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KINETICS AND MECHANISM OF THE REDUCTION OF TRIS-(1, 10-PHENANTHROLINE) COBALT (III) COMPLEX BY N-METHYLTHIOUREA IN AQUEOUS ACIDIC MEDIUM

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ABSTRACT

The kinetics and mechanism of the reduction of Tris(1,10-phenanthroline)cobalt(III) complex by N-methylthiourea has been studied in aqueous acidic medium. Stoichiometric determination shows that for one mole of the reductant, one mole of the oxidant was consumed. Kinetics study carried out under pseudo - first order condition showed that the rate of the reaction was acid dependent and first order with respect to the concentration of the both redox species. The rate of reaction was minimally affected by changes in ionic strength and dielectric constant of the medium. Added ions influenced the reaction rates. Michaelis-Menten plot started from the origin. Hence based on spectroscopic investigation, thermodynamic information from temperature dependence studies and kinetic evidences from Michaelis–Menten plot and interaction with added ions, an outer–sphere mechanism has been proposed for the $[Co(phen)_3]^{3+}$ − MTU reaction.

Keywords: Complex, Kinetics, N-methylthiourea, Reduction, Tris(1, 10-phenanthroline) cobalt (III).

INTRODUCTION

1, 10-Phenanthroline (phen) is a versatile heterocyclic bidentate chelating ligand that bond to metal atoms (ions) using the lone pairs of electrons on their nitrogen atoms resulting in a five-membered ring structure [1]. In the formation of complexes by these ligands, their σ-donation is complemented by their π-acceptor ability giving the complexes they form greater stability [2, 3, 4]. Compared to the 2, 2'-bipyridyl system (figure 2), 1, 10-phenanthroline has several distinct properties:

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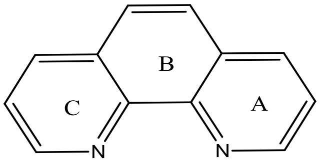

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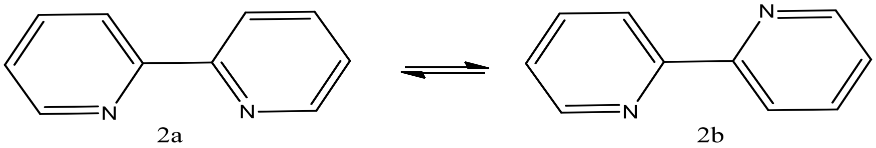

The rigid structure of the phen ligand (figure 1) imposed by the central ring (B) implies that the two nitrogen atoms are always held in proximityto each other resulting to a planar structure whereas in the 2,2’-bipyridyl system, free rotation about the linking bond allows the two nitrogen atoms to separate as in 2a$\rightleftharpoons$2b, precisely under basic or strongly acidic conditions [5]. This ability in phen enables them to readily form complexes with metal ions. Such complexes have potential applications in chemical, biochemical, photochemical and biological reactions. The planar structure of phen is also responsible for its ability to participate as an intercalating or groove-binding species with DNA and RNA [5]. The nucleus of phen has the ability to act as a triple-state photosensitizer especially in lanthanide complexes. The metal chelating properties of phen have been utilized in a range of analytical reagents including herbicides. Several natural products incorporating this heterocyclic nucleus have been isolated, several of which possesses interesting anti-cancer properties. For instance, Tris-(1, 10-phenanthriline) lanthanum(III) trithiocyanate has been reported to have anti-cancer activity [6]. Based on the distinct properties of phen such as its rigid planar nature, its aromatic nitrogen atoms in juxtaposition, its chelating capabilityand its basicity, it can enter into coordination with several metal ions [1] including cobalt which is an important biological element present in various enzymes [7]. Despite the previous several researches on phen complexes scattered in the literature, the kinetic behaviours of these complexes especially those chelating with cobalt have not really been explored and thus their kinetic data tends to be lacking. Hence, the synthesis of Tris-(1,10-phenanthroline) cobalt(III) complex was carried out in this work and subsequently a redox reaction with N-methylthiourea reductant was done in order to determine the kinetics of this complex in solution which will further throw light on its reaction mechanism taking cognizance of the Innersphere and Outersphere mechanistic classifications of Taube and co-workers [8].

EXPERIMENTAL

Materials

Analytical grade reagents were used throughout this work without further purification. Cobaltous chloride (BDH), hydrogen peroxide (30%) and methanol (70%) were reacted with 1, 10-phenanthroline monohydrate (Sigma-Aldrich) to prepare $[Co(phen)_3]^{3+}$. The reductant used was N-Methylthiourea (MTU). Hydrochloric acid (HCl) was used to maintain $[H^+]$ for the reactions while Sodium chloride (NaCl) was used to keep them at constant ionic strength. Magnesium chloride ($MgCl_2$), Ammonium chloride (NH_4^+), Sodium acetate (CH_3COO^-) and Sodium formate ($HCOO^-$) were used to test for the effect of ions on reaction rate. Acrylamide with methanol were used for free radical tests in all the reactions. Standard glass wares (Pyrex) were used at all times, temperature was checked with a thermometer. Kinetic runs were made using a Corning Colorimeter 252 model. A Grant JB1 thermostated water bath was used for temperature dependence studies. Rate of the reaction was monitored with a digital stop watch.

Methods

Following the preparatory route of [9], $[Co(phen)_3]^{3+}$ solution was prepared by dissolving 1.19 g (5.0×10^3 mole) of $Co(H_2O)_6Cl_2$ in 70 cm^3 of water in a beaker, then a solution of 3.05 g (15.0×10^3 mole) of 1,10-phanthroline monohydrate in 20 $cm^3$of methanol was added to the cobaltous chloride solution, 10 $cm^3$of H_2O_2 was also added to ensure oxidation from Co(II) to Co(III) [9]. The UV-Visible spectrum of the synthesized complex has a characteristic λ_{max} at 495 nm.Standard solution of hydrochloric acid (SigmaAldrich) was prepared by diluting concentrated hydrochloric acid (70 %, specific gravity 1.67) using distilled water. A 0.5 mol dm^{-3} stock solution of MTU was prepared from N-methythiourea (Sigma-Aldrich), with molecular weight of 90.15 g mol^{-1}. 4.5 g of MTU was dissolved in a 100 cm^3 volumetric flask and topped up to the mark with freshly prepared distilled water.Standard solutions of NaCl, NH_3Cl, $MgCl_2$, CH_3COOH, and HCOOH were all prepared by weighing known amount and dissolving in known volume of distilled water.

Stoichiometric Determination

The stoichiometry of the reactionwas determined by spectrophotometric titration using the mole ratio approach. The concentration of $[Co(phen)_3]^{3+}$ was kept constant at 2.0×10^{-3} mol $dm^{-3}$and that of MTUwas varied between (5.0 to 60.0) × 10^{-3} mol dm^{-3} at $[H^+] = 7.0 \times 10^{-2}$ mol dm^{-3}, μ = 0.20 mol dm^{-3} and T = 28 ± 1.0˚C. The reaction mixtures were monitored at 495 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

The rate of the reaction was monitored following the rate of increase in absorbance of the complexes at λ_{max} = 560 nm. All kinetic measurements were performed under pseudo first order conditions with the reductants in at least 10-15 fold excess over those of the complexes (Table 1). From the logarithmic plot of log ($A_\infty - A_t$) against time in seconds (where A_∞ and A_t are the absorbance at infinity and at time, t 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: $k_2 = k_1/[MTU]^n$, where'n' = reaction order with respect to the reductant.

Effect of Hydrogen ion

The effect of changes in $[H^+]$ on the reaction rate was investigatedat constant concentration of $[Co(phen)_3]^{3+}$and MTU. $[H^+]$ was varied between (1.0 – 13.0) × 10^{-2} mol dm^{-3} at constant ionic strength of 0.2 mol dm^{-3}(NaCl)and Temperature at 28 ± 1˚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 $k_2(H^+)$ against $[H^+]$.

Effect of Changes in Ionic Strength and Dielectric Constant of the reaction medium

The ionic strength of the reaction mixture, μ, was varied between 0.2 and 0.5 mol dm^{-3} (NaCl) while maintaining the concentration of other reactants constant at 28 ± 1.0˚C. The relationship of the reaction rate with changes in the ionic strength was determined by plotting log k_2 against $\sqrt{\mu}$. The effect of medium dielectric constant, D, on the rate was investigated by using a binary solvent mixture of water and acetone. A plot of log k_2 against $\frac{1}{D}$ gave the pictorial view of the effect of dielectric constant on the reaction medium.

Effect of Added Ions in the reaction medium

The effect of added ions on the reaction rate was observed by the addition of various amounts of ions (Mg^{2+}, NH_4^+, CH_3COO^-, $HCOO^-$) while maintaining the concentrations of the complex, reductant and acid constant. The ionic strength and temperature were also kept constant.

Temperature Dependence Studies

The temperature dependence study was carried out in order to determine thermodynamic parameters like activation enthalpy and entropy and how their results determine the mechanism of the reaction.

Test for Free Radicals

About $2cm^3$ of acrylamide 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 the oxidant and the reductant separately which served as control. Gel formation indicates the presence of free radicals in the reaction mixture.

Tests for Intermediate Complex

Test for the presence of stable, detectable intermediate formed during the course of the reaction was carried out spectrophotometrically. Electronic spectra of partially reacted reaction mixtures were recorded at various time intervals. A similar run was made for reactants separately in each case. This was carried out in order to determine whether enhancement of peak or shift in λ_{max} resulted as the reaction progresses.Furthermore, Michaelis-Menten plot of$1/k_1$ versus 1/[MTU] was plotted which provided information on the presence or absence of intermediate complex formation through the identification or non-identification of intercept.

Product Analysis

At the completion of the reaction, the reaction mixtures were analysed for the type of products formed. The presence of Co(II) product was identified spectrophotometrically by scanning the spectrum of reaction product between wavelength ranges of 400 – 700 nm respectively. The test for the presence of disulphide formed was carried out according to literature:The reaction product was extracted six times with diethylether. Then, the combined ether extract were washed and dried with Na_2SO_4 and left overnight to dry. Appearance of crystals suggested that the product of the reaction included disulphides (10, 11).

RESULTS AND DISCUSSION

Stoichiometry

The stoichiometry of the reaction was found to be 1:1 with respect to their oxidant-reductant mole ratio. The overall equation for the reaction of $[Co(phen)_3]^{3+}$ and MTU is:

$$2[Co(phen)_3)^{3+}] + 2RSH \longrightarrow 2[Co(phen)_3)^{2+}] + RSSR + 2H^+ \qquad (1)$$

This is consistent with reactions involving thiourea and its N-substituted derivatives seen in literature [10, 11, 12, 13, 14, 15, 16]. The stoichiometry is further supported by the result from product analysis: the spectroscopic test of the post reaction mixture giving a λ_{max} of 507 nm and the classical test successfully carried out on the reaction product to ascertain the presence of disulphide as earlier reported.

Order of the Reaction

The linearity of the pseudo-first order plot for the reaction for more than 80% of the reaction time as presented in figure 2 is an indication of first order dependence with respect to the $[\{Co(phen)_3\}^{3+}]$complex. The logarithmic plot of $k_1$versus [MTU] was linear with a gradient approximately equal to unity (Figure 3), suggesting a first order with respect to MTU, thus a second order overall. Similar second order kinetics had been reported for other reactions of MTU [10, 11,15].

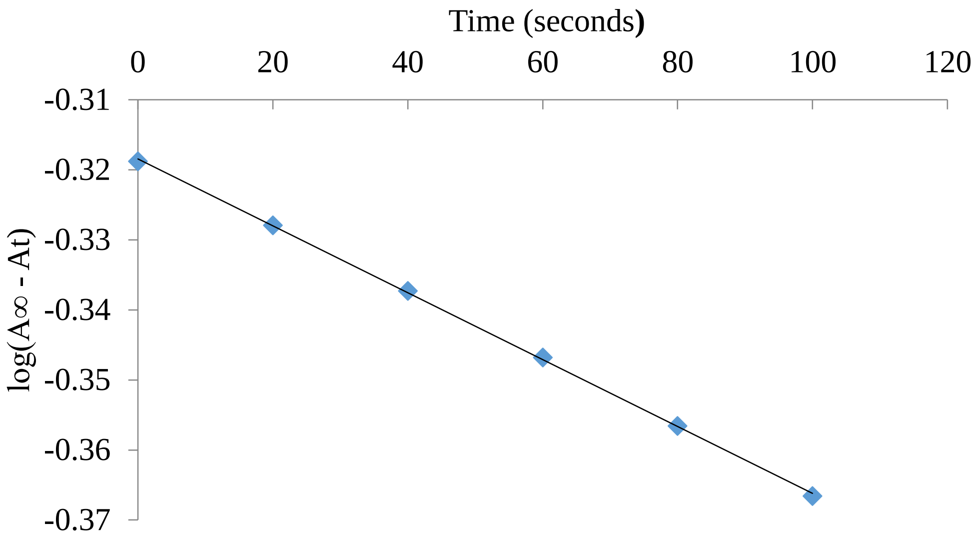

Figure 1: Pseudo-first order plot for the reaction of $[Co(phen)_3]^{3+}$ and MTU

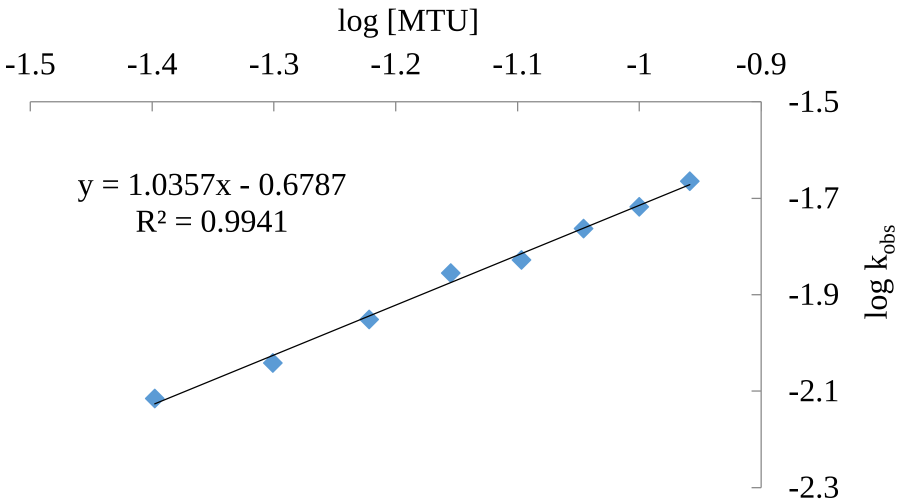

Figure 2:Plot of log k_{obs} versus log [MTU} for the reaction of $[Co(phen)_3]^{3+}$ and MTU

Acid Dependence Test

The result from study of the effect of acid on the reaction showed that reaction rate increased markedly with corresponding increase in hydrogen ion concentration (Table 1), the plot of k_2 versus $[H^+]$ has an intercept of 3.72 dm^3 mol^{-1} s^{-1} (Figure 4) and therefore signifies that the reaction occurs via twoparallel pathways of acid dependence and acid non-dependence [18,19]. The acid dependence is attributable to the protonation of MTU which behaves as a thiol, possessing asulphyhydryl (–SH) group [15].Hence the overall equation for the reaction of $[Co(phen)_3]^{3+}$ and MTU is presented as:

$$-\frac{d}{dt}[\{Co(phen)_3\}^{3+}] = b + a[H^+][\{Co(phen)_3\}^{3+}][MTU] \qquad (2)$$

Similarly, an acid dependence reaction was observed in the redox reaction between Cerium(II) and Cobalt(III) ion with thiourea and its N−substituted derivatives, where a mono-protonated species (RSH^+) as in $NH_3.CS.NH_2^+$is formed before the electron transfer [10,11]. Similar result were also reported by Osunkwo*et al* [20], on the electron transfer reaction of Tris(1,10-phenanthroline)cobalt(III) complex and thiosulphate ion in an aqueous acidic medium.

Effect of Ionic Strength and Dielectric Constant on the Reaction Rate

Investigation on the effect of ionic strength on the reaction species showed that changes in ionic strength concentration had no effect on the rate of the reaction (Table 1).Non-dependence of rate of reaction on ionic strength will likely be due to no charge on one or both of the reactants or the presence of an ion-pair. Ion-pair complexesdo not possess a formal charge, therefore, rate of reactions involving an ion pair would also not be affected by changes in ionic strength [15, 21]. By using water-acetone mixture at various proportions, the dielectric constant of the reaction medium was varied between 80.1 – 69.8. This study showed that changes in D had no effect on the reaction rates (Table 2). This suggests that the reaction occurred between an ion and a neutral molecule or a free radical. This is also consistent with a reaction involving ion-pairs with outersphere character [15, 21].

Table 1: Pseudo-first order and second order rate constants for the reaction of $[Co(phen)_3]^{3+}$ and N-methylthiourea at$[Co(phen)_3]^{3+}$ = 2.0 × 10^{-3} mol dm^{-3}, T = 28 ± 1˚C and λ_{max} = 495 nm

10^2 [MTU], mol dm^{-3}	10^2 $[H^+]$ mol dm^{-3}	[I] mol dm^{-3}	10^2 k_{obs}, s^{-1}	k_2 dm^3 mol^{-1} s^{-1}
4.00	7.00	0.20	0.76	0.19
5.00	7.00	0.20	0.91	0.18
6.00	7.00	0.20	1.12	0.19
7.00	7.00	0.20	1.40	0.20
8.00	7.00	0.20	1.49	0.19
9.00	7.00	0.20	1.73	0.19
10.00	7.00	0.20	1.92	0.19
11.00	7.00	0.20	2.17	0.20
7.00	1.00	0.20	0.40	0.05

7.00	3.00	0.20	0.76	0.11
7.00	5.00	0.20	1.30	0.19
7.00	7.00	0.20	1.48	0.21
7.00	9.00	0.20	2.34	0.33
7.00	11.00	0.20	2.60	0.37
7.00	13.00	0.20	2.52	0.36
7.00	7.00	0.20	1.39	0.20
7.00	7.00	0.25	1.47	0.21
7.00	7.00	0.30	1.41	0.20
7.00	7.00	0.35	1.52	0.22
7.00	7.00	0.40	1.54	0.22
7.00	7.00	0.45	1.47	0.21

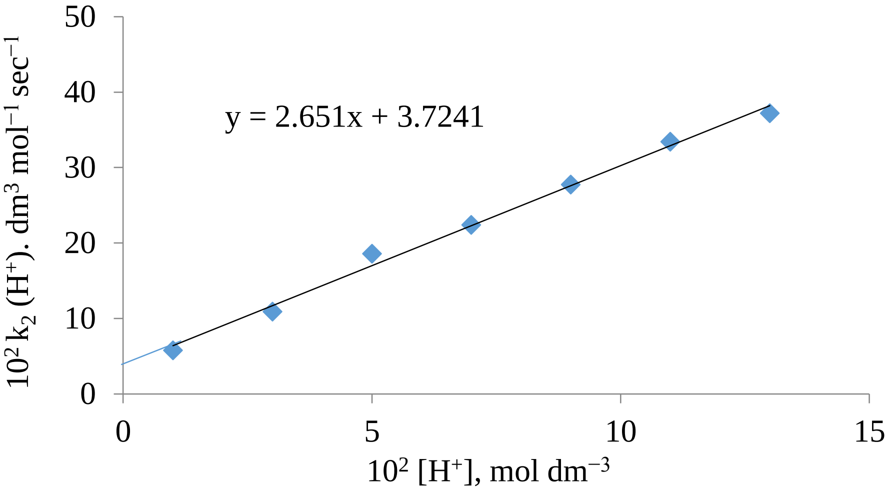

Figure 3:Plot of $k_2(H^+)$ against $[H^+]$ for the Reaction of $[Co(phen)_3]^{3+}$ and MTU

Table 2:Effect of Changes in Dielectric Constant of Reaction Medium for the Reaction of $[Co(phen)_3]^{3+}$ and N-methylthiourea at$[Co(phen)_3]^{3+} = 2.0 \times 10^{-3}$ mol dm^{-3}, $[MTU] = 7.0 \times 10^{-2}$ mol dm^{-3}, $[H^+] = 7.0 \times 10^{-3}$ mol dm^{-3}, I = 0.2 mol dm^{-3} (NaCl), D = (80.1 – 69.8), T = 28 ± 1˚C and λ_{max} = 495 nm.

D	**10^2 1/D**	**$10^2\,k_{obs}$, s^{-1}**	**k_2, $dm^3\,mol^{-1}\,s^{-1}$**
80.1	1.43	1.39	0.20
78.6	1.40	1.54	0.22
77.2	1.37	1.58	0.23
75.7	1.35	1.45	0.21
74.2	1.32	1.55	0.22
72.8	1.30	1.41	0.20

71.3	1.27	1.60	0.23
69.8	1.25	1.51	0.22

Effect of Added Ions

The inhibition in the reaction rate with increase in added anions ($HCOO^-$ and CH_3COO^-) indicate the absence of bridged intermediate ligands at the activated complex, making the effect of foreign ions possible in the activated complex. Ion catalysis and inhibition has been reported to be a characteristic of the outer-sphere reaction mechanism [22, 23, 24].

Temperature Dependence Studies

The rate of reaction was markedly catalysed when the temperature of the system was increased. The result is presented in Table 3. The plot of $ln({}^{k}/_{T})$ versus ${}^{1}/_{T}$ based on Eyring Polanyi equation (Equation 2) was linear; the gradient equals $-{}^{\Delta H^{\ddagger}}/_{R}$ while $ln\,{}^{k_b}/_{h} + {}^{\Delta S^{\ddagger}}/_{R}$ is the intercept.

$$ln({}^{k}/_{T}) = -{}^{\Delta H^{\ddagger}}/_{RT} + ln({}^{k_b}/_{h}) + {}^{\Delta S^{\ddagger}}/_{R} \qquad (3)$$

Where: k = rate constant, T = Temperature; $\Delta H^{\ddagger}$ = Enthalpy of Activation ($J\ mol^{-1}$), $\Delta S^{\ddagger}$ = Entropy of Activation ($J\ K^{-1}\ mol^{-1}$), R = Molar gas constant, k_b= Boltzmann constant and h = Planck constant.

The values of the activation parameters obtained from the study are: $\Delta S^{\ddagger} = 90.87\ JK^{-1}\ mol^{-1}$ and $\Delta H^{\ddagger}$= 11.99 KJ/mol. The positive value of $\Delta S^{\ddagger}$can be attributed to an activated complex where there is disorderliness of solvated particles as a result of dominance of bond breakage [25]. This agrees with an outersphere mechanism.

Table 3: Effect of Added ions to Reaction Medium for the Reaction of $[Co(phen)_3]^{3+}$ and N-methylthiourea at$[Co(phen)_3)^{3+}]$ = 2.0×10^{-3} mol dm^{-3}, [MTU] = 7.0×10^{-2} mol dm^{-3}, $[H^+]$ = 7.0×10^{-3} mol dm^{-3}, I = 0.2 mol dm^{-3} (NaCl), T = 28 ± 1˚C and λ_{max} = 495 nm

Ion	**10^3 [ion] mol dm^{-3}**	**10^2 k_{obs}, s^{-1}**	**k_2, $dm^3\ mol^{-1}\ s^{-1}$**

Mg^{2+}	0.00	1.39	0.20
	1.00	1.45	0.21
	10.00	1.63	0.23
	30.00	1.84	0.26
	50.00	2.07	0.29
	70.00	2.26	0.32
NH_4^+	0.00	1.39	0.20
	1.00	1.53	0.22
	10.00	1.70	0.24
	30.00	1.92	0.27
	50.00	2.13	0.30
	70.00	2.29	0.33
$HCOO^-$	0.00	1.41	0.20
	1.00	1.40	0.19
	10.00	1.16	0.17
	20.00	1.03	0.15
	30.00	0.87	0.12
	40.00	0.76	0.11
	50.00	0.61	0.09
CH_3COO^-	0.00	1.44	0.21
	1.00	1.35	0.19
	10.00	1.20	0.17
	20.00	1.04	0.15
	30.00	0.90	0.13
	40.00	0.69	0.10
	50.00	0.47	0.07

Table 4: Pseudo–first order and second order rate constants for the effect of change in temperature for the reaction of $[Co(phen)_3]^{3+}$ and N-methylthiourea at$[Co(phen)_3]^{3+} = 2.0 \times 10^{-3}$ mol dm^{-3}, [MTU] = 4.0×10^{-2} mol dm^{-3}, $[H^+] = 7.0 \times 10^{-3}$ mol dm^{-3}, I = 0.2 mol dm^{-3} (NaCl) and λ_{max} = 495 nm.

Temperature K	**10^2 [MTU] mol dm^{-3}**	**10^2 $[H^+]$ mol dm^{-3}**	**[I] mol dm^{-3}**	**10^2 k_{obs} s^{-1}**	**10 k_2 dm^{-3}mol^{-1} s^{-1}**
311	4.00	7.00	0.20	0.20	0.51
321	4.00	7.00	0.20	1.37	3.43
326	4.00	7.00	0.20	2.38	5.96
331	4.00	7.00	0.20	4.32	10.81
338	4.00	7.00	0.20	9.39	23.47

Test for Free Radicals

Polymerization test involving addition of acrylamide to the partially reduced reaction mixture followed by excess methanol produced a gelatinous precipitate; this implies the presence of free radical in this reaction [26, 27].

Test for the formation of Intermediate Complex prior to Electron transfer

Results obtained from comparison of the electronic spectrum of the $[Co(phen)_3]^{3+}$ complex with that of the reaction mixture 3 minutes after the start of reaction indicatedno significant shift in λ_{max} suggesting the absence of intermediate complex of a significant formation constant in the reaction. However, the Michaelis – Menten plot of $1/k_1$ versus 1/[MTU] was linear with no intercept (Figure 7), confirming the non-occurrence of intermediate complex formation during the course of the reaction [28]. Hence a reaction proceeding via an outer-sphere mechanistic pathway is implicated.

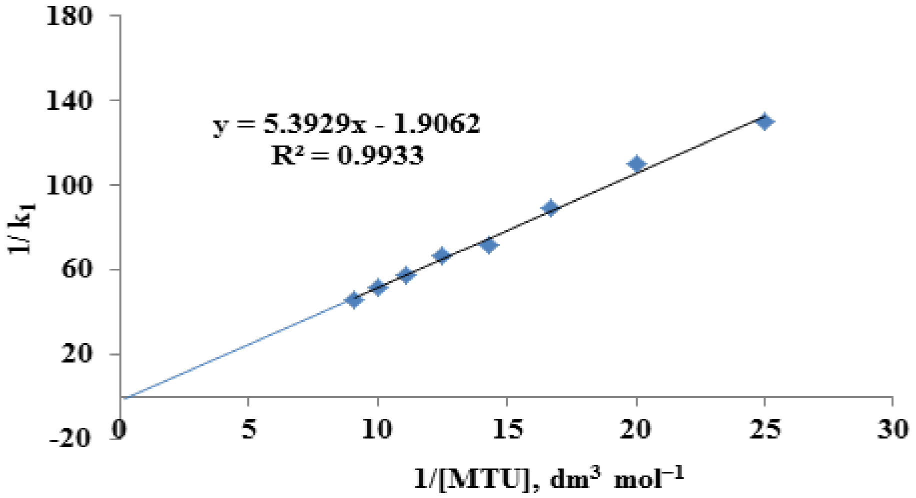

Figure 4:Plot of $1/k_1$ versus 1/ [MTU] for the Reaction of $[Co(phen)_3]^{3+}$ and MTU

Taking into account the under-listed shreds of evidence, the reduction of $[Co(phen)_3]^{3+}$by N-methylthiourea in aqueous HCl medium most probably occur by the outer-sphere mechanism;

1. The absence of an intercept in the Michaelis-Menten plot.
2. The catalysis and inhibition of reaction rate by added cations and anions respectively.
3. The absence of complex intermediates.
4. The positive $\Delta S^{\ddagger}$ value of 90.87 JK^{-1} mol^{-1}.

Mechanism of the reaction

$$\mathrm{RSH} + \mathrm{H^+} \xrightleftharpoons{K_{eq}} \mathrm{HRSH^+} \tag{4}$$

$$[\mathrm{Co(phen)_3}]^{3+} + \mathrm{RSH} \xrightleftharpoons[k_{-1}]{k_1} [(\mathrm{Co(phen)_3}]^{3+}, \mathrm{RSH}] \tag{5}$$

$$[(\mathrm{Co(phen)_3}]^{3+}, \mathrm{RSH}] \xrightarrow[\text{slow}]{k_2} (\mathrm{Co(phen)_3})^{2+} + \mathrm{RS}^* + \mathrm{H^+} \tag{6}$$

$$[\mathrm{Co(phen)_3}]^{3+} + \mathrm{HRSH^+} \xrightleftharpoons[k_{-3}]{k_3} [(\mathrm{Co(phen)_3}]^{3+}, \mathrm{HRSH^+}] \tag{7}$$

$$[(\mathrm{Co(phen)_3}]^{3+}, \mathrm{HRSH^+}] \xrightarrow[\text{slow}]{k_4} (\mathrm{Co(phen)_3})^{2+} + \mathrm{RS}^* + 2\mathrm{H^+} \tag{8}$$

$$\mathrm{RS}^* + \mathrm{RS}^* \xrightarrow[\text{fast}]{k_5} \mathrm{RSSR} \tag{9}$$

$$\text{Rate} = k_2\,[(\mathrm{Co(phen)_3})^{3+}, \mathrm{RSH^+}] + k_4\,[(\mathrm{Co(phen)_3})^{3+}, \mathrm{HRSH^+}] \tag{10}$$

We have it that;

$$[(\mathrm{Co(phen)_3})^{3+}, \mathrm{RSH^+}] = k_{-1}[(\mathrm{Co(phen)_3})^{3+}]\,[\mathrm{RSH}] \tag{11}$$

$$[(\mathrm{Co(phen)_3})^{3+}, \mathrm{HRSH^+}] = k_{-3}\,[(\mathrm{Co(phen)_3})^{3+}]\,[\mathrm{HRSH^+}] \tag{12}$$

$$[\mathrm{HRSH^+}] = K_{eq}\,[\mathrm{RSH}]\,[\mathrm{H^+}] \tag{13}$$

Substituting Equations (11), (12) and (13) into Equation (10), we get;

$$\text{Rate} = k_2k_{-1}[(\mathrm{Co(phen)_3})^{3+}]\,[\mathrm{RSH}] + k_4k_{-3}K_{eq}\,[\mathrm{H^+}][(\mathrm{Co(phen)_3})^{3+}]\,[\mathrm{RSH}] \tag{14}$$

Simplifying Equation (14) further, we have:

$$\text{Rate} = k_2k_{-1} + k_4k_{-3}K_{eq}\,[\mathrm{H^+}]\,[(\mathrm{Co(phen)_3})^{3+}][\mathrm{RSH}] \tag{15}$$

The rate law in Equation (15) can thus be written as;

$$\text{Rate} = b + a\,[\mathrm{H^+}]\,[(\mathrm{Co(phen)_3})^{3+}]\,[\mathrm{RSH}] \tag{16}$$

Equation (16) agrees with the experimental rate law in Equation (2), where $a = k_4k_{-3}K_{eq} = 2.65$ dm^6 mol^{-2} s^{-1} and $b = k_2k_{-1} = 3.72$ dm^3 mol^{-1} s^{-1}.

CONCLUSION

The reduction of Tris (1, 10-phenanthroline) cobalt (III) complex by N-methylthiourea was studied in aqueous hydrochloric acidic medium. Stoichiometric analysis gave a mole ratio of 1:1. Analysis of other kinetic data obtained under the pseudo-first order condition gave an overall second order; first order with respect to the concentrations of both the oxidant and the reductant. Effect of acid study showed a reaction proceeding via two routes of acid dependence and non-acid dependence. The mechanism of the reaction, based on the available kinetic and spectroscopic pieces of evidence was rationalized on the basis of an outersphere mechanism.

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