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Kinetics Study of the Reduction of $[(bipy)_2Mn^{III}O_2Mn^{IV}(bipy)_2]^{3+}$ by Thiocyanate Ion in Aqueous Hydrochloric Acid.

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ABSTRACT

The kinetics of the reduction of $[(bipy)_2Mn^{III}O_2Mn^{IV}(bipy)_2]^{3+}$ *by thiocyanate ion* (SCN^-) *has been studied in aqueous hydrochloric acid medium. The stoichiometric determination showed a mole ratio of 1:3. Kinetics study was carried out under pseudo - first order condition and showed that the rate of reaction was first order with respect to both* $[(bipy)_2Mn^{III}O_2Mn^{IV}(bipy)_2]^{3+}$ *and* $[SCN^-]$. *The rate of the reaction was acid dependent and was found to decrease with increase in ionic strength, suggesting a negative salt effect. The addition of added cations and anions* (Ni^{2+}, Mg^{2+}, NO_3^- *and* CH_3COO^-) *increased the rate of reaction and Michaelis-Menten's plot showed a zero intercept. Based on the results of the spectroscopic studies, kinetic evidences from Michaelis–Menten's plot and interaction with added ions, an outer–sphere mechanism has been proposed for the reaction of* $[(bipy)_2Mn^{III}O_2Mn^{IV}(bipy)_2]^{3+}$ *-* SCN^- *system.*

Keywords: Kinetics, Reaction, $[(bipy)_2Mn^{III}O_2Mn^{IV}(bipy)_2]^{3+}$, Thiocyante Ion.

INTRODUCTION

Manganese has been reported in literature to have a very important role in the active site of organisms. It is now clearly established that at least four enzymes (the photosynthetic oxygen-evolving complex, manganese catalase, manganese superoxide dismutase and ribonuleotide reductase) use bi- or multi-nuclear manganese complex as their redox catalytic center Vincent *et al.*, [1]; Andreasson and Vanngard[2]; Penner[3].

Thiocyanates (SCN) has antioxidant properties that include the ability to protect cells against oxidizing agents such as hypochlorous acid (HOCl) and repair protein chloramines. SCN is an important endogenous molecule that has the potential to interact in complex and elegant ways with its host environment and foreign organisms. SCN's diverse properties as both host defense and antioxidant agent make it a potentially useful therapeutic "Chandler and Day[4]. They are found in various foods and plants; they are produced primarily from the reaction of free cyanide with sulphur Pedemonte *et al.*, [5]. It is sometimes called sulphocyanate or simply "yam vitamin" a natural substance produced in certain plants called nitrilosides among which are the foods, African yams and cassava. These edible plants were once included in the diet of native Africans before the introduction of grains such as rice and wheat. It is also known to be an important part in biosynthesis, thus the complete absence of thiocyanate according to Childers *et al.,*[6] or reduced thiocyanate as reported by Minarowski *et al.,*[7] in the human body is damaging to the human host defence system Moskwa *et al.,* [8] ; Xu *et al.,*[9] . It is used as a precursor for the synthesis of pharmaceuticals and other specialty chemicals. The role of manganese as well as that of thiocyanate in humans has therefore prompted the investigation of the kinetics and mechanism of the reduction of $[(bipy)_2Mn^{III}O_2Mn^{IV}(bipy)_2]^{3+}$ (referred to in the text as $[Mn^{III}O_2Mn^{IV}]^{3+}$ by (SCN^-).

EXPERIMENTAL METHODS

Materials

Analytical grade reagents were used throughout this work without further purification. Hydrochloric acid (HCl) was used to maintain $[H^+]$ for the reactions while Sodium chloride (NaCl) was used to maintain constant ionic strength. Magnesium chloride ($MgCl_2$), Nickel nitrate ($NiNO_3$), Sodium acetate (CH_3COO^-) and Sodium nitrate (NO_3^-) were used to test for the effect of added species on reaction rate. Acrylamide with methanol were used for free radical tests in all the reactions.

Stoichiometric Determination

The stoichiometry of the reaction was determined by spectrophotometric titration using the mole ratio approach. The concentration of the $[Mn^{III}O_2Mn^{IV}]^{3+}$ was kept constant at 5.0×10^{-3} mol dm^{-3} and that of SCN^- was varied between **(**3.0 – 12.0) x 10^{-3} mol dm^{-3} at $[H^+] = 1 \times 10^{-3}$ mol dm^{-3}, I = 0.5 mol dm^{-3}, T = 30.0 ± 1.0 ^oC. The reaction mixtures were monitored at λ_{max} = 683 nm and the absorbance (A_∞) was plotted against the mole ratio of the reactants and the point of sharp inflection in the plot gave the stoichiometry of the reaction.

Kinetic Measurements

All kinetic measurements were performed under pseudo-first order conditions with that of SCN^- in at least 10 folds excess over that of the complex. From the logarithmic plot of log ($A_t - A_\infty$) against time (t) in seconds (where A_t and A_∞ are the absorbance at time, t and at infinity respectively), the slope of the plot was obtained and the pseudo-first order rate constant (k_1) was determined. The second order rate constant (k_2) was subsequently estimated from the relation: $k_2 = k_1/[SCN^-]^n$, where'n' = reaction order with respect to SCN^-.

Effect of Hydrogen Ion Concentration

The effect of changes in $[H^+]$ on the reaction rate was investigated at constant concentration of $[(bipy)_2Mn^{III}O_2Mn^{IV}[(bipy)_2]^{3+}$ and SCN^-.

$[H^+]$ was varied between $(0.4 – 2.8) \times 10^{-3}$ mol dm^{-3} at constant ionic strength of 0.5 mol dm^{-3} (NaCl) and Temperature at 30.0 ± 1.0˚C. The order of reaction with respect to $[H^+]$ was obtained as the slope of the plot of log k_1 against log $[H^+]$. Variation of acid dependent rate constant with $[H^+]$ was obtained by plotting k_2 against $[H^+]$.

Effect of Changes in Ionic Strength and Dielectric Constant of the Reaction Medium

The ionic strength of the reaction mixture, I, was varied between (0.2 – 1.4) mol dm^{-3} (NaCl) while maintaining the concentration of the complex and SCN^- constant at 30.0 ± 1.0˚C. The relationship of the reaction rate with changes in the ionic strength was determined by plotting log k_2 vs $\sqrt{I}$. The effect of medium dielectric constant, D, on the rate was investigated by using a binary solvent mixture of water and acetone.

Effect of Added Ions on the Reaction Medium

The effect of added ions on the reaction rate was achieved by the addition of various amounts of ions (Mg^{2+} , Ni^+, CH_3COO^-, NO_3^-) while maintaining the concentrations of the complex, SCN^- and HCl constant. The ionic strength and temperature were also kept constant.

Test for Free Radicals

About two (2 cm^3) of 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 $[Mn^{III}O_2Mn^{IV}]^{3+}$ and SCN^- separately which served as control. Addition of excess methanol did not give a gel, indicating the probable absence of free radicals in the reaction mechanism.

Tests for Intermediate Complex

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 determine whether enhancement of peak or shift in λ_{max} will result as the reaction progresses. Furthermore, Michaelis-Menten’s plot of $1/k_1$ versus 1/[SCN] was plotted which provided information on the presence or absence of intermediate complex formation through the identification or non-identification of intercept.

RESULTS AND DISCUSSION

Stoichiometry Studies

A mole ratio of 1:3 was observed for the stoichiometry result between $[Mn^{III}O_2Mn^{IV}]^{3+}$ - SCN^- . This is consistent with the report of “Lohdip and Iyun[10] for the reaction of $[(phen)_2Mn^{III}O_2Mn^{IV}(phen)_2]$ and SCN^-. Based on the stoichiometry observed, the overall equation for the redox reaction can be represented by the following equation:

$$[Mn^{III}O_2Mn^{IV}]^{3+} + 3SCN^- + 4H^+ \longrightarrow 2Mn^{2+} + \tfrac{3}{2}(SCN)_2 + 2H_2O \qquad \mathbf{1.0}$$

Order of Reaction

The kinetics investigation indicated an order of one with respect to $[Mn^{III}O_2Mn^{IV}]^{3+}$ from the plot of log (A_t -A_∞) versus time which was linear over 80 % extent of the reaction (Fig. 1.0). The logarithmic plot of k_1 verses log [SCN^-] was linear with a gradient approximately equal to unity (Fig. 2.0), suggesting a first order with respect to SCN^-, thus a second order overall. A second order rate constant, k_2, was obtained from $k_2 = k_1/[SCN^-]$ and were found to be fairly constant for the system (Table 1.0), further confirming first order with respect to the [SCN^-]. The rate law for the reaction is presented as:

$$\frac{-d[Mn^{III}O_2Mn^{IV}]^{3+}}{dt} = k_2[Mn^{III}O_2Mn^{IV}]^{3+}[SCN^-] \qquad \mathbf{2.0}$$

where $k_2 = 12.59 \pm 0.25$ dm^3 mol^{-1} s^{-1}

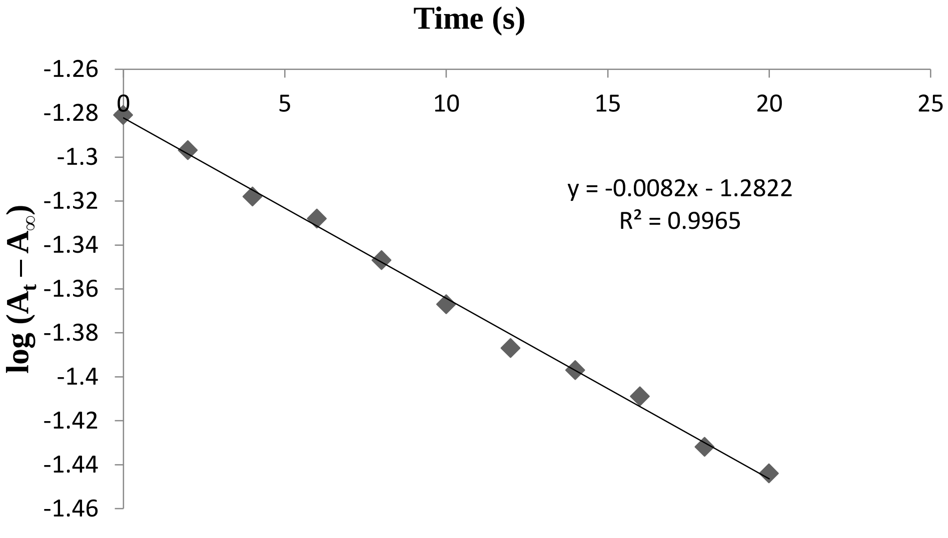

Figure 1.0: Typical Pseudo-first Order Plot of $[Mn^{III}O_2Mn^{IV}]^{3+}$ - SCN^- System.

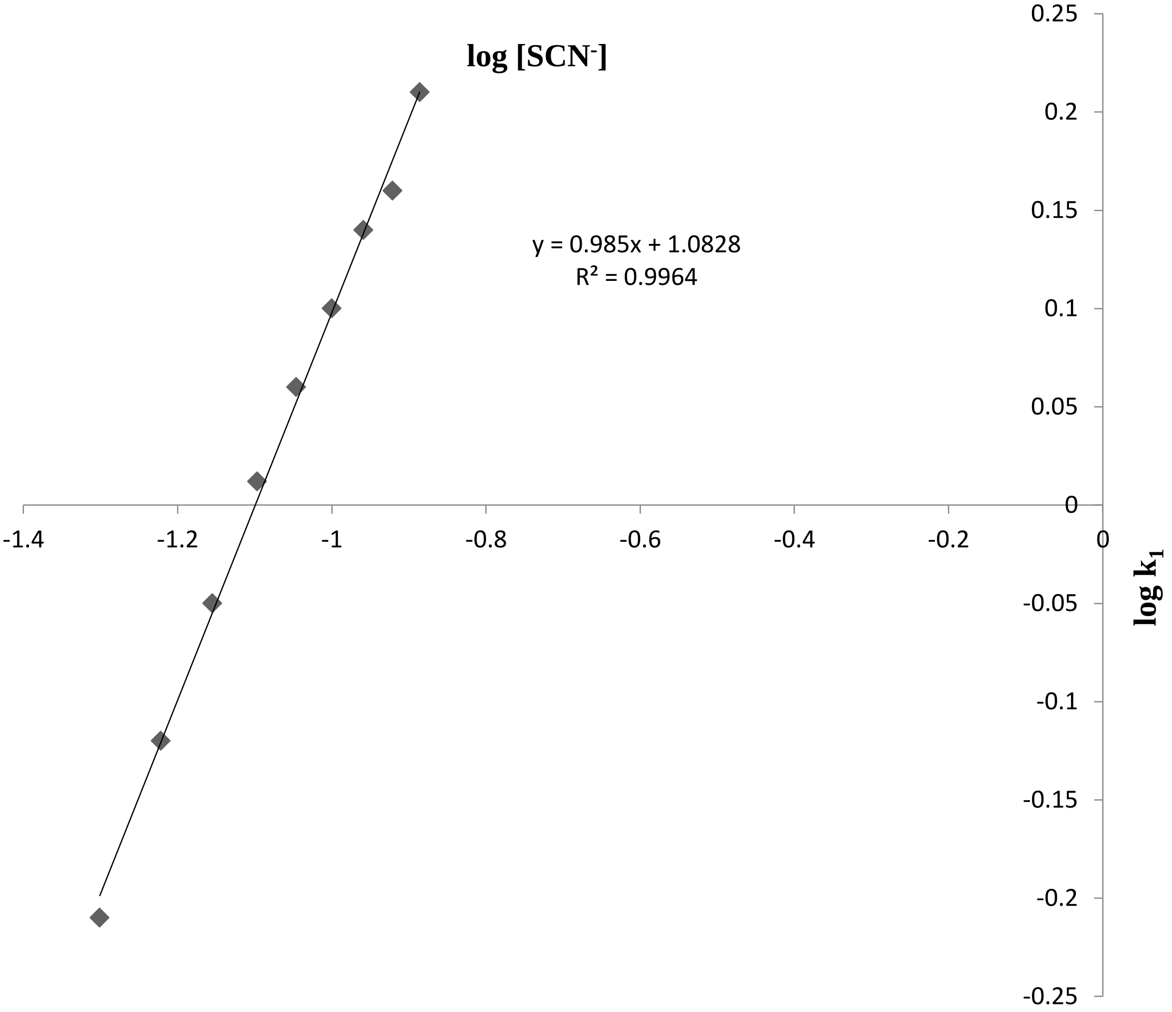

Figure 2.0: Plot of log k_1 vs log $[SCN^-]$ for the Reaction of $[Mn^{III}O_2Mn^{IV}]^{3+}$ - SCN^- System.

Table 1.0: Pseudo-first Order and Second Order Rate Constant for the Reaction of $[Mn^{III}O_2Mn^{IV}]^{3+}$ = 5 x 10^{-3} mol/dm^3 by SCN^-, $[H^+]$ = 1.0 x 10^{-3} mol dm^{-3}, I = 0.5 mol dm^{-3} at 30.0 ±1.0 ^{O}C and λ_{max} = 683 nm.

10^2 [SCN^-] mol dm^{-3}	[H^+], 1.0 x 10^{-3} mol dm^{-3}	I, 0.5 mol dm^{-3}	10^1 k_1, s^{-1}	$k_{2,}$ dm^3 mol^{-1} s^{-1}
5.0	1.0	0.5	6.17	12.34
6.0	1.0	0.5	7.66	12.77
7.0	1.0	0.5	8.90	12.71
8.0	1.0	0.5	10.34	12.93
9.0	1.0	0.5	11.29	12.54
10.0	1.0	0.5	12.68	12.68
11.0	1.0	0.5	13.83	12.57
12.0	1.0	0.5	14.59	12.16
13.0	1.0	0.5	16.04	12.34
8.0	0.4	0.5	5.75	7.19
8.0	0.8	0.5	6.95	8.69
8.0	1.2	0.5	8.08	10.10
8.0	1.6	0.5	9.21	11.51
8.0	2.0	0.5	10.34	12.92
8.0	2.4	0.5	11.44	14.30
8.0	2.8	0.5	12.64	15.80
8.0	1.0	0.2	11.37	14.21
8.0	1.0	0.4	10.32	12.90
8.0	1.0	0.6	9.61	12.01
8.0	1.0	0.8	8.65	10.82
8.0	1.0	1.0	8.47	10.59
8.0	1.0	1.2	7.43	9.92
8.0	1.0	1.4	7.02	8.78

Effect of Hydrogen Ion Concentration

The results for the effect of [H^+] indicated that the rate of reaction increased with increase in the concentration of HCl (Fig. 3.0). This result is in good agreement with the reports of Banerjee *et al.*,[11] for the reduction of $[Mn^{III}O_2Mn^{IV}]^{3+}$ and hydrogen peroxide, Lohdip and Iyun[10], for the reaction of $[(phen)_2Mn^{III}O_2Mn^{IV}(phen)_2]^{3+}$ with SCN^- and Chaudhuri and Banerjee[12] for the reaction of $[Mn^{III}O_2Mn^{IV}]^{3+}$ with NO_2^- respectively. Hence the overall equation for the reaction is presented as:

$$\frac{-1/3\mathrm{d}[Mn^{III}O_2Mn^{IV}]^{3+}}{dt} = (a + b\,[H^+])[Mn^{III}O_2Mn^{IV}]^{3+}[SCN^-] \qquad \mathbf{3.0}$$

where a = 5.805 $dm^3\ mol^{-1}\ s^{-1}$, b = 3.56 x 10^{-3} $dm^3\ mol^{-1}\ s^{-1}$**:** a = intercept and b = slope.

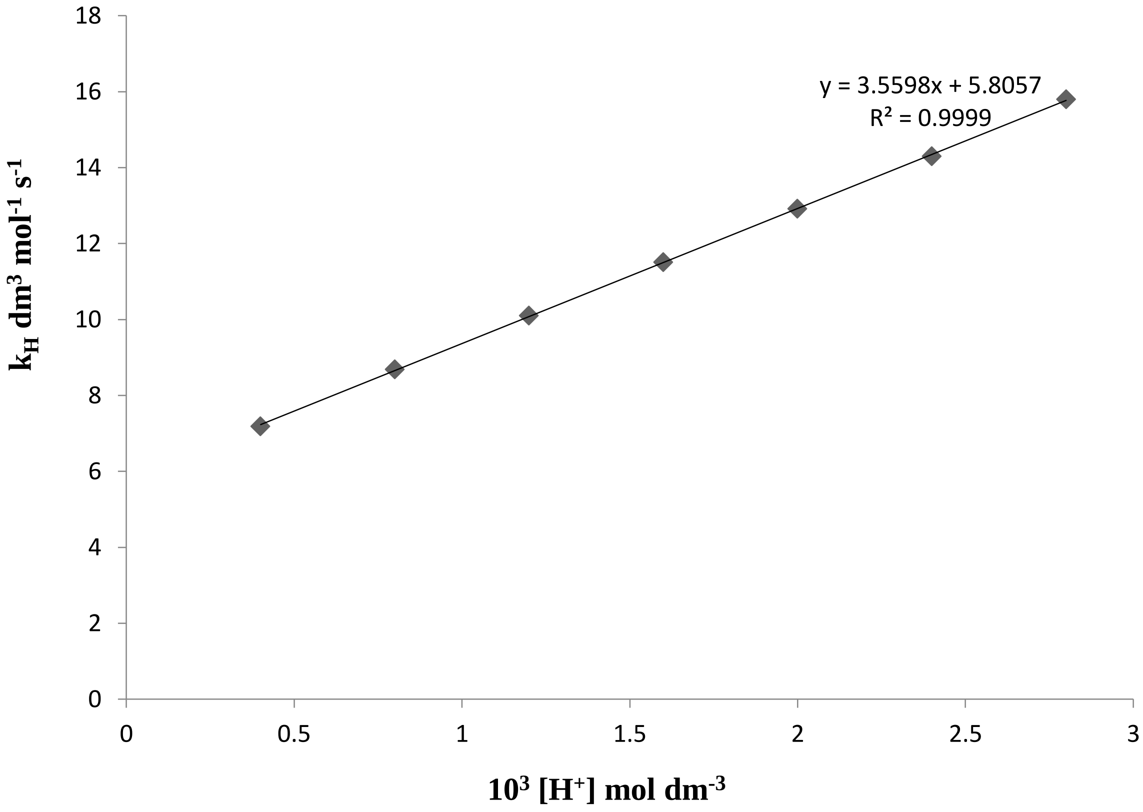

Figure 3.0: Plot of log k_2 vs [H^+] for $[Mn^{III}O_2Mn^{IV}]^{3+}$ - SCN^- System.

Effect of Changes in Ionic Strength and Dielectric Constant of the Reaction Medium

The rate constant was found to decrease with increase in ionic strength from a plot of log k_2 vs $\sqrt{I}$ (Fig. 4.0), suggesting a negative salt effect. This observation suggests that the activated complex is formed from two ions of unlike charges. This result is in good agreement with the reports of Arabel *et al.,*[13] for the reaction of $[(bipy)_2Mn^{III}O_2Mn^{IV}(bipy)_2]^{3+}$ and hydroxyacids; Leal *et al.,*[14] for the reactions of hexacyanoferrate(III) and L-ascorbic acid and Iyun *et al.,*[15] for $[diaquotetrakis(2, 2' – bipyridine) - \mu - oxodiruthenium(III)]^{3+}$ and ascorbic acid respectively.

The effect of change in dielectric constant showed that the rate constant increased as the concentration of acetone increased.

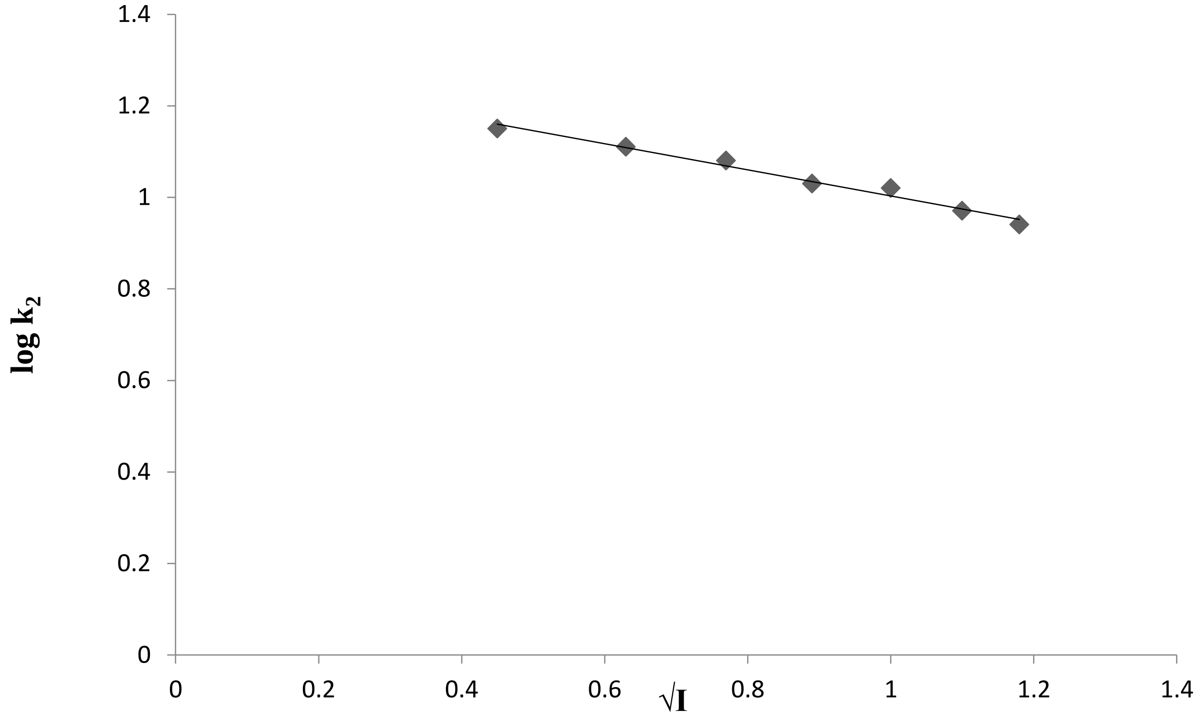

Figure 4.0: Plots of log k_2 vs $\sqrt{I}$ for $[Mn^{III}O_2Mn^{IV}]^{3+}$ - SCN^- System.

Effect of Added Ions in the Reaction Medium

The addition of added cations and anions (Mg^{2+}, Ni^{2+}, CH_3COO^- and NO_3^-) increased the rate of reaction (Table 2.0). The catalysis of the added cations and anions is consistent with the reports of Lohdip and Iyun[10] for the reaction of $[(phen)_2Mn^{III}O_2Mn^{IV}(phen)_2]^{3+}$ and SCN^-. The cations and anions catalysis for this reaction indicates that the reaction did proceed via outer-sphere mechanism. This result is also consistent with the result reported by "Mohammed *et al.*[16] for the reaction of $[(bipy)_2(H_2O)RuORu(H_2O)(bipy)_2]^{4+}$ and thiourea.

Test for Free Radicals

Addition of a solution of acrylamide to partially reacted mixture did not give a gel even in the presence of excess methanol, indicating the probable absence of free radicals in the reaction mechanism.

Tests for Intermediate Complex

The results of spectroscopic studies indicated no shift from λ_{max} of 683 nm this suggests the absence of the formation of an intermediate complex in the reaction. Furthermore, the plot of $1/k_1$ versus $1/[SCN^-]$ (Fig. 5.0) gave a straight line which passed through the origin also suggesting absence of intermediate complex formation prior to redox reaction process. This result is also consistent with the results of "Lohdip and Iyun[17]; "Iyun *et al.,* [18] for the reaction of (diaquotetrakis (2, 2' – bipyridine) - μ - oxodiruthenium(III)]$^{3+}$ and 2-mercaptoethanl and diAquotetrakis(2, 2' - bipyridine) - μ - OxoDiRuthenium(III)$^{3+}$ and L- ascorbic acid respectively.

Table 2.0: Effect of Added Cations and Anions for the $[Mn^{III}O_2Mn^{IV}]^{3+}$ - SCN^- System. $[Mn^{III}O_2Mn^{IV}]^{3+}$ = 5 x 10^{-3} mol/dm^3, $[H^+]$ = 1.0 x 10^{-3} mol dm^{-3} , I = 0.5 mol dm^{-3} at 30.0 ±1.0 ^{O}C and λ_{max} = 683 nm.

Ion	**10^3 [Ion], mol dm^{-3}**	**k_1, s^{-1}**	**k_2, dm^3 mol^{-1} s^{-1}**
Mg^{2+}	0.2	0.97	12.13
	0.4	0.99	12.41
	0.6	1.01	12.71
	0.8	1.03	12.90
	1.0	1.05	13.11
	1.2	1.07	13.32
Ni^{2+}	0.2	16.42	12.32
	0.4	16.56	12.42
	0.6	16.65	12.49
	0.8	16.88	12.66
	1.0	17.25	12.94
	1.2	17.36	13.02
CH_3COO^-	0.2	0.94	11.73
	0.4	0.94	11.80
	0.6	0.99	12.38
	0.8	1.01	12.65
	1.0	1.04	12.99
	1.2	1.07	13.40
NO_3^-	0.2	1.01	12.68
	0.4	1.03	12.83
	0.6	1.05	13.06
	0.8	1.06	13.25
	1.0	1.09	13.68
	1.2	1.12	14.04

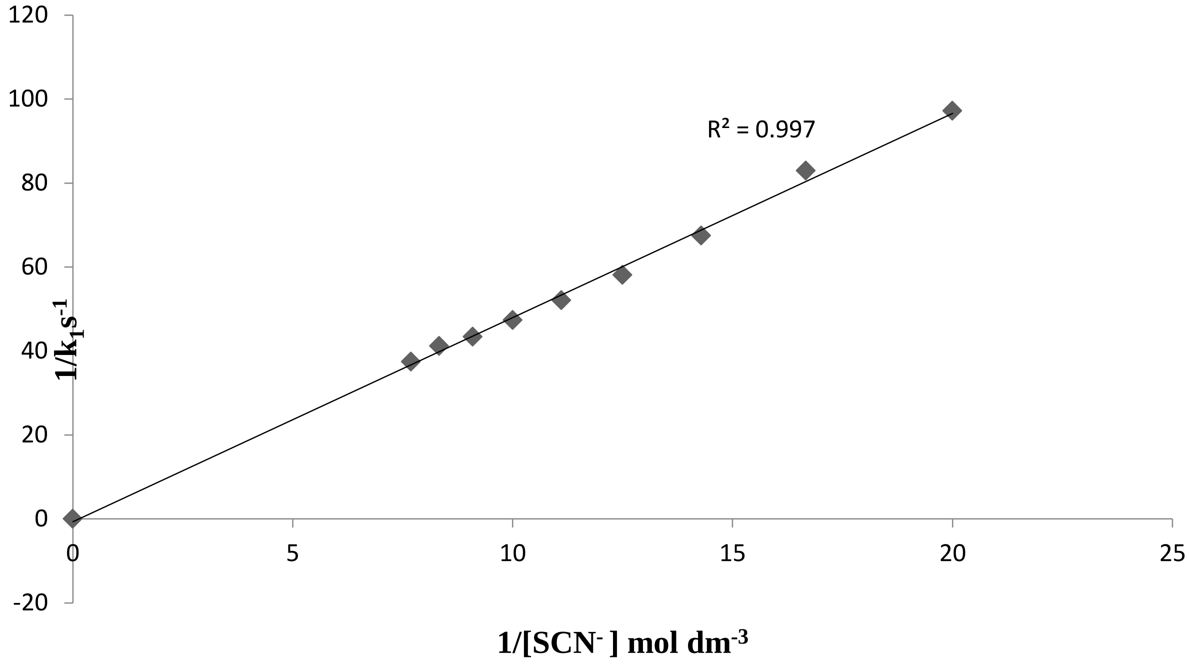

Figure 5.0: Plot of $1/k_1$ versus $1/[SCN^-]$ for $[Mn^{III}O_2Mn^{IV}]^{3+}$ - SCN^- System.

Reaction Mechanism k_2

The observed acid catalysis was due to successive protonation and hydration of the complex Chaudhuri and Banerjee[12]. Under the acid condition used for the system, the following reaction mechanism was proposed:

$$[Mn^{III}O_2Mn^{IV}]^{3+} + H^+ \overset{K_1}{\rightleftharpoons} [HMn^{IV}O_2Mn^{IV}]^{4+} \qquad \mathbf{4.0}$$

$$[HMn^{IV}O_2Mn^{IV}]^{4+} + SCN^- \xrightarrow[\text{slow}]{k_2} [HMn^{III}O_2Mn^{IV}]^{3+} + \tfrac{1}{2}(SCN)_2 \qquad \mathbf{5.0}$$

$$[HMn^{III}O_2Mn^{IV}]^{3+} + SCN^- \xrightarrow[\text{slow}]{k_3} [HMn^{III}O_2Mn^{III}]^{2+} + \tfrac{1}{2}(SCN)_2 \qquad \mathbf{6.0}$$

$$[HMn^{III}O_2Mn^{III}]^{2+} + SCN^- + 3H^+ \xrightarrow[\text{fast}]{k_4} 2Mn^{2+} + 2H_2O + \tfrac{1}{2}(SCN)_2 \qquad \textbf{7.0}$$

Equations 5 and 6 are the rate determining steps:

$$\text{Rate} = k_2[HMn^{IV}O_2Mn^{IV}]^{4+}[SCN^-] + k_3[HMn^{III}O_2Mn^{IV}]^{3+}[SCN^-] \qquad \textbf{8.0}$$

From equation 4

$$[HMn^{IV}O_2Mn^{IV}]^{4+} = K_1[Mn^{III}O_2Mn^{IV}]^{3+}[H^+] \qquad \textbf{9.0}$$

Substituting equation 9.0 into 8.0

$$\text{Rate} = k_2K_1[Mn^{III}O_2Mn^{IV}]^{3+}[SCN^-][H^+] + k_3[HMn^{III}O_2Mn^{IV}]^{3+}[SCN^-] \qquad \textbf{10.0}$$

Rearranging equation 10.0

$$\text{Rate} = k_3 + k_2K_1[H^+][Mn^{III}O_2Mn^{IV}]^{3+}[SCN^-] \qquad \textbf{11.0}$$

where k_3 = a, k_2K_1 = b

Equation 11.0 becomes:

$$\text{Rate} = (a + b\,[H^+])[Mn^{III}O_2Mn^{IV}]^{3+}[SCN^-] \qquad \textbf{12.0}$$

where a = 5.805 $dm^3\ mol^{-1}\ s^{-1}$, b = 3.56 x 10^{-3} $dm^3\ mol^{-1}\ s^{-1}$

This equation is similar to the rate equation in 3.0 above.

CONCLUSION

The kinetics of the reduction of $[Mn^{III}O_2Mn^{IV}]^{3+}$ by thiocyanate ion (SCN^-) in aqueous hydrochloric acid medium showed a mole ratio of 1:3, order of reaction is first order with respect to the complex and thiocyanate ions respectively - second order overall. The rate of reaction increased with increase in hydrogen ion concentration, decreased with increase in ionic strength of the reaction medium. The rate of reaction was affected by added ions and an intermediate complex was not detected.

Based on the above results, the reaction system has been rationed to proceed via outer-sphere mechanism.

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