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Research Article

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Reduction of tris(2,2'-bipyridine)cobalt(III) complex by thiosulphate ion in an aqueous acidic medium

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Abstract

The reduction of tris(2,2'-bipyridine)cobalt(III) complex by thiosulphate ion in an aqueous acidic medium gave a notable outcome. The stoichiometric evaluation indicates that one mole of the reducing agent has been consumed by one mole of the oxidant, and the reaction complies with an overall equation:



The kinetics study conducted under a pseudo-first-order method shows that the rate of the reaction was acid-reliant and third-order overall; zero-order in the [oxidant], second-order in the [reductant], and first-order in the hydrogen ion concentration. The empirical rate expression complies with the equation:

$$-\frac{d}{dt} [\text{Co}(\text{bpy})_3^{3+}] = a [\text{H}^+][\text{S}_2\text{O}_3^{2-}]^2$$

'a' = 77.82 dm⁶ mol⁻² s⁻¹; at [H⁺] = 2.0 × 10⁻² mol dm⁻³, μ = 0.4 mol dm⁻³ (NaCl), T = 28 ± 1°C and λ_{max} = 560 nm.

With increased ionic strength and decreased medium dielectric constant, the reaction rate increased. The inclusion of cations and anions accelerate and constricted the reaction rates respectively. Spectroscopic examination and kinetic evidence indicate an outer sphere mechanism, and the mechanism was therefore proposed via an outer-sphere route.

Keyword: Kinetics, Reduction, Tris(2,2'-bipyridine)cobalt(III), Thiosulphate ion, Mechanism

1. Introduction

Thiosulphate ion ($S_2O_3^{2-}$) an oxyanion of sulphur, is a moderately strong reducing agent, that has a wide range of applications such as: fixing photographic images, extracting silver from their ore, a promising antidote for cyanide poisoning, a mordant in the dye industry for determining oxidizing agents by an indirect procedure that involves iodine as intermediate among others [1]. Tetrathionate ($S_4O_6^{2-}$) ions can be produced from the oxidation of thiosulphate (SO_4^{2-}) ions by mild oxidants such as iodine and iron(III) in a neutral aqueous medium, while stronger oxidizing agents like bromine and chlorine produce sulphate ions. However, with H_2O_2 , both SO_4^{2-} and $S_4O_6^{2-}$ ions are formed. Oxidation by iodine in an alkaline medium yields SO_4^{2-} ions and the ratio of SO_4^{2-} to $S_4O_6^{2-}$ increases with the increasing negative logarithm of hydrogen ion of the reaction medium [2]. Hence, the oxidation product of $S_2O_3^{2-}$ ions is determined by two influences: the redox potential of the oxidant, and the reaction medium's pH [3].

Osunkwo *et al.* [4] reported a third order overall in the reaction of tris-(1,10-phenanthroline)cobalt(III) complex with $S_2O_3^{2-}$ ion; zero-order in the [oxidant], second-order in the [reductant], and first-order in the $[H^+]$. The empirical rate law is the same as:

$$- \frac{d[Co^{III}(phen)_3^{3+}]}{dt} = k[H^+][S_2O_3^{2-}]^2$$

Dennis *et al.* [3] documented a zero-order with respect to $[W(CN)_8^{3-}]$ for the reaction of thiosulphate with octacyanotungstate(V) ions, and a notable second-order in $[S_2O_3^{2-}]$ with a rate law:

$$- \frac{d[W(CN)_8^{3-}]}{dt} = k[H^+][S_2O_3^{2-}]^2$$

Similarly, the work reported by Sandved and Holte on the reaction of thiosulphate ions with $[Fe(CN)_8]^{3-}$ ions was zero-order with the complex concentration [5]. The rate law was presented thus:

$$- \frac{d[Fe(CN)_8^{3-}]}{dt} = k[H^+][S_2O_3^{2-}]^2$$

The rate expression for the reaction of octacyanomolybdate(V) ion with $S_2O_3^{2-}$ ion in a weakly acidic medium [6] has been reported:

$$- \frac{d[Mo(CN)_8^{3-}]}{dt} = k[Mo(CN)_8^{3-}][S_2O_3^{2-}][M^+]$$

Taking into account the above results, this paper presents kinetic data on the kinetic study of the reduction of tris-(2,2-bipyridine)cobalt(III) by thiosulphate ion in a strong acidic media in order to provide more information on the reactivity of complexes with thiosulphate ions.

2.0 Materials and Methods

$[Co(bpy)_3]^{3+}$ complex was prepared using the method of Gaëlle *et al.* [7]. 1.19 g (5.0×10^{-3} moles) of $Co(H_2O)_6Cl_2$ was dissolved in 70 cm³ of water in a beaker, a separate beaker containing 20 cm³ of methanol was added 2.44 g (15.0×10^{-3} moles) of 2,2'-bipyridine. The first solution was then added to the second solution in the beaker, 10 cm³ of H_2O_2 was then added to oxidise the Co(II) to Co(III). The solution was then boiled for *ca* half an hour and refilled into a 100 cm³ flask to obtain a 0.05 molar concentration. The complex was characterised by its λ_{max} of 560 nm.

A known concentration solution of hydrochloric acid (Sigma Aldrich) was prepared by diluting concentrated hydrochloric acid (70%, specific gravity 1.67 g/cm³) by means of distilled water. The solution was standardised titrimetrically using sodium carbonate as the primary standard and phenolphthalein indicator. A 1.37 molar concentration stock solution of NaCl was prepared from sodium chloride with a molecular weight of 58.5 g mol⁻¹. 20.0 g of NaCl was dissolved in a 100 cm³ volumetric flask and topped up to the mark with freshly prepared distilled H₂O. A 0.5 mol dm⁻³ stock solution of Na₂S₂O₃ was prepared from sodium thiosulphate (May and Baker, Analar grade, 99%) with a molecular weight of 158.11 g mol⁻¹. 7.91 gram of Na₂S₂O₃ was dissolved in a 100 cm³ volumetric flask and made up to the mark with distilled H₂O. Also, the preparation of stock solutions of ammonium chloride and sodium formate was done by dissolving a known amount with distilled H₂O.

2.1 Stoichiometric studies

The spectrophotometric titration was used in the determination of mole ratio of the redox partner at a constant [Co(bpy)₃³⁺], [H⁺], temperature, and ionic strength while varying [S₂O₃²⁻] from 5.0 × 10⁻³ to 60.0 × 10⁻³ mol dm⁻³. A plot of absorbance (A_∞) versus the mole ratio of the redox partner was made, and the point of inflexion in the plot indicates the mole ratio of the reactants [8-12].

2.2 Kinetic measurements

The increase in absorbance of the reaction mixture was observed for the determination of the reaction rate at 560 nm maximum absorption on a Corning Colorimeter 252 model. A 10-fold excess of reductant over the [Co(bpy)₃³⁺] was used for the kinetic determination (Table 1). The graphs of log (A_∞-A_t) against time were used to ascertain the order of [Co(bpy)₃³⁺], and the order of [S₂O₃²⁻] from the logarithm plot of k_{obs} versus [S₂O₃²⁻].

The influence of [H⁺] (10.0 – 70.0) × 10⁻² mol dm⁻³ and ionic strength, 0.20 – 0.70 mol dm⁻³ using NaCl was studied for the reaction [4,8,9,10]. The influence of the addition of NH₄⁺ and HCOO⁻ ions on the reaction mixture while keeping other reaction participants constant was studied.

The examination of participation of free radical was done by the addition of 0.2 cm³ of acrylamide solution to an incompletely reacted mixture and excess methanol.

2.3 Reaction's Temperature Study

The reaction medium temperature was varied across (301 – 341) K, and other conditions were fixed. Using Eyring Polanyi equation (Equation 1), the plot of ln(k₂/T) versus 1/T, and the activation parameters were evaluated from the slopes and the intercept [12].

$$\ln(k_2/T) = -\Delta H^\ddagger/RT + \ln(k_b/h) + \Delta S^\ddagger/R \quad (1)$$

2.4 Intermediate Specie Investigation

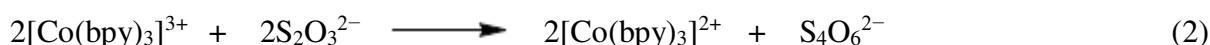
A wavelength range of 400 to 700 nm was used for the scanning of the reaction mixture to check the presence of measurable intermediate. Also, Michaelis-Menten's plot of reciprocal of k_{obs} and [reductant]² was made.

2.5 Analysis of Products

The products formed were examined classically and spectroscopically. The possible formation of Co^{2+} ion was investigated by making use of KCN based on Hahn and Welcher (1963) method [13], and the tetrathionate ion was by the use of excess mercury(I) nitrate [3]. The spectroscopic determination of Co^{2+} ion was done by using an ultraviolet–visible spectrophotometer to obtain the λ_{max} of the post-reaction mixture.

3.0 Results and Discussion

The result obtained from stoichiometric studies on the redox reaction of $[\text{Co}(\text{bpy})_3]^{3+}$ and $\text{S}_2\text{O}_3^{2-}$ shows that one mole of the oxidant was consumed by one mole of the reductant. The overall equation of the reaction is represented as;



Analogous stoichiometry of this nature has been documented by the reaction of thiosulphate ion with hexacyanoferrate(III) ion [1], tris-(1,10-phenanthroline)cobalt(III) complex [4], copper ions [14], and oxo-bridged ruthenium dimer (Ru_2O^{4+}) [15]. In support of the stoichiometry, the absorption maxima displayed a peak at 505 nm, a blue colouration is formed on the addition of KCN to the product mixture [13], and adding Mercury(I) nitrate to the reacted solution produced a yellow precipitate which turns black on heating [3], all indicating the actual reduction to Co^{2+} and the presence of tetrathionate ion respectively.

The $[\text{Co}(\text{bpy})_3]^{3+} - \text{S}_2\text{O}_3^{2-}$ reaction was zero-order with respect to the $[\text{Co}(\text{bpy})_3]^{3+}$ complex and second-order with respect to $[\text{S}_2\text{O}_3^{2-}]$, thus a second order overall. The evidence for zero-order dependence on the $[\text{Co}(\text{bpy})_3]^{3+}$ was ascertained from a non-linear pseudo-first-order plot of $\log(A_\infty - A_t)$ against time (Fig. 1). The curve of A against time gave a linear graph (Fig. 2), and the steadiness of k_2 values at different $[\text{Co}(\text{bpy})_3]^{3+}$ as represented in Table 1 further confirms the zero-order. However, the graph of $\log k_{\text{obs}}$ against $\log [\text{S}_2\text{O}_3^{2-}]$ with a gradient of 2.02 (Fig. 3) was rationalised second-order on $[\text{S}_2\text{O}_3^{2-}]$. An analogous outcome with respect to $\text{S}_2\text{O}_3^{2-}$ has been reported earlier for other reactions [3,4,5].

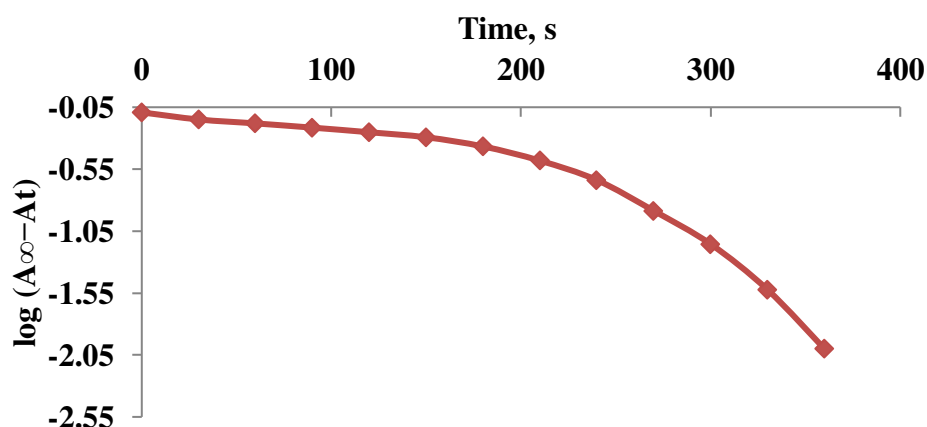


Fig. 1: Pseudo-first order plot for the $[\text{Co}(\text{bpy})_3]^{3+} - \text{S}_2\text{O}_3^{2-}$ reaction

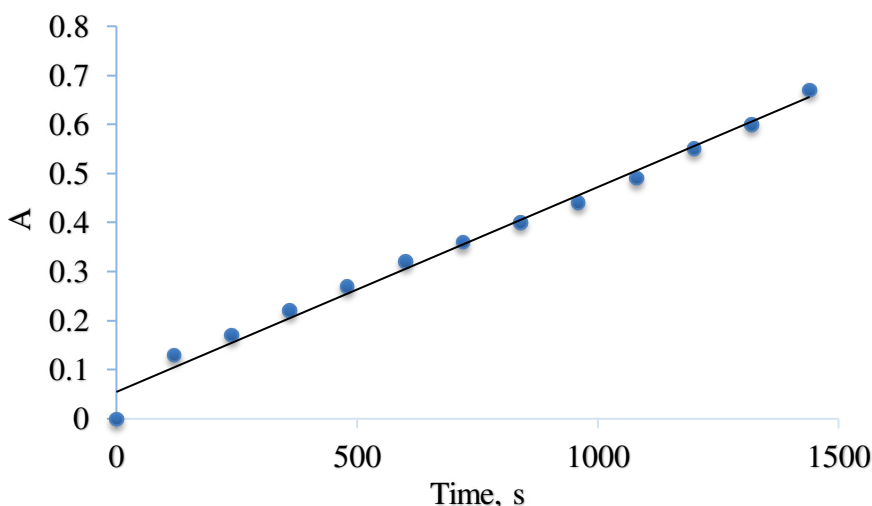


Fig. 2: Plot of A against time

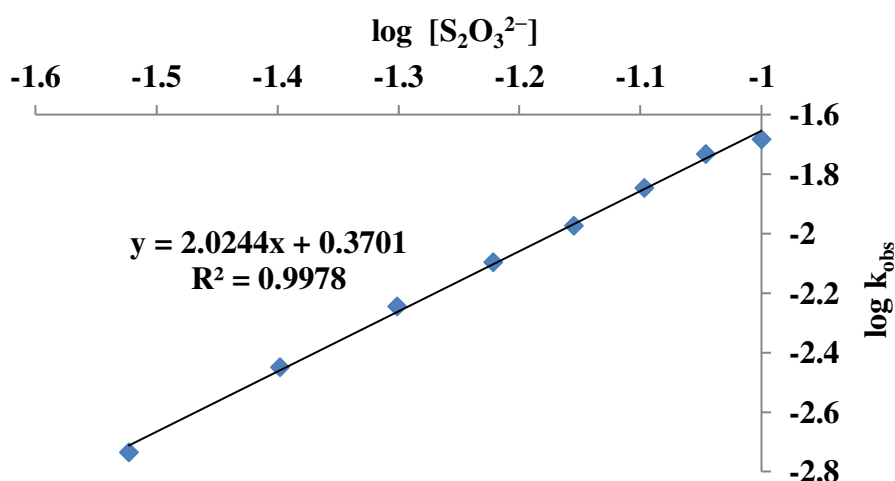


Fig. 3: Plot of $\log k_{\text{obs}}$ against $\log [\text{S}_2\text{O}_3^{2-}]$ for the $[\text{Co}(\text{bpy})_3]^{3+}$ and $\text{S}_2\text{O}_3^{2-}$ reaction

A marked increase in the rate of reaction with $[\text{H}^+]$ (Table 1) implies the protonation of $\text{S}_2\text{O}_3^{2-}$ to another reactive species, HS_2O_3^- and the probable participation of both HS_2O_3^- and $\text{S}_2\text{O}_3^{2-}$ in the reduction process (Equations 3 and 4) [15]. The acid dependence plot of k_2 versus $[\text{H}^+]$ starts from the origin (Fig. 4), and therefore signifies that the reaction occurs via a single acid dependence pathway [15,16,17], its slope of 0.78 infers a first-order dependence on the [acid] [18].

The increase in the rate of reaction was possible as the ionic strength was varied (Table 1), and a slope of 1.80 was obtained from the curve of $\log k_2$ versus $\sqrt{\mu}$ (Fig. 5) which suggests that the product of the charges on the reactants at the slow step is 1.80, and the positive value suggesting that the interaction is between like charges [18-20]. The differing magnitude of the slope as against 2.04 which is the expected value according to the linear equation $\log k = \log k_o + 1.02 Z_a Z_b \mu^{1/2}$ could be a result of interferences by other ions. The decrease in dielectric constant resulted in a marked rise in the observed rate (Table 2), the outcome is uncommon with reaction in an aqueous acidified solution.

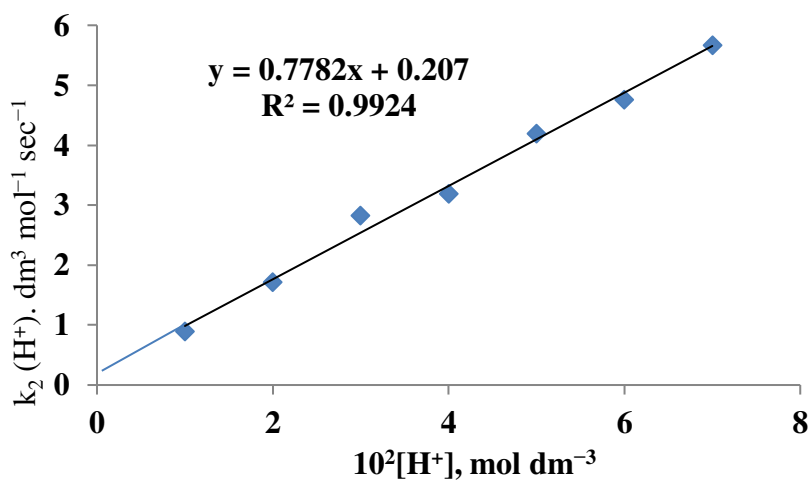


Fig. 4: Plot of $k_2 (\text{H}^+)$ against $[\text{H}^+]$ for the Reaction of $[\text{Co}(\text{bpy})_3]^{3+}$ and $\text{S}_2\text{O}_3^{2-}$

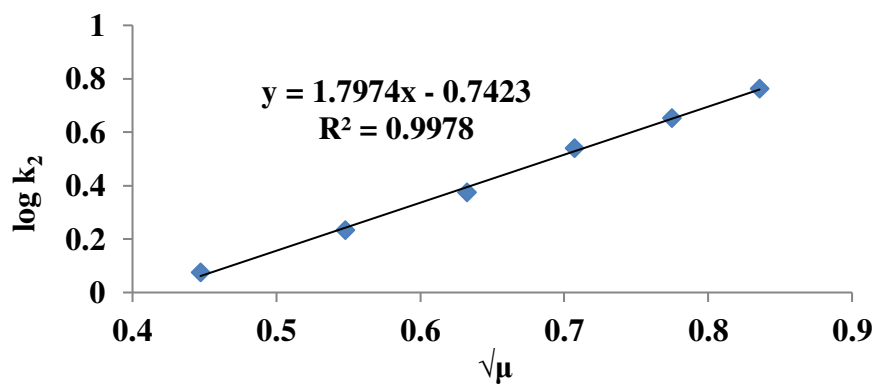


Fig. 5: graph of $\log k_2$ versus $\sqrt{\mu}$ for the Reaction of $[\text{Co}(\text{bpy})_3]^{3+}$ and $\text{S}_2\text{O}_3^{2-}$

Table 1: Rate constants for the reaction of $[\text{Co}(\text{bpy})_3]^{3+}$ and $\text{S}_2\text{O}_3^{2-}$ ion at $28 \pm 1^\circ\text{C}$ and $\lambda_{\text{max}} = 560 \text{ nm}$

$10^3[\text{Co}(\text{bpy})_3]^{3+}$, mol dm^{-3}	$10^2[\text{S}_2\text{O}_3^{2-}]$, mol dm^{-3}	$10^2[\text{H}^+]$, mol dm^{-3}	$[\mu]$, mol dm^{-3}	$10^2 k_{\text{obs}}$, s^{-1}	k_2 , $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
1.00	7.00	2.00	0.40	1.05	2.15
2.00	7.00	2.00	0.40	1.06	2.17
3.00	7.00	2.00	0.40	1.06	2.17
4.00	7.00	2.00	0.40	1.07	2.19
5.00	7.00	2.00	0.40	1.06	2.17
2.00	3.00	2.00	0.40	0.18	2.04
2.00	4.00	2.00	0.40	0.36	2.22
2.00	5.00	2.00	0.40	0.57	2.28
2.00	6.00	2.00	0.40	0.80	2.23
2.00	7.00	2.00	0.40	1.06	2.17
2.00	8.00	2.00	0.40	1.43	2.23
2.00	9.00	2.00	0.40	1.85	2.28
2.00	10.00	2.00	0.40	2.08	2.08
2.00	7.00	1.00	0.40	0.84	1.71
2.00	7.00	2.00	0.40	1.06	2.17
2.00	7.00	3.00	0.40	1.38	2.82
2.00	7.00	4.00	0.40	1.56	3.19
2.00	7.00	5.00	0.40	2.06	4.20
2.00	7.00	6.00	0.40	2.33	4.76
2.00	7.00	7.00	0.40	2.78	5.67
2.00	7.00	2.00	0.20	0.58	1.19
2.00	7.00	2.00	0.30	0.84	1.71
2.00	7.00	2.00	0.40	1.06	2.17
2.00	7.00	2.00	0.50	1.69	3.46
2.00	7.00	2.00	0.60	2.20	4.50
2.00	7.00	2.00	0.70	2.83	5.78

Table 2: Influence of medium dielectric constant for the reaction of $[\text{Co}(\text{bpy})_3]^{3+}$ and $\text{S}_2\text{O}_3^{2-}$ at $[\text{Co}(\text{bpy})_3]^{3+} = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{S}_2\text{O}_3^{2-}] = 7.0 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{H}^+] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$, $\mu = 0.4 \text{ mol dm}^{-3}$ (NaCl), $T = 28 \pm 1^\circ\text{C}$ and $\lambda_{\text{max}} = 560 \text{ nm}$

D	$10^2/\text{D}$	$10^2 k_{\text{obs}}$, s^{-1}	k_2 , $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
80.1	1.25	0.91	1.86
78.7	1.27	0.98	2.00
77.2	1.30	1.06	2.15
75.8	1.32	1.14	2.33
74.4	1.34	1.24	2.52
72.9	1.37	1.35	2.75
71.5	1.40	1.41	2.87
70.1	1.43	1.51	3.08

Table 3: Added ions effect on the reaction of $[\text{Co}(\text{bpy})_3]^{3+}$ and $\text{S}_2\text{O}_3^{2-}$ at $[\text{Co}(\text{bpy})_3]^{3+} = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$ and $[\text{S}_2\text{O}_3^{2-}] = 7.0 \times 10^{-2} \text{ mol dm}^{-3}$

Ion	$10^3[\text{Ion}],$ mol dm^{-3}	$10^2 k_{\text{obs}},$ s^{-1}	$k_2,$ $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
NH_4^+	0.00	1.06	2.17
	1.00	1.06	2.16
	10.00	1.06	2.17
	30.00	1.11	2.27
	50.00	1.22	2.49
	70.00	1.26	2.58
	100.00	1.36	2.77
HCOO^-	0.00	0.96	1.95
	1.00	0.82	1.66
	3.00	0.76	1.56
	5.00	0.71	1.45
	7.00	0.51	1.04
	10.00	0.41	0.83

Added cation (NH_4^+) led to an increase in the rate of the reaction while added anion (HCOO^-) decelerated the rate (Table 3). The cation catalysis and anion inhibition detected have been linked with the outer sphere electron transfer process [21]. The active participation of free radical in the reaction was negative.

The zero intercept from the plot of $1/k_{\text{obs}}$ versus $1/[\text{S}_2\text{O}_3^{2-}]^2$ (Fig. 6) reveals the possibility of the non-existence of an intermediate complex with an appreciable equilibrium constant [22]. The test of spectroscopically determinable intermediate showed a shift in the λ_{max} from 560 to 600 nm, this could suggest the presence of an ion-pair at the rate-determining step which would have inhibited the presence of a complex intermediate spectroscopically detectable [22], hence, in conformity with the kinetic evidence from $1/k_{\text{obs}}$ versus $1/[\text{S}_2\text{O}_3^{2-}]^2$ plot.

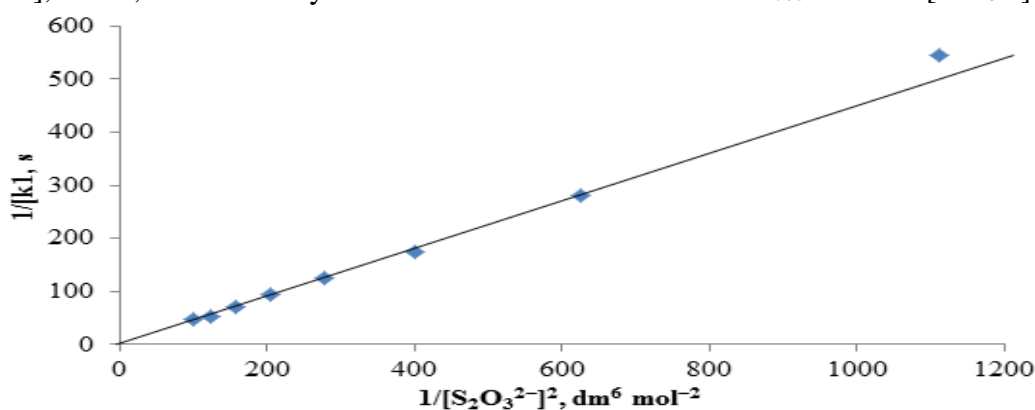


Fig. 6: Plot of $1/k_{\text{obs}}$ against $1/[\text{S}_2\text{O}_3^{2-}]^2$ for the reaction of $[\text{Co}(\text{bpy})_3]^{3+} - \text{S}_2\text{O}_3^{2-}$

Results for the effect of the temperature change on the reaction rate showed an increase in the reaction rate as the temperature rises in the study reaction (Table 4). The activation parameters ΔS^\ddagger and ΔH^\ddagger ($-14.56 \text{ JK}^{-1} \text{ mol}^{-1}$ and 71.79 Jmol^{-1} respectively) were evaluated from the intercept and slope of the graph in Fig. 7, and it backs an inner-sphere mechanism of electron transfer. The negative ΔS^\ddagger suggests a reaction where there is a mutual ordering of

solvated molecules at the slow stage of the reaction as a result of the dominance of bond formation [23]. An inner-sphere mechanism has been obtained by some researchers [24,25].

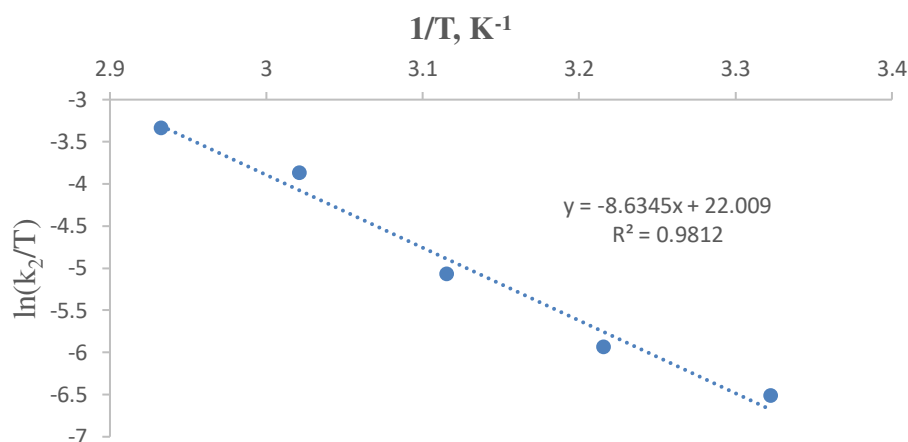


Fig. 7: The plot of $\ln(k_2/T)$ versus $1/T$ for the $[\text{Co}(\text{bpy})_3]^{3+} - \text{S}_2\text{O}_3^{2-}$ reaction

Table 4: Result for the effect of temperature change for $[\text{Co}(\text{bpy})_3]^{3+}$ and $\text{S}_2\text{O}_3^{2-}$ reaction at $[\text{Co}(\text{bpy})_3]^{3+} = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{S}_2\text{O}_3^{2-}] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{H}^+] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$, $\mu = 0.4 \text{ mol dm}^{-3}$ (NaCl), $T = 28 \pm 1^\circ\text{C}$ and $\lambda_{\text{max}} = 560 \text{ nm}$

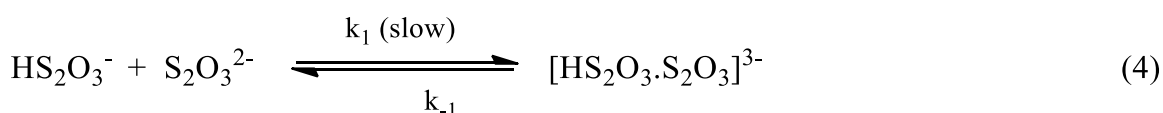
Temperature, K	$10^2[\text{S}_2\text{O}_3^{2-}]$, mol dm^{-3}	$10^2[\text{H}^+]$, mol dm^{-3}	$[\mu]$, mol dm^{-3}	$10^2 k_{\text{obs}}$, s^{-1}	k_2 , $\text{dm}^{-3} \text{mol}^{-1} \text{s}^{-1}$
301	5.00	2.00	0.40	0.11	0.45
311	5.00	2.00	0.40	0.21	0.83
321	5.00	2.00	0.40	0.50	2.02
331	5.00	2.00	0.40	1.74	6.95
341	5.00	2.00	0.40	3.05	12.18

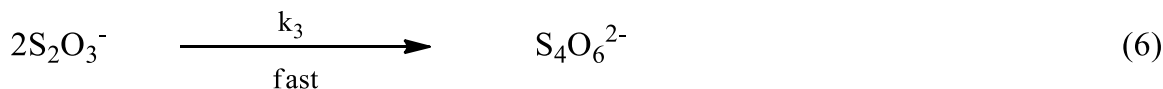
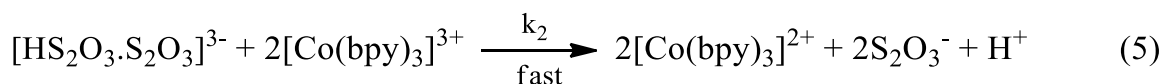
3.1 Mechanism of the Reaction

The reaction of $[\text{Co}(\text{bpy})_3]^{3+} - \text{S}_2\text{O}_3^{2-}$ is rationalised in favour of an outer sphere mechanism and a possible inner sphere route taken recourse to the following criteria;

1. The absence of complex intermediates observed from kinetic studies
2. The catalytic and inhibitory result of added ions
3. The values of the activation parameters.

On the basis of the results ascertained from the study, the following mechanistic steps (Equation 3 – 6) are proposed for the $[\text{Co}(\text{bpy})_3]^{3+} - \text{S}_2\text{O}_3^{2-}$ reaction;





$$\text{Rate} = k_1 [\text{HS}_2\text{O}_3^-][\text{S}_2\text{O}_3^{2-}] \quad (7)$$

From Equation 3,

$$K_{\text{eq}} = \frac{[\text{HS}_2\text{O}_3^-]}{[\text{S}_2\text{O}_3^{2-}][\text{H}^+]} \quad (8)$$

$$[\text{HS}_2\text{O}_3^-] = K_{\text{eq}} [\text{S}_2\text{O}_3^{2-}][\text{H}^+] \quad (9)$$

replacing Equation (9) into (7),

$$\text{Rate} = k_1 K_{\text{eq}} [\text{H}^+][\text{S}_2\text{O}_3^{2-}]^2 \quad (10)$$

$$\text{Rate} = a [\text{H}^+][\text{S}_2\text{O}_3^{2-}]^2 \quad (11)$$

where $a = k_1 K_{\text{eq}} = 77.82 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$.

The HS_2O_3^- and the $\text{S}_2\text{O}_3^{2-}$ ions are active species in the elementary steps scheme. Nevertheless, they interact together at the slow step, thereby, producing an ion associate (Equation 4). Since the reaction proceeded via one pathway as obtained from acid-dependence studies, hence subsequent reactions occurred in a succession of fast steps including the reaction of $[\text{Co}(\text{bpy})_3]^{3+}$ complex and the ion associate (Equation 5). This is sharp conformity with the zero-order dependence displayed by the complex concentration and the second order, seen on that of the reductant.

Conclusion

The reduction of $[\text{Co}(\text{bpy})_3]^{3+}$ in an aqueous acidic medium by $\text{S}_2\text{O}_3^{2-}$ ion was studied. The interacting number of moles was in the ratio of 1:1. Analysis of other kinetic data gave an overall third-order; zero-order for the [oxidant], second-order for [reductant], and first-order for hydrogen ion concentration. The mechanism of the reaction based on the available evidence has been rationalised in favour of the outer sphere mechanism but with a possible inner sphere route. The formation of bimolecular ion-pair was electrostatically important in bringing about electron transfer in the moieties of redox species as it is vital for proteins and nucleic acids to perform their function.

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