± 1 °C, μ = 1.0 mol dm^{-3}. The reaction was monitored spectrophotometrically by taking the absorbance at λ_{max} of 683 nm. The pseudo-first order plot of log $(A_t−A_\infty)$ versus time (t) in seconds were made (A_t and A_∞ are the absorbance at time, t and at infinity respectively).

The influence of hydrogen ion concentration on the reaction rate was investigated in the range of $0.5 \leq [H^+]$ 4.0×10^{-4} mol dm^{-3} using HCl, at constant ionic strength of μ = 1.0 mol dm^{-3} and T = 30 ± 1 °C (NaCl).

The effect of ionic strength of the reaction medium on the rate was investigated in the range of 0.2 – 1.2

mol dm^{-3} (NaCl) while the concentrations of other reactants were kept constant. The relationship between of the reaction rate and changes in ionic strength was investigated by plotting log k$_2$versus√μ. The effect of medium dielectric constant, D, on the rate was also investigated by using a binary solvent mixture of 20 % ethanol/water respectively. The effect of added ions on the reaction rate was achieved by varying the concentrations of (Ni$^+$, NO$_3^-$ and HCOO$^-$) while the concentrations of other reactants were kept constant.

To test for the presence of free radical in the reaction mixture, acrylamide solution was added to a partially reduced reaction mixture, followed by an addition of methanol in excess. The same treatment was applied to the solutions of $[(bipy)_2Mn^{III}O_2Mn^{IV}(bipy)_2]^{3+}$ and H_2Q separately which served as control.

Electronic spectra of partially reacted reaction mixtures were recorded at various time intervals. A similar run was carried out for reactants separately in each case. This was carried out in order to observe enhancement of peak or shift in λ$_{max}$ will result as the reaction progresses. Furthermore, Michaelis-Menten's type plot of1/k$_1$ versus 1/[H_2Q] was carried out which provided information on the presence or absence of intermediate complex formation through the identification or non-identification of intercept.

The products of the reaction were analyzed for quinine and Mn^{2+}. The solution at the end of the reaction was divided into two parts. One part was kept in the dark for 2 days. A dirty yellow precipitate was obtained. This was filtered and reacted with 2,4-dinitrophenylhydrazine. Red crystals indicating the presence of Quinone were obtained. To the second part of the completely reacted solution, dilute solution of H$_2$SO$_4$ and KIO$_3$were added and warmed for 2 mins, the solution turned pinkish indicating the presence of Mn^{2+}.

3.0 Results and Discussion

The Uv visible spectrum of the synthesized compound, $[(bipy)_2Mn^{III}O_2Mn^{IV}(bipy)_2]^{3+}$ indicated a wavelength of maximum absorption (λ$_{max}$) of the compound as 683 nm (Fig. 1).

A mole ratio of 2:3 was obtained as the stoichiometry between the reaction of $[(bipy)_2Mn^{III}O_2Mn^{IV}(bipy)_2]^{3+}$and H_2Q. This is consistent with the report of Lohdip and Iyun (2003) for the reaction of $[(phen)_2Mn^{III}O_2Mn^{IV}(phen)_2]$and thiocynate. The overall equation for the redox reaction can be represented by equation 1:

$$2[(bipy)_2Mn^{III}O_2Mn^{IV}(bipy)_2]^{3+} + 3H_2Q + 2H^+ \rightarrow 3Q + 4Mn^{2+} + 4H_2O \qquad (1)$$
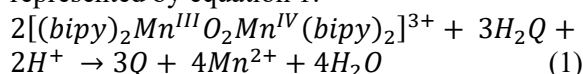
The reaction indicated an order of one with respect to$[(bipy)_2Mn^{III}O_2Mn^{IV}(bipy)_2]^{3+}$. The plot of log (A$_t$ -A$_∞$) versus time was linear for over 90 % extent of the reaction (Fig. 2). Also plot of log k$_0$ versus log [H_2Q] was linear and the slope was 1.02 (Fig. 3), indicating first order with respect to H$_2$Q. Therefore, the overall order of the reaction is second order with a second order rate constant, k$_2$ obtained from k$_2$ = k$_0$/[H_2Q] fairly constant (Table 1.0). This is consistent with what was reported by Iyun and Ukoha (1999). The rate law for the reaction is:

$$-\frac{2}{3}\frac{[(bipy)_2Mn^{III}O_2Mn^{IV}(bipy)_2]^{3+}}{dt} = k_2[(bipy)_2Mn^{III}O_2Mn^{IV}(bipy)_2]^{3+}[H_2Q] \qquad (2)$$
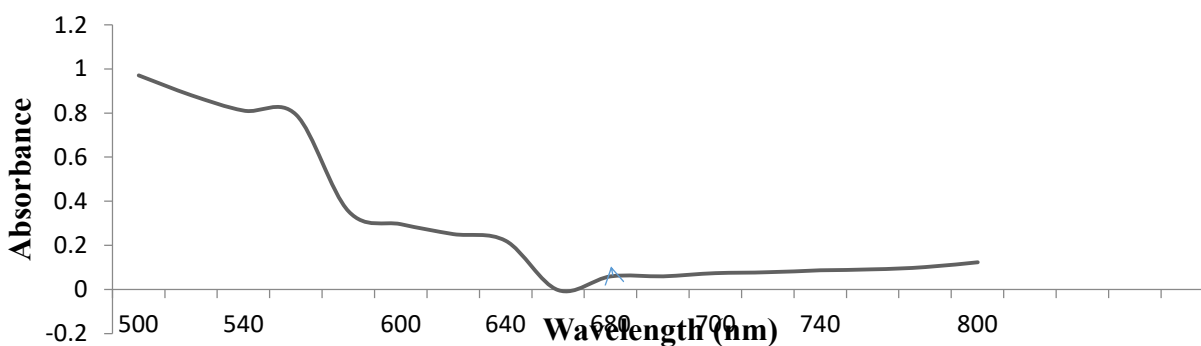
where k$_2$ = 7.64 ± 0.03 dm^3 mol^{-1} s^{-1}

Fig. 1: Uv/visible Spectrum of $[(bipy)_2Mn^{III}O_2Mn^{IV}(bipy)_2]^{3+}$.
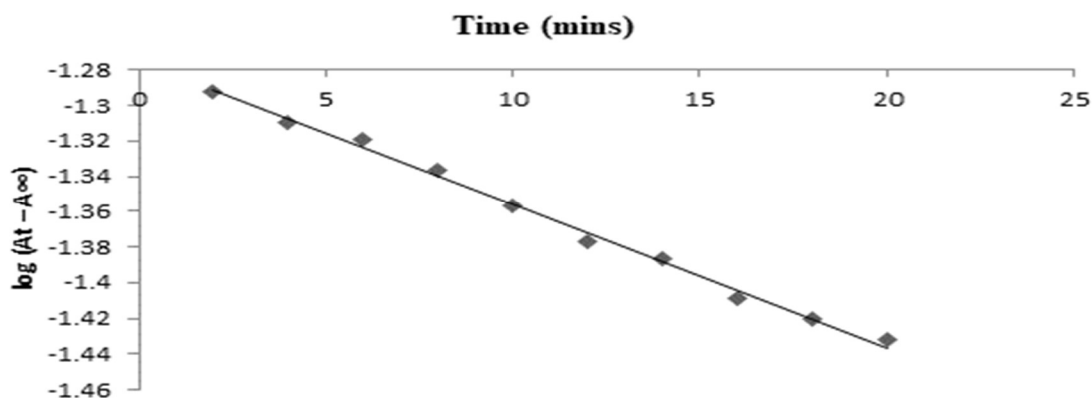
Fig. 2: Pseudo-first order plot for the reaction of $[(bipy)_2Mn^{III}O_2Mn^{IV}(bipy)_2]^{3+}$ and H_2Q. $[(bipy)_2Mn^{III}O_2Mn^{IV}(bipy)_2]^{3+} = 5.0 \times 10^{-5}$, $[H_2Q] = (1.2\text{-}3.0) \times 10^{-3}$, $H^+ = 1.0 \times 10^{-4}$, $\mu = 1.0$ mol dm^{-3}, $\lambda_{max} = 683$ nm and T= 30.0 ±1^{O}C.
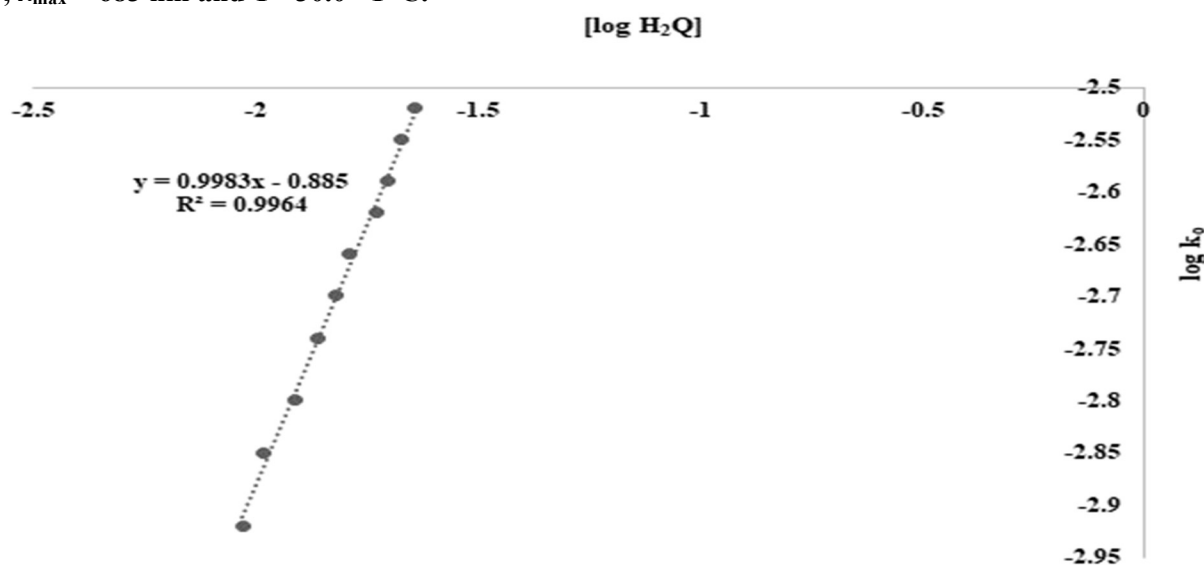

Fig.3: Variation of log k_0 vs log $[H_2Q]$ for $[(bipy)_2Mn^{III}O_2Mn^{IV}(bipy)_2]^{3+} = 5 \times 10^{-5}$, $[H_2Q] = (1.2 – 3.0) \times 10^{-3}$, $H^+ = 1 \times 10^{-4}$, $\mu = 1.0$ mol dm^{-3}, $\lambda_{max} = 683$ nm and T= 30.0 ±1^{O}C.

Observation of the effect of hydrogen ion concentration on the reaction rate revealed increase in rate with increase in the concentration of acid (Fig. 4). In the range of $0.5 \leq [H^+] \leq 3.5$ mol/dm^3 as shown in Table 1. A plot of k_2 vs $[H^+]$ was linear with a slope of 1.76×10^{-4} dm^3 mol^{-1} s^{-1} and an intercept of 5.73 dm^3 mol^{-1} s^{-1}. This result is in good agreement with the findings reported by Banerjee et al. (1997) for the reduction of $[Mn^{III}O_2Mn^{IV}]^{3+}$ by hydrogen peroxide and also the those reported by Chaudhuri et al. (1995) for the reaction of $[(bipy)_2Mn^{III}O_2Mn^{IV}(bipy)_2]^{3+}$ with NO_2^- respectively. However, the results are at variance with those reported by Iyun et al. (1996) for the oxidation of I, 3-dihydroxybenzene by $[RuORu]^{4+}$ where the rate of reaction decreases as $[H^+]$ increases, hence the overall equation for the reaction is presented as:

$$\frac{-d[(bipy)_2Mn^{III}O_2Mn^{IV}(bipy)_2]}{dt} = \{5.73 + 1.76 \times 10^{-4}[H^+][(bipy)_2Mn^{III}O_2Mn^{IV}(bipy)_2][H_2Q] \quad (3)$$

where a = 5.73 dm^3 mol^{-1} s^{-1}, b = 1.76 $\times$ 10^{-4} dm^3 mol^{-1} s^{-1}: a = intercept and b = slope.

Table 1: Pseudo-first and pseudo second order rate constants for the reaction of $[(bipy)_2Mn^{III}O_2Mn^{IV}(bipy)_2]^{3+}$ and H_2Q at = 5.0×10^{-5}, $[H_2Q]$ = $(1.2\text{-}3.0) \times 10^{-3}$, H^+ = 1.0×10^{-4}, μ = 1.0 mol dm^{-3}, λ_{max} = 683 nm and T= 30.0 ± 1^{O}C.

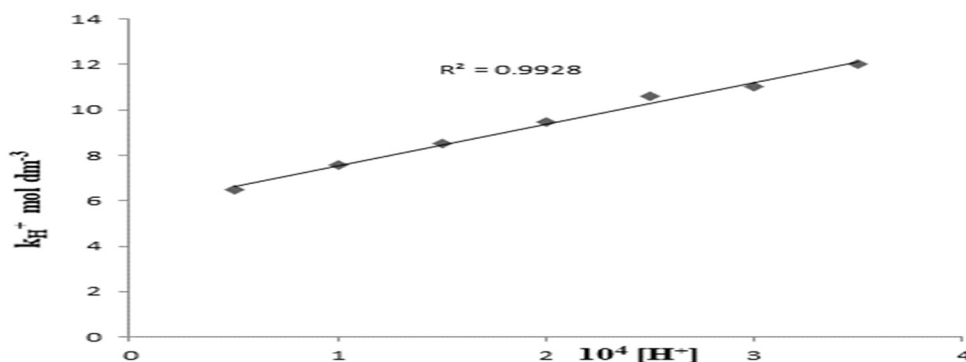| $10^3[H_2Q]$ mol dm^{-3}	$[H^+]$ = 1.0×10^{-4} mol dm^{-3}	μ= 1.0 mol dm^{-3}	$10^1 k_0$s^{-1}	k_2 dm^3 mol^{-1} s^{-1}
1.2	1	1	9.26	7.72
1.4	1	1	10.43	7.45
1.6	1	1	12.23	7.64
1.8	1	1	13.91	7.73
2	1	1	15.31	7.66
2.2	1	1	16.37	7.44
2.4	1	1	18.52	7.72
2.6	1	1	20.04	7.71
2.8	1	1	21.39	7.64
3	1	1	23.05	7.68
2	0.5	1	12.92	7.46
2	1	1	15.31	7.66
2	1.5	1	17.07	8.53
2	2	1	18.93	9.47
2	2.5	1	21.16	10.58
2	3	1	22.06	11.03
2	3.5	1	24.02	10.01
2	1	0.2	15.5	7.75
2	1	0.4	15.41	7.7
2	1	0.6	15.52	7.76
2	1	0.8	15.5	7.75
2	1	1	15.38	7.69
2	1	1.2	15.59	7.8

Fig.4: Plot of k_2 vs $[H^+]$ for the reaction of $[(bipy)_2Mn^{III}O_2Mn^{IV}(bipy)_2]^{3+}$ with H_2Q $[(bipy)_2Mn^{III}O_2Mn^{IV}(bipy)_2]^{3+}$= 5.0×10^{-5}, $[H_2Q]$ = 2.0×10^{-3}, H^+ =1.0×10^{-4}, μ = 1.0 mol dm^{-3}, λ_{max} = 683 nm and T= 30.0 ± 1^{O}C.

Table 2: Effect of dielectric constant on the reaction of $[(bipy)_2Mn^{III}O_2Mn^{IV}(bipy)_2]^{3+}$ with H₂Q. $[(bipy)_2Mn^{III}O_2Mn^{IV}(bipy)_2]^{3+}= 5.0 \times 10^{-5}$, $[H_2Q] = 2.0 \times 10^{-3}$, $H^+ = 1.0 \times 10^{-4\#}$, $\mu = 1.0$ mol dm⁻³, D = 20 % Ethanol, $\lambda_{max} = 683$ nm and T= 30.0 ± 1ᴼC.

10^3 [H_2Q] mol dm⁻³	10^4[H^+] mol dm⁻³	$\mu = 1.0$ mol dm⁻³	$10^3 k_0$ s⁻¹	k_2 dm³ mol⁻¹ s⁻¹
2	1	1	15.34	7.67
2	1	1	15.58	7.79
2	1	1	15.69	7.85
2	1	1	15.45	7.73
2	1	1	15.44	7.72
2	1	1	15.34	7.67

The rate of reaction was also found to be unaffected by added cation and anion as shown in Table 3, which also agrees with the findings reported by Lohdip and Iyun (2003). Addition of acrylamide solution to the partially reacted mixture (in the presence of excess methanol) indicated the absence of gel formation, which also confirm the absence of free radicals in the reaction. This result is contrary to that reported by Gosh *et al.,* (2002) where little gel was formed in the presence of excess methanol. Michelis Menten's type was linear with zero intercept indicating the absence of intermediate complex formation (Fig. 5). Also spectroscopic data is consistent with kinetic data for the absence of intermediate.

Table 3: Effect of cation and anions for the reaction of $(bipy)_2Mn^{III}O_2Mn^{IV}(bipy)_2]^{3+}$ with H_2Q. $[(bipy)_2Mn^{III}O_2Mn^{IV}(bipy)_2]^{3+}= 5.0 \times 10^{-5}$, $[H_2Q] = 2.0 \times 10^{-3}$, $H^+ =1.0 \times 10^{-4}$, $\mu = 1.0$ mol dm⁻³, $\lambda_{max} = 683$ nm and T= 30.0 ± 1ᴼC.

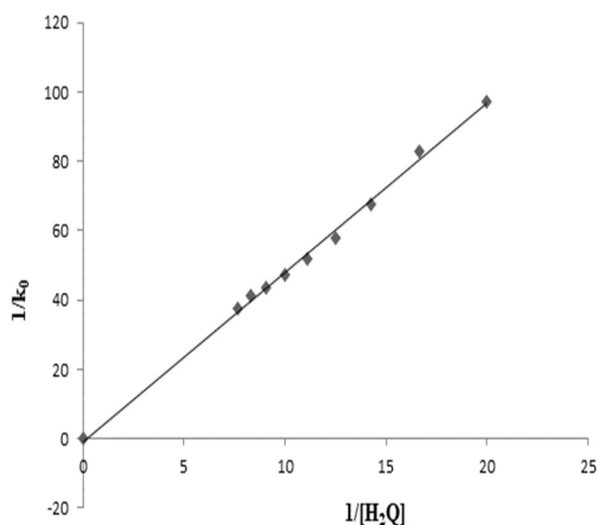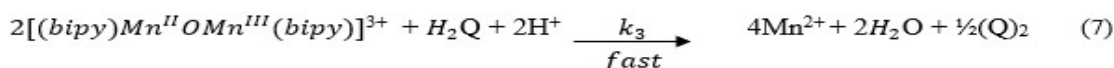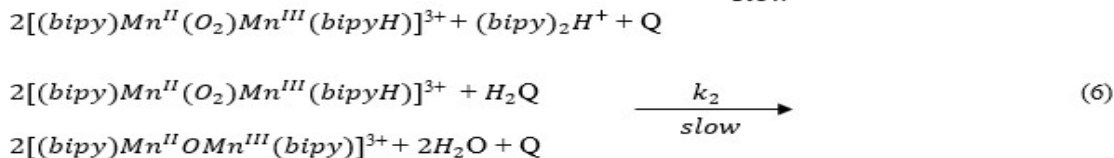| Ion	10^3 [Ion] mol dm⁻³	$10^3 k_0$ s⁻¹	k_2 dm³ mol⁻¹ s⁻¹
Ni²⁺	0.3	21.99	11.00
	0.5	22.45	11.23
	0.7	21.99	11.00
	0.9	21.99	11.00
	1.0	21.97	11.04
	1.3	22.09	11.05
HCOO⁻	0.3	23.95	11.98
	0.5	23.98	11.99
	0.7	23.91	11.95
	0.9	23.93	11.96
	1.0	23.88	11.94
	1.3	23.88	11.94
NO₃⁻	0.3	23.99	11.75
	0.5	23.86	11.93
	0.7	23.58	11.79
	0.9	23.49	11.75
	1.0	23.17	11.58
	1.3	23.49	11.75

Fig. 5: Plot of $1/k_0$ versus $1/[H_2Q]$ for reaction of with H_2Q. $[(bipy)_2Mn^{III}O_2Mn^{IV}(bipy)_2]^{3+}= 5.0 \times 10^{-5}$, $[H_2Q] = 2.0 \times 10^{-3}$, $H^+ = 1.0 \times 10^{-4}$, $\mu = 1.0$ mol dm⁻³, $\lambda_{max} = 683$ nm and T= 30.0 ± 1ᴼC

The result obtained in these tests are consistent with the results of Mohammed *et al.,* (2017) for the reduction of diaquotetrakis (2, 2′-bipyridine)-μ-oxodiruthenium(III) ion by hypophosphorous. The following reaction mechanism was proposed for the system:

$$2[(bipy)_2 Mn^{III} O_2 Mn^{IV}(bipy)_2]^{3+} + H^+ \; \underset{}{\overset{K}{\rightleftharpoons}} \quad (4)$$

$$2[(bipy)_2 Mn^{III} O_2 Mn^{IV}(bipy)]^{3+} + (bipy)_2 H^+$$

$$2[(bipy)_2 Mn^{III} O_2 Mn^{IV}(bipy)]^{3+} + H^+ + H_2Q \; \xrightarrow[slow]{k_1} \quad (5)$$

$$2[(bipy) Mn^{II}(O_2) Mn^{III}(bipyH)]^{3+} + (bipy)_2 H^+ + Q$$

$$2[(bipy) Mn^{II}(O_2) Mn^{III}(bipyH)]^{3+} + H_2Q \; \xrightarrow[slow]{k_2} \quad (6)$$

$$2[(bipy) Mn^{II} O Mn^{III}(bipy)]^{3+} + 2H_2O + Q$$

$$2[(bipy) Mn^{II} O Mn^{III}(bipy)]^{3+} + H_2Q + 2H^+ \; \xrightarrow[fast]{k_3} \quad 4Mn^{2+} + 2H_2O + \frac{1}{2}(Q)_2 \quad (7)$$
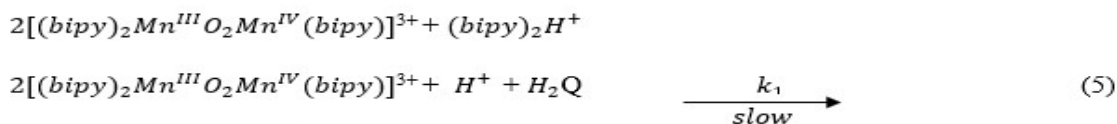
4.0 Conclusion

The reaction rate increased with increase in the concentration of hydrochloric acid and was unaffected by ionic strength concentration and added ions. The reaction system has been rationed to proceed via Proton Coupled Electron Transfer Mechanism due to the non-catalysis by added ions.

5.0 References

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Conflict of Interest
The authors declare no conflict of interest