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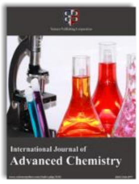

Electron transfer reaction of Tris(1,10-phenanthroline) cobalt(III) complex $[Co(phen)_3]^{3+}$ and thiosulphate ion ($S_2O_3^{2-}$) in an aqueous acidic medium

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Abstract

The electron transfer reaction of Tris (1,10-phenanthroline)cobalt(III) complex by thiosulphate ion has been studied in an aqueous acidic medium. Stoichiometric determination shows that for one mole of the oxidant that was reduced, one mole of the reductant was consumed; the reaction conforms to an overall equation:

$$2[Co(phen)_3]^{3+} + 2S_2O_3^{2-} \rightarrow 2[Co(phen)_3]^{2+} + S_4O_6^{2-}$$

Kinetics study carried out under pseudo-first order condition shows that the reaction proceeded via a one-way acid-dependent pathway and was third order overall; zero order with respect to the oxidant concentration, second order with respect to the reductant concentration and first order with respect to the hydrogen ion concentration. The empirical rate law conforms to the equation:

$$-\,{}^{d}\!/_{dt}\{Co(phen)_3\}^{3+}] = a\,[H^+]\,[S_2O_3^{2-}]^2$$

'a' = 128.26 $dm^6\ mol^{-2}\ s^{-1}$: at $[H^+] = 2.0 \times 10^{-2}$ mol dm^{-3}, $\mu = 0.4$ mol dm^{-3} (NaCl), T = 28 ± 1˚C and $\lambda_{max} = 495$ nm.
The rate of reaction increased at the increase in ionic strength and at the decrease in medium dielectric constant. Added cations and anions catalyzed and inhibited the reaction rates respectively. The Michaelis-Menten plot of $1/k_1$ versus $1/[S_2O_3^{2-}]^2$ started from the origin. Hence based on spectroscopic investigation, thermodynamic information from temperature dependence studies and kinetic evidence from Michaelis–Menten plots and the interactions with added ions, an outer-sphere mechanism has been rationalized for this reaction. The mechanistic scheme of the reaction was proposed via the stated mechanistic route.

Keywords: *Complex; Electron transfer; Kinetics; Thiosulphate ion; Tries (1-10-phenanthroline) cobalt (III).*

1. Introduction

Over the past few decades, the study of chemical kinetics and reaction mechanism of electron transfer reactions have found much relevance in modern chemistry because of its wide applicability. Since chemical kinetics deals with rates of chemical reaction, and of the factors upon which the rates depends (Santosh 2006); hence Inorganic chemists through kinetic studies seeks to examine these factors such as temperature, concentration, pressure, the effect of catalyst etc. and consequently explain how these factors affect the rate of reaction. The knowledge of the variation and effect of these factors on reaction rates can aid proper interpretation of stepwise elementary steps a reaction undertakes which constitute its mechanism (Asperger 2003). In view of this, Taube and co-workers based on experimental facts have successfully classified these reaction mechanisms into two broad mechanistic pathways thus: Inner-sphere and outer-sphere mechanism of electron transfer (Taube 1953). Kinetic studies have been previously carried out on several chemical and biological compounds but there has been growing interest towards transition metal complexes, this is because of the wide range of applications of metal complexes resulting from the peculiarity in the physical and chemical properties of transition metals that form such complexes. The metal complexes of diimine ligands such as 1,10-phenanthroline and 2,2'-bipyridine have received much research interest because of their versatile roles as building blocks in synthesis as well as their bioinorganic and biomedicinal applications (Wang et al. 2014, Ahmed & Khaled 2015, Gopinathan & Arumugham 2015, Molphy et al. 2015). Based still on the peculiarity of transition metal properties, metal complexes can either function as a reductant or an oxidant in an electron transfer reaction with other metal complexes or with other compounds, thus have attracted a lot of kinetic studies on them. Interestingly in spite of the numerous kinetic data on various metal complexes, kinetic study on them seems to persevere and has proven inexhaustible, this can only be attributed to the great potency of synthesising numerous metal complexes from different starting materials at different experimental conditions, and also the wide range of other available reducing and oxidizing agents. Hence this fact informed the step taken towards this kinetic study.

Electron transfer reactions of $[Co(phen)_3]^{3+}$ complex with thiosulphate ion was investigated in a low pH medium under the pseudo-first order conditions. Just as illustrated above, several factors such as; effect of temperature, effect of hydrogen ion concentration, effect of added ions, salt effect, and solvent effect among others will be considered and their influence in the rate of reaction will be ascertained. Kinetic data and thermodynamic information generated from the effect of these parameters on the reaction rate will guide rationalizing mechanistic pathway the reaction followed and consequently a plausible mechanistic scheme that will stand alongside other documented kinetic data will be deduced.

2. Materials and method

All reagents used were of analytical grade and was not purified further. Sodium thiosulphate was the reductant, 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 and methanol were used for the free radical test in the reaction. Standard glass wares (Pyrex) were used at all times, temperature was checked with a thermometer. Kinetic runs were done using a Corning Colorimeter 252 model, a Grant JB1 thermostated water bath was used for the temperature dependence studies and the rate of reaction was monitored with a digital stopwatch. The preparation of $[Co(phen)_3]^{3+}$ complex was done according to literature (Gaelle et al. 2016) involving the reaction of $CoCl_2.6H_2O$ and phenanthroline monohydrate in the mole ratio of 1:3 respectively. The UV-Visible characterization of the complex gave a λ_{max} of 495 nm. Standard solutions were prepared by weighing the known amount of the chemical and dissolving in a known volume of distilled water.

2.1. Stoichiometric determination

The stoichiometry, under the reaction condition $[\{Co(phen)_3\}^{3+}] = 4.0 \times 10^{-3}$ mol dm^{-3}, $[S_2O_3^{2-}] = (5.0$ to $60.0) \times 10^{-3}$ mol dm^{-3}, $[H^+] = 2.0 \times 10^{-2}$ mol dm^{-3}, $\mu = 0.10$ mol dm^{-3} and $T = 28 \pm 1.0$˚C was determined by spectrophotometric titration using the mole ratio approach. The reaction product was analysed classically and spectroscopically where possible.

2.2. Kinetic measurement

The rate of the reaction for the reduction of $[Co(phen)_3]^{3+}$ and the concomitant oxidation of $S_2O_3^{2-}$ was monitored following the rate of increase in absorbance of the reaction mixture at λ_{max} of 495 nm. All kinetic measurements were performed under pseudo-first order conditions with the reductants in at least 15 fold excess over those of the complexes (Table 1). The kinetic curves obtained under this condition were exponential and the rate constant was obtained from the logarithmic plot of ($\log A_\infty - A_t$) against time (t). Pseudo-first order rate constants were determined from the slopes of the plots, based on the following equation;

$$\text{Log}\,(A_\infty - A_t) = -\frac{k_1 t}{2.303} + \text{Log}\,(A_\infty - A_o) \qquad (1)$$

Where A_∞ = final absorbance, at = absorbance at time t, A_0 = Initial absorbance and k_1 = pseudo-first order rate constant as reported elsewhere (Onu et al. 2015, Ukoha et al. 2015).

The second order rate constant (k_2) was subsequently estimated from the relation: $k_2 = k_1/[S_2O_3^{2-}]^n$, where 'n' = reaction order with respect to the reductant. The influence of $[H^+]$ $(0.70 - 5.00) \times 10^{-2}$ mol dm^{-3} and ionic strength, 0.20 – 0.80 mol dm^{-3} using NaCl was investigated for the reaction. 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 formation of free radical intermediates was detected by monitoring gel formation by acrylamide in partially reacted reaction mixture in excess methanol (Onu et al. 2015).

2.3. Thermodynamic studies

The temperatures were varied across (311 – 341) K. All other experimental conditions were maintained, and a plot of ln(k/T) versus 1/T gave a slope and an intercept from which thermodynamic parameters like activation enthalpy and entropy will be estimated and how their results determine the mechanism of the reaction will also be ascertained (Ukoha et al. 2015).

2.4. Product analysis

Completely reacted solution was analysed classically and spectroscopically where possible for the type of product(s) that will be formed. Qualitative analysis using potassium thiocyanate (KSCN) according to the method developed by Hahn and Welcher (1963) was carried out to determine if Co^{2+} ions were present in the product mixtures, Addition of mercury(I)nitrate to the reaction mixture was used to ascertain the formation of tetrathionate ion (Patil et al. 2009). Furthermore, spectrophotometric analysis of the Co(II) complex products was carried out using a UV-visible spectrophotometer by determining the λ_{max} of the post-reaction mixture to see if it matches to that expected for Cobalt(II) complexes of 1,10-phenanthroline..

3. Results and discussion

3.1. Stoichiometry

Spectrophotometric titration showed that one mole of reduced $[Co(phen)_3]^{3+}$ was consumed per mole of $S_2O_3^{2-}$ oxidized implying that a one-electron transfer process takes place at the rate determining step. This is illustrated in equation (2) below:

$$[Co(phen)_3]^{3+} + S_2O_3^{2-} \rightarrow [Co(phen)_3]^{2+} + S_2O_3 \qquad (2)$$

The $S_2O_3^-$ readily dimerizes to $S_4O_6^{2-}$ a tetrathionate ion (Patil et al. 2009), thus leading to the general equation of the reaction as presented in equation (3). The reaction process agrees with other reactions of $S_2O_3^{2-}$ from previous literature (Byerley et al. 1973, Patil et al. 2009, Mohammed 2015).

$$2[Co(phen)_3]^{3+} + 2S_2O_3^{2-} \rightarrow 2[Co(phen)_3]^{2+} + S_4O_6^{2} \qquad (3)$$

In support of the result from stoichiometric study, evidence from spectroscopic products analysis of the reaction mixture showed an increase in the λ_{max} from 495 nm to 600 nm, implying actual reduction of the $[Co(phen)_3]^{3+}$ to $[Co(phen)_3]^{2+}$, classical product analysis with KSCN carried out on the product to confirm the actual reduction from Co(III) to Co(II) complex was successful as blue colouration was detected. The formation of tetrathionate ion as a product was also ascertained from the yellow precipitate produced when mercury(I)acetate was added to the reaction mixture and which becomes black on heating (Patil et al. 2009).

3.2. Kinetic study

The $[Co(phen)_3]^{3+} - (S_2O_3^{2-})$ reaction was zero order with respect to the $[\{Co(phen)_3\}^{3+}]$ complex and second order with respect to $[S_2O_3^{2-}]$, thus a second order overall. The evidence for zero order dependence on the $[\{Co(phen)_3\}^{3+}]$ was ascertained from the pseudo-first order plot of log (A_∞ - A_t) against time that was non-linear (fig 1), the constancy of k_2 values at different concentrations of $[Co(phen)_3]^{3+}$ as depicted in Table (1), coupled with the linearity of the integrated rate plot of [A_∞ - A_t] versus time for zero order reactions (fig 2). In the same vein, the second order rationalized on $[S_2O_3^{2-}]$ was evidenced by the plot of log k_{obs} versus log $[S_2O_3^{2-}]$ that gave a slope of 2.02 (Fig 3). Similar result with respect to $S_2O_3^{2-}$ has been previously reported (Dennis et al. 1985). The constancy of k_2 values obtained from $\frac{k_{obs}}{[S_2O_3^{2-}]^2}$ further confirms the second order with respect to $S_2O_3^{2-}$ (Table 1).

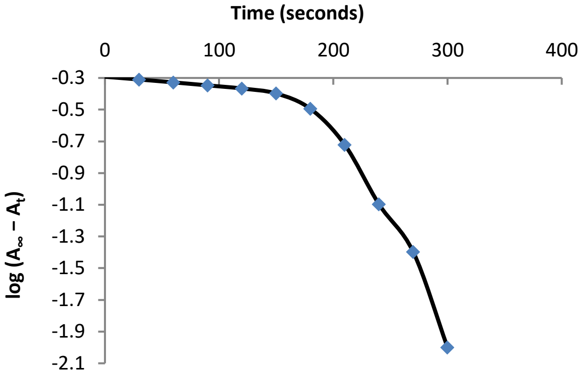

Fig. 1: Pseudo-First Order Plot.

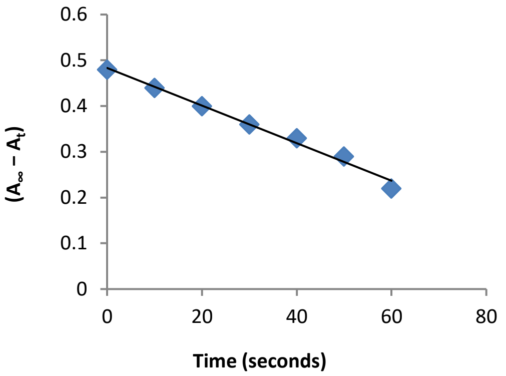

Fig. 2: Plot of (A∞ − At) Against Time

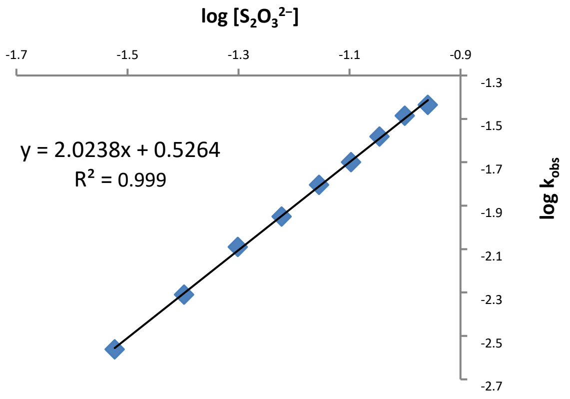

Fig. 3: Plot of Log k_{obs} versus Log $[S_2O_3^{2-}]$.

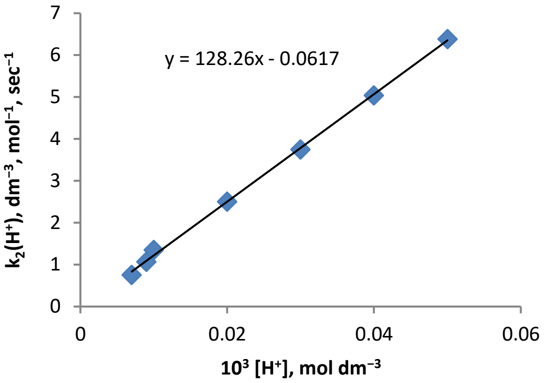

Fig. 4: Plot of $k_2(H^+)$ versus $[H^+]$

3.3. Acid dependence studies

Results obtained from the acid dependence study showed a marked increase in the rate of reaction with an increase in $[H^+]$ as seen in Table (1). This result agrees with acid dependence studies on $S_2O_3^{2-}$ oxidation previously reported (Dennis et al. 1985, Patil et al. 2009, Mohammed 2015), implicating the protonation of $S_2O_3^{2-}$ to its reactive species, $HS_2O_3^-$ (Dereven'kov et al. 2013) as depicted in equation (4). The participation of both thiosulpuric acid ($HS_2O_3^-$) and thiosulphate ion ($S_2O_3^{2-}$) in the reduction process as shown in equations (5) indicates a reaction where the $S_2O_3^{2-}$ was not completely protonated (Goyal et al. 1995); hence both the $HS_2O_3^-$ and the unprotonated $S_2O_3^{2-}$ species were active in the reaction mechanism. Furthermore, the acid dependence plot of k_2 versus $[H^+]$ started from the origin as shown in figure (4), implicating a reaction process occurring via a single acid dependent pathway (Mshelia et al. 2010; Onu et al. 2015), thus the forward reaction in an equilibrium association of these active species becomes the rate determining step of the reaction in which an ion associate is formed (Equation 5). The concentration of the complex assuming a zero order with respect to the reaction, $S_2O_3^{2-}$ assuming a second order and the $[H^+]$ taking up a first order was as a result of the equilibrium association of these species. Subsequent reactions that occurred including the backward reaction in equation (5) took place in a series of fast steps as shown below in the reaction mechanism.

$$S_2O_3^{2-} + H^+ \xrightleftharpoons{K_{eq}} HS_2O_3^- \tag{4}$$

$$HS_2O_3^- + S_2O_3^{2-} \xrightleftharpoons[k_{-1}]{k_1\text{ (slow)}} [HS_2O_3.S_2O_3]^{3-} \tag{5}$$

Thus, this result of acid dependence on rate is in agreement with equation (6)

$$-\,{}^{d}\!/_{dt}[\{Co(phen)_3\}^{3+}] = a\,[H^+]\,[S_2O_3^{2-}]^2 \tag{6}$$

Where slope = 'a' = 128.26 $dm^6\,mol^{-2}\,s^{-1}$

Table 1: Observed Order and Second Order Rate Constants for the Reaction of $[Co(phen)_3]^{3+}$ and Thiosulphate Ion ($S_2O_3^{2-}$) At T = 28 ± 1˚C and λ_{max} = 495 nm.

10^3 $[Co(phen)_3]^{3+}$ mol dm^{-3}	10^2 [$S_2O_3^{2-}$], mol dm^{-3}	10^2 [H^+] mol dm^{-3}	[I] mol dm^{-3}	10^3 k_{obs}, s^{-1}	k_2 dm^3 mol^{-1} s^{-1}
1.00	7.00	2.00	0.40	15.80	3.22
2.00	7.00	2.00	0.40	15.77	3.22
3.00	7.00	2.00	0.40	15.65	3.19
4.00	7.00	2.00	0.40	15.59	3.18
5.00	7.00	2.00	0.40	15.56	3.18
2.00	3.00	2.00	0.40	2.74	3.05
2.00	4.00	2.00	0.40	4.90	3.06
2.00	5.00	2.00	0.40	8.13	3.25
2.00	6.00	2.00	0.40	11.22	3.12
2.00	7.00	2.00	0.40	15.72	3.21
2.00	8.00	2.00	0.40	19.96	3.12
2.00	9.00	2.00	0.40	26.2	3.23
2.00	10.00	2.00	0.40	32.74	3.27
2.00	11.00	2.00	0.40	36.69	3.03
2.00	7.00	0.70	0.40	3.69	0.75
2.00	7.00	0.90	0.40	5.25	1.07
2.00	7.00	1.00	0.40	6.63	1.35
2.00	7.00	2.00	0.40	12.28	2.51
2.00	7.00	3.00	0.40	18.39	3.75
2.00	7.00	4.00	0.40	24.69	5.04
2.00	7.00	5.00	0.40	31.27	6.38
2.00	7.00	2.00	0.20	0.66	1.35
2.00	7.00	2.00	0.30	1.16	2.36
2.00	7.00	2.00	0.40	1.58	3.22
2.00	7.00	2.00	0.50	2.28	4.65
2.00	7.00	2.00	0.60	3.22	6.57
2.00	7.00	2.00	0.70	4.07	8.31
2.00	7.00	2.00	0.80	5.53	11.28

3.4. Effect of changes in ionic strength and dielectric constant of the medium

Study on the effect of changes in the ionic strength of the reaction medium using an inert salt (NaCl) led to an increase in the rate of reaction as the ionic strength increased (Table 1). Based on the Debye-Hückel equation for the reaction of ions in solution (Equation 7), Least square plot of log k_2 versus $\sqrt{\mu}$ was linear with a slope of 2.02 (Fig 5). This suggests a positive salt effect at the rate determining step where there is an interaction between two like charges (Equation 5). By varying the dielectric constant, D, of the reaction medium from 80.1 – 70.1 using $(CH_3)_2CO$-H_2O mixture, it was observed that the reaction rate increased with a decrease in D (Table 2, Fig 6). This suggests that the unlike charges were reacting in the rate-determining step, confirming the suggestion made earlier on the observation of the effect of change of ionic strength of reaction medium on rate. Conformity of the result of the variation of ionic strength with that due to effect of varying D could suggest one route for the reaction (Gupta & Gupta 1970).

$$\text{Log } k = \log k_o + 1.02\, Z_A Z_B \mu^{1/2} \qquad (7)$$

Where k = rate constant of the Equation, k_o = hypothetical rate constant in a medium of infinite dielectric constant, Z_A, Z_B = charges on reactants A and B respectively, μ = ionic strength. The plot of log k versus $\sqrt{\mu}$ would be linear with slope $1.02Z_aZ_b$ (at 25˚C) and log k_o as the intercept.

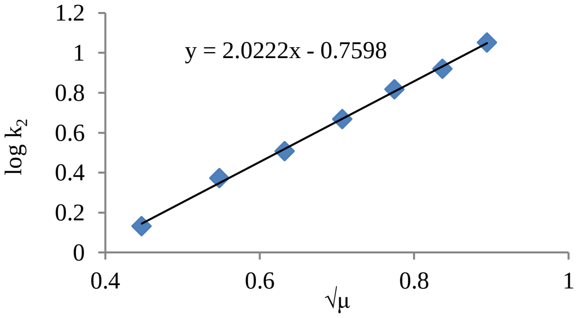

Fig. 5: Plot of Log K2 Versus √M.

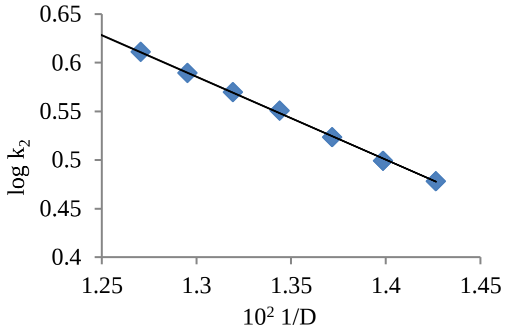

Fig 6: Plot of Log K_2 versus 1/D.

Table 2: Effect of Changes in Dielectric Constant of Reaction Medium for the Reaction of $[Co(phen)_3]^{3+}$ and Thiosulphate Ion ($S_2O_3^{2-}$) at $[Co(phen)_3]^{3+}$ = 2.0 × 10^{-3} mol dm^{-3}, $[S_2O_3^{2-}]$ = 7.0 × 10^{-2} mol dm^{-3}, $[H^+]$ = 2.0 × 10^{-2} mol dm^{-3}, I = 0.4 mol dm^{-3} (NaCl), D = (80.1 – 70.1), 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	1.25	1.47	3.01
78.7	1.27	1.55	3.16
77.2	1.30	1.64	3.34
75.8	1.32	1.74	3.56
74.4	1.34	1.82	3.72
72.9	1.37	1.90	3.89
71.5	1.40	2.00	4.09
70.1	1.43	2.08	4.25

3.5. Effect of added ions and temperature on the rate and mechanism of the reaction

Added cations (Mg^{2+} and NH_4^-) led to increasing in rates of reaction (Table 3) while added anions (CH_3COO^- and $HCOO^-$) led to decrease in rates (Table 4). The cation catalysis and anion inhibition observed has been associated with outer-sphere electron transfer process (Pryztas & Sutin 1973).

Table 3: Effect of Added Cations to Reaction Medium for the Reaction of $[Co(phen)_3]^{3+}$ and Thiosulphate ion ($S_2O_3^{2-}$) at $[Co(phen)_3]^{3+}$ = 2.0 × 10^{-3} mol dm^{-3}, $[S_2O_3^{2-}]$ = 7.0 × 10^{-2} mol dm^{-3}, $[H^+]$ = 2.0 × 10^{-2} mol dm^{-3}, I = 0.4 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+}	1.00	1.73	3.71
	10.00	1.81	3.76
	30.00	1.84	3.82
	50.00	1.87	3.89
	70.00	1.92	3.98
	100.00	1.96	4.05
	140.00	1.98	4.18
NH_3^+	1.00	1.65	3.36
	10.00	1.70	3.48
	30.00	1.73	3.62
	50.00	1.81	3.70
	70.00	1.91	3.90
	100.00	1.99	4.06
	140.00	2.12	4.32

Table 4: Effect of Added Anions to Reaction Medium for the Reaction of $[Co(phen)_3]^{3+}$ and Thiosulphate Ion ($S_2O_3^{2-}$) at $[Co(phen)_3]^{3+}$ = 2.0 × 10^{-3} mol dm^{-3}, $[S_2O_3^{2-}]$ = 7.0 × 10^{-2} mol dm^{-3}, $[H^+]$ = 2.0 × 10^{-2} mol dm^{-3}, I = 0.4 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}
CH_3COO^-	0.00	1.97	4.02

	1.00	1.66	3.39
	3.00	1.45	2.95
	5.00	1.11	2.27
	7.00	1.01	2.07
	10.00	0.68	1.38
	15.00	0.24	0.48
$HCOO^-$	1.00	1.97	4.02
	10.00	1.63	3.32
	30.00	1.33	2.72
	50.00	1.18	2.41
	70.00	0.96	1.97
	100.00	0.72	1.48
	140.00	0.37	0.77

The rate of the reaction was greatly catalysed by a corresponding increase in temperature (Fig 7, Table 5). The values of the activation parameters obtained from temperature dependence study of the reaction just as reported for added ions support the rationalization of an outer-sphere route for this reaction where $\Delta S^{\ddagger} = 68.51$ JK^{-1} mol^{-1} and $\Delta H^{\ddagger} = 115.49$ KJ/mol. A positive value of entropy of activation (high entropy) implies a reaction where species at the activated complex are loosely held together (James, 2002). Similar activation parameters have been obtained from past studies on other forms of Co (III) complexes (Asemave et al. 2012).

Table 5: Pseudo–First Order and Second Order Rate Constants for the Effect of Change in Temperature for the Reaction of $[Co(phen)_3]^{3+}$ and Thiosulphate Ion ($S_2O_3^{2-}$) At $[Co(phen)_3]^{3+} = 2.0 \times 10^{-3}$ mol dm^{-3}, $[S_2O_3^{2-}] = 3.0 \times 10^{-2}$ mol dm^{-3}, $[H^+] = 2.0 \times 10^{-2}$ mol dm^{-3}, I = 0.4 mol dm^{-3} (NaCl), T = 28 ± 1°C and λ_{max} = 560 nm.

Temperature K	$10^2\,[S_2O_3^{2-}]$ mol dm^{-3}	$10^2\,[H^+]$ mol dm^{-3}	[I] mol dm^{-3}	10^3 k_{obs} s^{-1}	k_2 dm^{-3} mol^{-1} s^{-1}
311	3.00	2.00	0.40	0.94	0.19
326	3.00	2.00	0.40	8.56	1.75
336	3.00	2.00	0.40	29.80	6.08
341	3.00	2.00	0.40	51.75	10.56

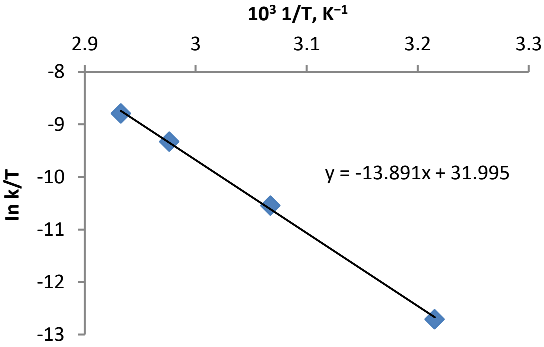

Fig. 7: The Plot of Ln(K/T) versus $1/T$.

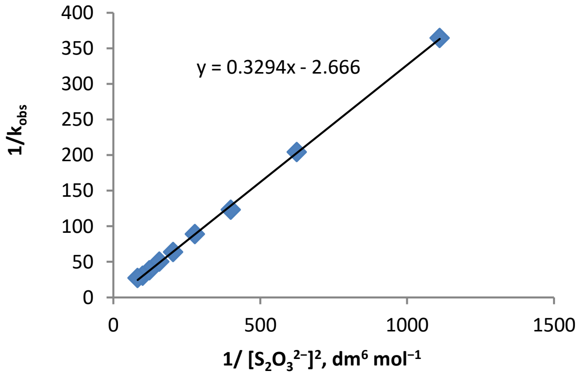

Fig. 8: Plot of 1/ k_{obs} versus 1/ $[S_2O_3^{2-}]^2$

Spectroscopic study for the presence or absence of intermediate in the reaction scheme indicated a shift from the absorption maxima of 495 nm to 600 nm suggesting the formation of intermediate complexes prior to electron transfer. However, Michaelis-Menten plot of $1/k_1$ versus $1/[S_2O_3^{2-}]^2$ was linear without any appreciable intercept (Fig 8). This implies the absence of stable intermediates with large enough formation constants. This fact supports the suggestion of outer-sphere mechanistic pathway as the route for $[Co(phen)_3]^{3+}$–($S_2O_3^{2-}$) reaction.

A polymerisation was not induced on the addition of acrylamide to the reaction mixture followed by excess methanol 1 minute, 2 minutes and 3 minutes after onset of reaction. This suggests that free radicals were not produced in the $[Co(phen)_3]^{3+}$–($S_2O_3^{2-}$) reaction. This agrees with the lack of free radical participation in the reaction of Ru_2O^{4+} and $S_2O_3^{2-}$ (Mohammed 2015).

3.6. Mechanism of the reaction

Summarily an outer-sphere mechanism is proposed for this reaction, guided by the following evidence:

1) The non-appreciable negative intercept of the Michaelis-Menten's plot.
2) The catalysis and inhibition of added cations and anions respectively.
3) The absence of complex intermediate of large formation constant.
4) The high entropy of the system where $\Delta S^{\ddagger}$ is 68.51 JK^{-1} mol^{-1}.

Based on the above findings, the following mechanistic scheme is proposed for the reduction of $[Co(phen)_3]^{3+}$ by $S_2O_3^{2-}$ in acidic medium:

$$S_2O_3^{2-} + H^+ \underset{}{\overset{K_{eq}}{\rightleftharpoons}} HS_2O_3^- \qquad (8)$$

$$HS_2O_3^- + S_2O_3^{2-} \underset{k_{-1}}{\overset{k_1\ (slow)}{\rightleftharpoons}} [HS_2O_3.S_2O_3]^{3-} \qquad (9)$$

$$[HS_2O_3.S_2O_3]^{3-} + 2[Co(phen)_3]^{3+} \xrightarrow[fast]{k_2} 2[Co(phen)_3]^{2+} + 2S_2O_3^- + H^+ \qquad (10)$$

$$2S_2O_3^- \xrightarrow[fast]{k_3} S_4O_6^{2-} \qquad (11)$$

$$Rate = k_1\,[HS_2O_3^-]\,[S_2O_3^{2-}] \qquad (12)$$

$[HS_2O_3^-]$ is the protonated active species that is produced at the equilibrium step in Equation 8, we have it that;

$$K_{eq} = \frac{[HS_2O_3^-]}{[S_2O_3^{2-}]\,[H^+]} \qquad (13)$$

$$[HS_2O_3^-] = K_{eq}\,[S_2O_3^{2-}]\,[H^+] \qquad (14)$$

Substituting Equation (14) into Equation (12), we get;

$$Rate = k_1K_{eq}\,[H^+]\,[S_2O_3^{2-}]^2 \qquad (15)$$

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

$$Rate = a\,[H^+]\,[S_2O_3^{2-}]^2 \qquad (16)$$

Equation (16) corresponds to the experimental rate law in Equation (6), where $a = k_1K_{eq} = 128.26$ dm^6 mol^{-2} s^{-1}.

4. Conclusion

The Electron transfer reaction of Tris (1,10-Phenanthroline)Cobalt(III) complex and Thiosulphate ion was studied in an aqueous Hydrochloric Acidic medium. A mole ratio of 1:1 was obtained. Analysis of other kinetic data obtained under the pseudo-first order condition gave an overall third order; zero order with respect to the concentration of the oxidant, second order with respect to the concentration of the reductant and first order with respect to the hydrogen ion concentration. Based on the evidence obtained in the study, an outersphere mechanism has been rationalized for the reaction and a plausible mechanistic scheme which explains the kinetic data obtained was proposed.

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