

**Reaction of Thiosulphate with Coordinated Superoxide in
[(NH₃)₅Co(μ-O₂)Co(NH₃)₅]⁵⁺: A Mechanistic Study**

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ABSTRACT

The kinetics and mechanism of the electron transfer reactions of thiosulphate and μ-superoxo-bis[pentaamminecobalt(III)] pentachloride monohydrate, [(NH₃)₅Co(O₂)Co(NH₃)₅]Cl₅.H₂O, hereafter represented as Co(O₂)Co⁵⁺ was studied in aqueous perchloric acid under pseudo-first-order conditions at 27 ± 1 °C, I = 0.5 C² mol dm⁻³(NaClO₄) and λ_{max} = 660 nm. μ-superoxo-bis[pentaamminecobalt(III)] pentachloridemonohydrate was used as the oxidant and it was synthesized and characterized according to reported procedure. The reaction was found to be first-order in both reactants, second-order overall, acid dependent and displayed a zero Brønsted-Debye salt effect. Decreasing the dielectric constant from 80.1–74.01 (CH₃COCH₃/H₂O) has no effect on the rate of reaction. Inhibitory effect of Mg²⁺ and catalytic effect of NO₃⁻ rationalized the reaction in favour of outersphere mechanism. A large negative value of ΔS[‡] (–249.21 Jmol⁻¹K⁻¹) was obtained during the thermodynamic studies and that showed that the activated complex formed is more ordered. This confirmed that the reaction proceeded by associative mechanism. There was no evidence for the presence of free radicals during the course of the reaction and none to support the formation of an intermediate complex. The results suggest an outer-sphere mechanism for the reaction. A probable mechanism is proposed.

Key words: Kinetics, mechanism, oxidation, dioxygen complex, observed rate constant, thiosulphate, Ionic strength

INTRODUCTION

Metal–dioxygen complexes have long been the subject of thorough research due to their importance to the physiological metabolism of dioxygen (O₂) [1–3]. The singlet oxygen (³O₂), present in air is less reactive than its different reduced derivatives [4] like superoxide (O₂⁻), peroxide (O₂²⁻) and hydroxyl radical (·OH). These radicals having independent existence with one or more unpaired electrons form a part of reactive oxygen species (ROS) [5].

In living systems, different enzymes, such as xanthine oxidase [6, 7], lipoxygenase, and cyclooxygenase [8, 9], spontaneously but in limited extent produce ROS species in electron-rich environment. However, when the production of ROS exceeds the limit, it tips off the balance between the former and the natural antioxidant defense systems [10], causing severe damages to all the essential bio-macromolecules, like, carbohydrates, proteins, lipids and nucleic acids [11-13], resulting in metabolic and cellular disorders. This situation, called ‘oxidative stress’ may lead to critical diseases like cancer, heart problems [14-16] and diabetes [17, 18].

In pursuit of understanding the ROS chemistry, numerous metal-bound-oxygen complexes were synthesized. Among which was cobalt-bound superoxo complexes which were renowned since they are easy to study at ambient conditions [19]. Taube, Sykes, and others have reported the detailed studies on the reduction of these complexes with different metal ions [20, 21] and reducing agents such as sulphite, arsenite, nitrite, etc. [22, 23].

In this work we have chosen a metal bound superoxo species, $[(\text{NH}_3)_5 \text{Co} (\mu\text{-O}_2)\text{Co}(\text{NH}_3)_5]^{5+}$, as a suitable model for ROS and studied the kinetics of its reduction by thiosulphate anion ($\text{S}_2\text{O}_3^{2-}$). Thiosulphate ion can act as a reducing agent and thus also as an antioxidant. $\text{S}_2\text{O}_3^{2-}$ finds several medicinal applications, like in treatment of cisplatin induced nephrotoxicity [24]. It provides high antitumor activity with systemic chemoprotection [25, 26] and is effective at reducing carboplatin ototoxicity when administered in the guinea pig [27]. Combined administration of high dose cisplatin and $\text{S}_2\text{O}_3^{2-}$ have shown favourable results against ovarian cancer [26].

The mechanism, by which $\text{S}_2\text{O}_3^{2-}$ reduces nephrotoxicity and ototoxicity, has been proposed to involve the process of free-radical scavenging and covalent binding to the platinum compound [28, 29]. The potential role of $\text{S}_2\text{O}_3^{2-}$ as a radical scavenger to the best of our knowledge is yet to be studied in detail.

We herein present the kinetics of oxidation of $\text{S}_2\text{O}_3^{2-}$ by binuclear superoxo cobalt(III) complex. This interaction showcased the capacities of $\text{S}_2\text{O}_3^{2-}$ as a radical scavenger and a bridging ligand. The experimental observation revealed that $\text{S}_2\text{O}_3^{2-}$ reduces the bound-superoxo moiety through a consecutive reaction to form an intermediate bridging thiosulfato complex. We believe that the proposed mechanistic elucidation of the title work will offer an insight to the understanding of the prospective roles of sulphur-containing small molecules, such as $\text{S}_2\text{O}_3^{2-}$.

This study is aimed at generating kinetic data with respect to the oxidation of thiosulphate ions by μ -superoxo-bridged binuclear cobalt(III) complex of ammine and to propose plausible mechanism that underpin this reaction of interest. An investigation of this binuclear cobalt(III) species is worthwhile in part because of the possible relevance of the results as a comparative tool. It will also serve as an extension of earlier studies on dioxygen cobalt(III) complex and contribute to the conceptual development of inorganic reaction mechanisms in relation to this type of complexes.

EXPERIMENTAL

Analar grade reagents were used in this research. Reaction rates were monitored by following the decrease in absorbance of the reaction mixture at 660 nm on a CORNING colorimeter 253. $[\text{Co}_2(\text{O}_2)(\text{NH}_3)_{10}]\text{Cl}_5 \cdot 5\text{H}_2\text{O}$ was used as the oxidant and it was synthesized and characterized according to reported procedure [30]. Thiosulphate (Sigma- Aldrich) was used as the reducing agent, while sodium perchlorate (M&B) was used to maintain the ionic strength of the reaction medium.

The stoichiometry of the reaction was determined by spectrophotometric titration, using the mole ratio method [31] by keeping the concentration of the $\text{Co}(\text{O}_2)\text{Co}^{5+}$ constant at $2 \times 10^{-3} \text{ mol dm}^{-3}$ and varying the concentration of the reductant ($\text{S}_2\text{O}_3^{2-}$) within the range $(4\text{-}32) \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{H}^+] = 0.02 \text{ mol dm}^{-3}$, $I = 0.5 \text{ C}^2 \text{ mol dm}^{-3}$ (NaClO_4), $\lambda_{\text{max}} = 660 \text{ nm}$ and $T = 27.0 \pm 1.0 \text{ }^\circ\text{C}$.

Kinetic studies were conducted *via* spectrophotometry by monitoring the decrease in absorbance of the reaction mixture at 660 nm (λ_{max} of aqueous $\text{Co}(\text{O}_2)\text{Co}^{5+}$) as a function of time using Corning Spectrophotometer model 253 [32]. All measurements were made under pseudo-first order conditions with the concentration of thiosulphate ($\text{S}_2\text{O}_3^{2-}$) at least 20 times greater than that of $\text{Co}(\text{O}_2)\text{Co}^{5+}$ and at constant ionic strength of $0.5 \text{ C}^2 \text{ mol dm}^{-3}$ (using NaClO_4), $[\text{H}^+] = 0.02 \text{ mol dm}^{-3}$, and temperature of $27.0 \pm 1.0 \text{ }^\circ\text{C}$. Under such conditions, kinetic curves were exponential and rate constants were obtained from logarithmic plots of absorbance differences, $\log (A_t - A_\infty)$ against reaction time. Second order rate constants, k_2 , were derived for each run [33] as represented by equation (1) below

$$k_2 = \frac{k_{\text{obs}}}{[\text{S}_2\text{O}_3^{2-}]} \dots\dots\dots(1)$$

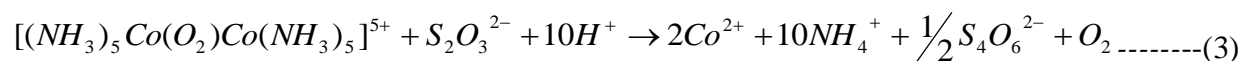
The effect of $[\text{H}^+]$ on the reaction rate was investigated by varying the $[\text{H}^+]$ between $0.2 \times 10^{-1} \leq [\text{H}^+] \leq 1.4 \times 10^{-1} \text{ mol dm}^{-3}$. Kinetic runs were carried out at constant ionic strength of $0.5 \text{ C}^2 \text{ mol dm}^{-3}$ (using NaClO_4) and temperature of $27.0 \pm 1.0 \text{ }^\circ\text{C}$, while keeping oxidant's and reductant's concentrations constant at $2 \times 10^{-3} \text{ mol dm}^{-3}$ and $1.6 \times 10^{-1} \text{ mol dm}^{-3}$ respectively [32]. The effect of varying the ionic strength of the reaction medium on the rate of the reaction was investigated in the range of $0.20 - 0.80 \text{ mol dm}^{-3}$ (using NaClO_4) while the concentrations of the reactants were kept constant at $27 \pm 1 \text{ }^\circ\text{C}$. The effect of added anion and cation on the reaction rates was investigated for $[\text{X}] = (0 - 10) \times 10^{-2} \text{ mol dm}^{-3}$ where X represents nitrate ion (NO_3^-) and Magnesium ion (Mg^{2+}) at constant $[\text{Co}(\text{O}_2)\text{Co}^{5+}]$, $[\text{S}_2\text{O}_3^{2-}]$, ionic strength and temperature [34]. The effect of changes in the dielectric constant (D) of the reaction medium on the rates of reaction of $\text{CoO}_2\text{Co}^{5+}$ and thiosulphate ($\text{S}_2\text{O}_3^{2-}$) was investigated at constant $[\text{CoO}_2\text{Co}^{5+}]$, $[\text{S}_2\text{O}_3^{2-}]$, ionic strength (I) and temperature of reaction by varying the dielectric constant of the medium using binary mixture of acetone-water (2-10%). The effect of temperature on the reaction rate was studied in the range of 300–340 K. The temperature dependence data were analysed using Eyring plot of $\ln(\frac{k_2}{T})$ versus $\ln(\frac{1}{T})$ (eq. 2) and thermodynamic parameters were determined at constant $[\text{Co}(\text{O}_2)\text{Co}^{5+}]$, $[\text{S}_2\text{O}_3^{2-}]$ and ionic strength.

$$\ln[\frac{k_2}{T}] = \ln[\frac{k_b}{h}] + \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{R} - [\frac{1}{T}] \dots\dots\dots(2)$$

Electronic spectra of partially reacted reaction's mixture at wavelength interval of 400 nm-700 nm were carried out. Similar run was made for the oxidant separately and the two results were compared. Michaelis–Menten plot of $1/k_{\text{obs}}$ versus $1/[\text{S}_2\text{O}_3^{2-}]$ was also carried out to detect the presence or absence of intermediate complex formation. Test for free radicals was carried out by adding about 5 cm^3 of $0.015 \text{ mol dm}^{-3}$ of acrylamide to a partially oxidised reaction mixture. A large excess of methanol was added to the reaction mixture. Control experiment was carried out by adding acrylamide to solutions of oxidant and reductant separately at the same conditions of $[\text{H}^+]$, ionic strength (I) and temperature [34-36].

RESULTS AND DISCUSSION

Plot of absorbance at completion of reaction *versus* $\frac{[S_2O_3^{2-}]}{[CoO_2Co^{5+}]}$ gave an inflexion at 1.25 (approx. 1) (Fig. 1). This result indicates a stoichiometry of one mole of $[S_2O_3^{2-}]$ reacting with one moles of CoO_2Co^{5+} as represented with eqn.3.



This result is similar to the finding of Osunlaja, 2013, where the mole ratio of the reaction of $Co(O_2)Co^{5+}$ with thiourea was found to be 1:1 [37]. Similarly, Adetoro *et.al.*, found the mole ratio of the reaction of CoO_2Co^{2+} and lysine to be 1:1 respectively [38].

In the kinetic analysis, the pseudo-first order plot of $\log (A_t - A_\infty)$ (where A_t and A_∞ are absorbances at time 't' and at infinity, respectively) against time was linear to more than 75% extent of reaction, indicating that the reaction is first order with respect to $[CoO_2Co^{5+}]$ under the experimental conditions (Fig. 2). This is further supported by the values of second order rate constant, k_2 , which were fairly constant (Table 1). The order of the reaction with respect to $[S_2O_3^{2-}]$ was found by plotting $\log k_{obs}$ against $\log [S_2O_3^{2-}]$. The plot of $\log k_{obs}$ against $\log [S_2O_3^{2-}]$ was linear with a slope of 1.025 (approx. 1) (Fig. 3). This suggests that the order of reaction with respect to $[S_2O_3^{2-}]$ is first order. Therefore, the rate equation for the reaction is represented by equation 4;

$$-d \frac{[Co(O_2)Co^{5+}]}{dt} = k_2 [Co(O_2)Co^{5+}] [S_2O_3^{2-}] \text{----- (4)}$$

where $k_2 = (0.906 \pm 0.03) \times 10^{-1} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

This finding is similar to the one observed by Osunlaja *et. al.*, in the reduction of this complex with thiourea [37].

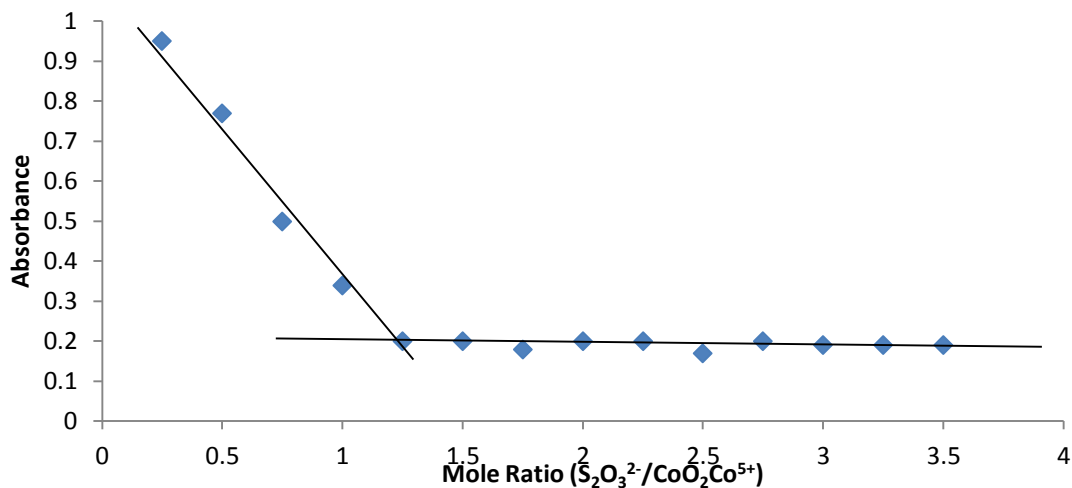


Figure 1: Stoichiometry of the oxidation of $[\text{S}_2\text{O}_3^{2-}]$ by $[\text{Co}(\text{O}_2)\text{Co}^{5+}]$

$[\text{Co}(\text{O}_2)\text{Co}^{5+}] = 2 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{C}_6\text{H}_4(\text{OH})_2] = (0.5 - 7.0) \times 10^{-3} \text{ mol dm}^{-3}$,
 $[\text{H}^+] = 2 \times 10^{-2} \text{ mol dm}^{-3}$, $I = 0.5 \text{ cm}^2 \text{ mol dm}^{-3}$ (NaClO_4), $T = 27.0 \pm 1.0^\circ\text{C}$ and
 $\lambda_{\text{max}} = 660 \text{ nm}$.

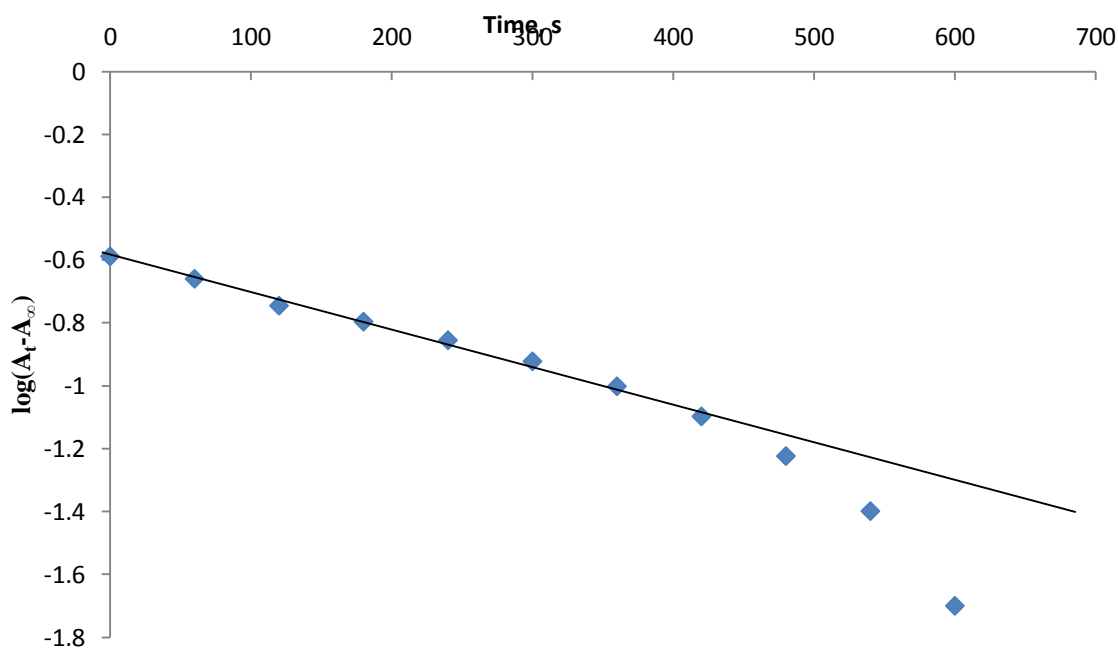


Figure 2: Typical Pseudo-first order plot for the oxidation of $S_2O_3^{2-}$ by CoO_2Co^{5+} at $[CoO_2Co^{5+}] = 2 \times 10^{-3} \text{ mol dm}^{-3}$, $[S_2O_3^{2-}] = 16 \times 10^{-2} \text{ mol dm}^{-3}$, $[H^+] = 0.02 \text{ mol dm}^{-3}$, $I = 0.5 \text{ C}^2 \text{ mol dm}^{-3}$ ($NaClO_4$), $T = 27.0 \pm 1.0^\circ\text{C}$ and $\lambda_{\text{max}} = 660 \text{ nm}$

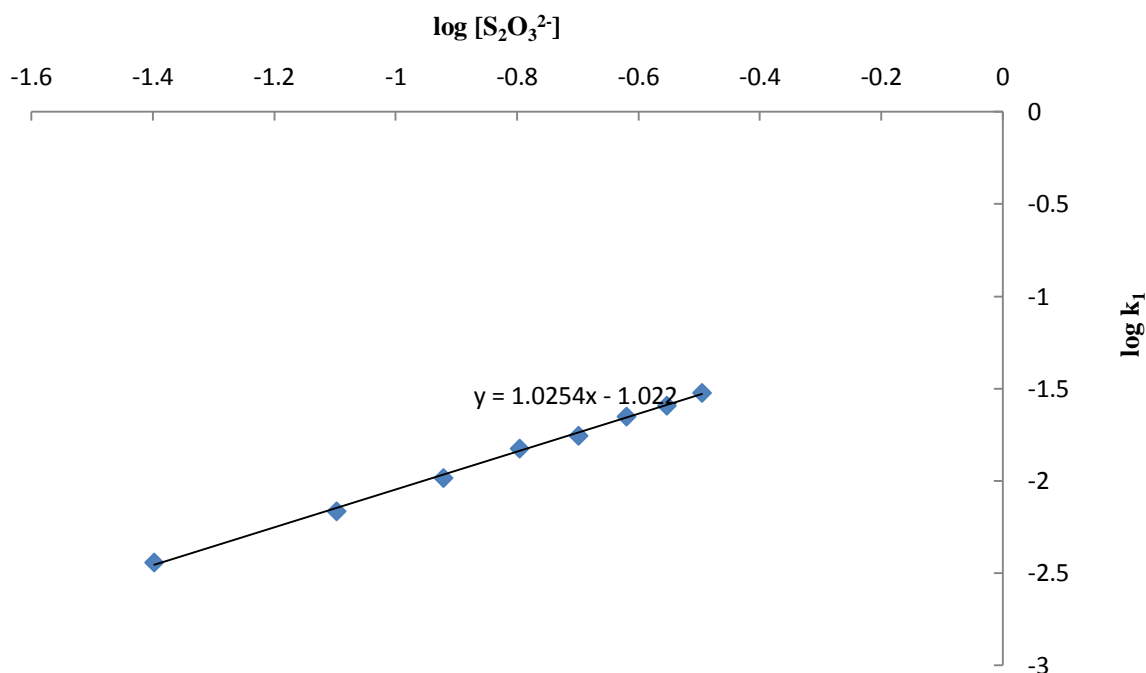


Figure 3: Plot of $\log k_1$ versus $\log [S_2O_3^{2-}]$ for the oxidation of $S_2O_3^{2-}$ by CoO_2Co^{5+} at $[CoO_2Co^{5+}] = 2 \times 10^{-3} \text{ mol dm}^{-3}$, $[S_2O_3^{2-}] = (4-32) \times 10^{-2} \text{ mol dm}^{-3}$, $[H^+] = 0.02 \text{ mol dm}^{-3}$, $I = 0.5 \text{ C}^2 \text{ mol dm}^{-3}$ ($NaClO_4$), $T = 27.0 \pm 1.0^\circ\text{C}$ and $\lambda_{\text{max}} = 660 \text{ nm}$

KINETIC STUDIES OF $[(NH_3)_5Co_2(O_2)(NH_3)_5]^{5+} - S_2O_3^{2-}$ REACTION

Table 1: Pseudo-first order and second order rate constants for the oxidation of $S_2O_3^{2-}$ by $[CoO_2Co]^{5+}$ at $T = 27.0 \pm 1.0^\circ\text{C}$, $[CoO_2Co^{5+}] = 2 \times 10^{-3} \text{ mol dm}^{-3}$ and $\lambda_{\text{max}} = 660 \text{ nm}$

$10^2[S_2O_3^{2-}]$ (mol dm^{-3})	$10^1[H^+]$ (mol dm^{-3})	I ($\text{C}^2 \text{ mol dm}^{-3}$)	10^2k_1 (s^{-1})	10^1k_2 ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)

4	0.2	0.50	0.36	0.91
8	0.2	0.50	0.69	0.86
12	0.2	0.50	1.04	0.87
16	0.2	0.50	1.50	0.94
20	0.2	0.50	1.76	0.88
24	0.2	0.50	2.24	0.93
28	0.2	0.50	2.58	0.92
32	0.2	0.50	3.01	0.94
16	0.2	0.20	1.50	0.94
16	0.2	0.30	1.52	0.95
16	0.2	0.40	1.51	0.94
16	0.2	0.50	1.49	0.93
16	0.2	0.60	1.50	0.94
16	0.2	0.70	1.52	0.95
16	0.2	0.80	1.49	0.93

The effect of ionic strength on the rate of the reaction is presented in Table 1. It shows that the rate constants are relatively constant with increase in ionic strength of the reaction medium, from 0.20 – 0.80 mol dm⁻³ (using NaClO₄), indicating a negligible Brønsted-Debye salt effect. It implies that the reaction proceeds via an interaction between a charged and an uncharged form of the reactants or the rate determining step is made up of only one reactant [39].

In order to investigate the effect of [H⁺] on the reaction rate, [H⁺] was varied within the range of $0.2 \times 10^{-1} \leq [\text{H}^+] \leq 1.4 \times 10^{-1}$ mol dm⁻³ at constant ionic strength (I), while keeping [CoO₂Co⁵⁺] and [S₂O₃²⁻] constant. The reaction rate increased with increase in [H⁺] at I = 0.5 C² mol dm⁻³ (using NaClO₄), and T = 27 ± 1 °C. The pseudo-first order and second order rate constants at increasing [H⁺], but constant [CoO₂Co⁵⁺], [S₂O₃²⁻], I and T are presented in Table 1.0. The plot of k₂(H⁺) versus [H⁺] is linear (Fig. 4). The dependence of rate constants on [H⁺] can be represented by Equation (5). This result is the reverse of the finding of Singh *et. al.*, for the reaction of $[(\text{NH}_3)_4\text{Co}^{\text{III}}(\mu\text{-NH}_2,\mu\text{-O}_2)\text{Co}^{\text{III}}(\text{NH}_3)_4]^{4+}$ with S₂O₃²⁻ [40]

$$k_{\text{obs}} = \frac{K_1 k_3 k_2 [\text{H}^+]}{(k_{-2} + k_3)} \dots\dots\dots (5)$$

Table 2: Effect of acid concentration on the rate of reaction of [CoO₂Co⁵⁺] with [S₂O₃²⁻] at [CoO₂Co⁵⁺] = 2 × 10⁻³ mol dm⁻³, [S₂O₃²⁻] = 16 × 10⁻² mol dm⁻³, I = 0.5 C² mol dm⁻³, T = 27 ± 1 °C and λ_{max} = 660 nm.

$10^2[S_2O_3^{2-}]$ (mol dm ⁻³)	$10^1[\text{H}^+]$ (mol dm ⁻³)	I (C ² mol dm ⁻³)	10^2k_1 (s ⁻¹)	10^1k_2 (dm ³ mol ⁻¹ s ⁻¹)
16	0.2	0.5	1.50	0.94
16	0.4	0.5	2.70	1.68
16	0.6	0.5	4.55	2.85
16	0.8	0.5	6.55	4.09
16	1.0	0.5	7.54	4.71
16	1.2	0.5	9.59	5.99
16	1.4	0.5	10.63	6.64

Table 3: Effect of added ions on $[(\text{NH}_3)_5 \text{Co}_2(\text{O}_2)(\text{NH}_3)_5]^{5+} - \text{S}_2\text{O}_3^{2-}$ reaction at $[\text{CoO}_2\text{Co}^{5+}] = 2 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{S}_2\text{O}_3^{2-}] = 16 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{H}^+] = 2 \times 10^{-2} \text{ mol dm}^{-3}$, $I = 0.5 \text{ C}^2 \text{ mol dm}^{-3}$ (NaClO₄), $T = 27.0 \pm 1.0^\circ\text{C}$ and $\lambda_{\text{max}} = 660 \text{ nm}$

X	$10^2[\text{X}]$ (mol dm ⁻³)	$10^2 k_1$ (s ⁻¹)	$10^1 k_2$ (dm ³ mol ⁻¹ s ⁻¹)
Mg ²⁺	0	1.50	0.94
	2	1.37	0.85
	4	1.19	0.74
	6	1.05	0.66
	8	0.93	0.58
	10	0.73	0.46
NO ₃ ⁻	0	1.50	0.94
	2	1.55	0.97
	4	1.59	0.99
	6	1.63	1.02
	8	1.66	1.04
	10	1.68	1.05

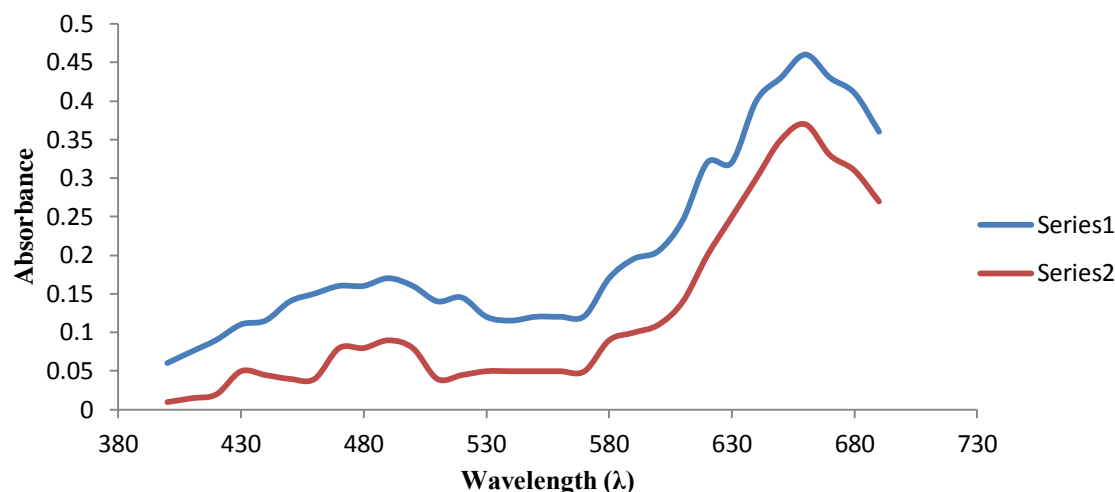


Figure 4: Spectra of CoO_2Co^{5+} and that of reaction mixture (Oxidant = CoO_2Co^{5+} and RM = reaction mixture)

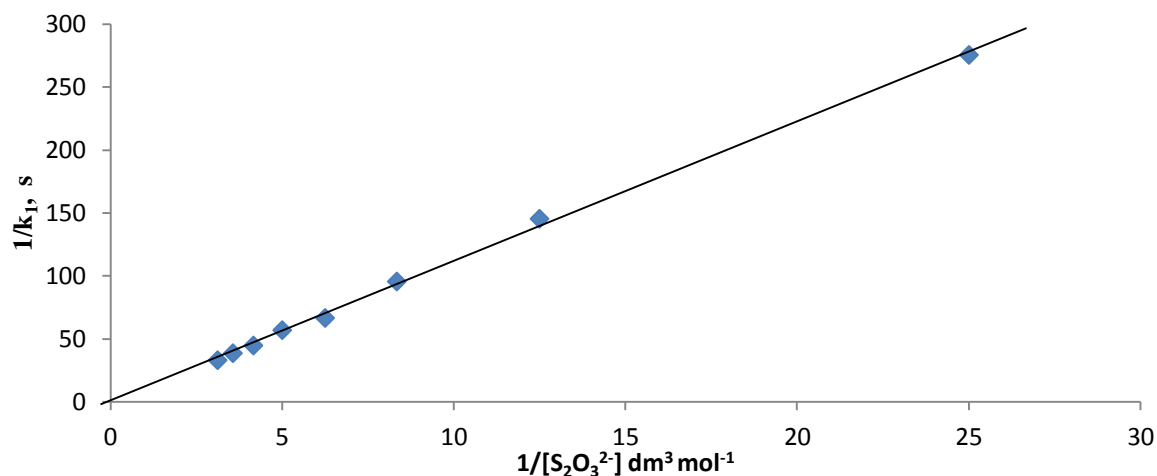


Figure 5: Michaelis-Menten plot of $1/k_1$ versus $1/[S_2O_3^{2-}]$ for the oxidation of $S_2O_3^{2-}$ by CoO_2Co^{5+} at $[CoO_2Co^{5+}] = 2 \times 10^{-3} \text{ mol dm}^{-3}$, $[S_2O_3^{2-}] = 16 \times 10^{-2} \text{ mol dm}^{-3}$, $[H^+] = 2 \times 10^{-2} \text{ mol dm}^{-3}$, $I = 0.5 \text{ C}^2 \text{ mol dm}^{-3}$, (NaClO₄), $T = 27.0 \pm 1.0 \text{ }^\circ\text{C}$ and $\lambda_{\text{max}} = 660 \text{ nm}$

Table 4: Effect of changes in temperature on $[(NH_3)_5Co_2(O_2)(NH_3)_5]^{5+} - S_2O_3^{2-}$ reaction at $[CoO_2Co^{5+}] = 2 \times 10^{-3} \text{ mol dm}^{-3}$, $[S_2O_3^{2-}] = 16 \times 10^{-2} \text{ mol dm}^{-3}$, $[H^+] = 2 \times 10^{-2} \text{ mol dm}^{-3}$, $I = 0.5 \text{ mol dm}^{-3}$ (NaClO₄) and $\lambda_{\text{max}} = 660 \text{ nm}$

Temp. (K)	$k_1 \cdot 10^2 (\text{s}^{-1})$	$k_2 \cdot 10$ ($\text{dm}^{-3}\text{mol}^{-1}\text{s}^{-1}$)	$k_2/T \cdot 10^4$ ($\text{dm}^{-3}\text{mol}^{-1}\text{s}^{-1}\text{K}^{-1}$)	$\ln(k_2/T)$	$1/T \cdot 10^3 (\text{K}^{-1})$
300	1.50	0.94	3.13	-8.07	3.33
310	1.69	1.06	3.42	-7.98	3.23

320	1.84	1.15	3.59	-7.93	3.13
330	1.97	1.23	3.73	-7.89	3.03
340	2.16	1.35	3.97	-7.83	2.94

$\Delta H^\ddagger = +4.575 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -249.21 \text{ J mol}^{-1} \text{ K}^{-1}$, $\Delta G^\ddagger = +79.34 \text{ KJ mol}^{-1}$ at 300K

$E_a = +7.45 \text{ kJ mol}^{-1}$

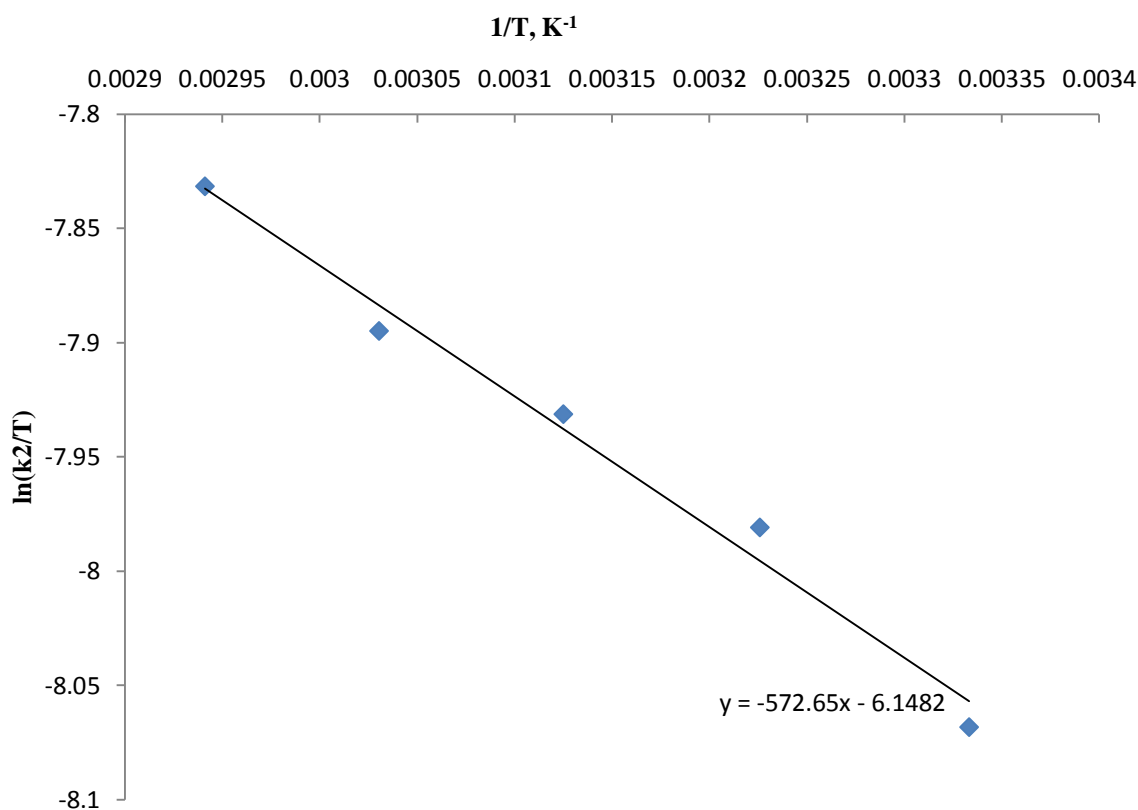


Figure 10: The plot of $\ln(k/T)$ versus $1/T$ for the reaction of $\text{S}_2\text{O}_3^{2-}$ and $\text{CoO}_2\text{Co}^{5+}$ at $[\text{CoO}_2\text{Co}^{5+}] = 2 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{S}_2\text{O}_3^{2-}] = 16 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{H}^+] = 2 \times 10^{-2} \text{ mol dm}^{-3}$, $I = 0.5 \text{ mol dm}^{-3}$ (NaClO_4), and $\lambda_{\text{max}} = 660 \text{ nm}$

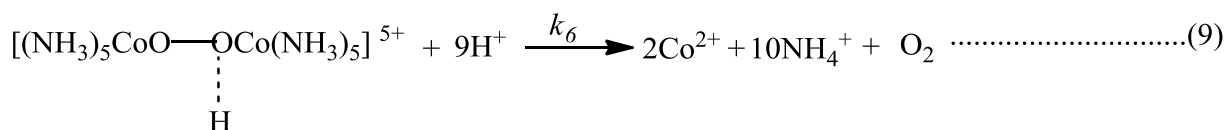
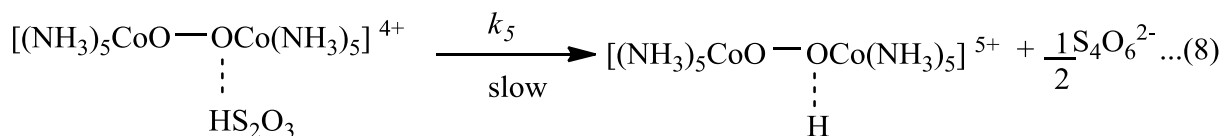
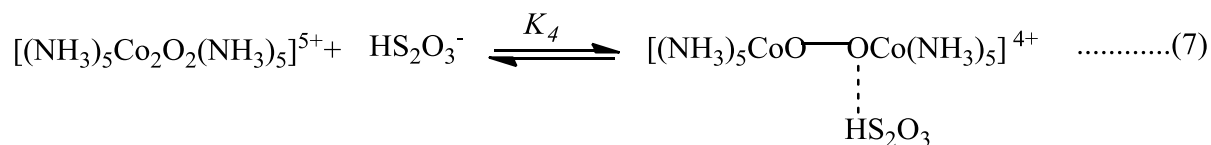
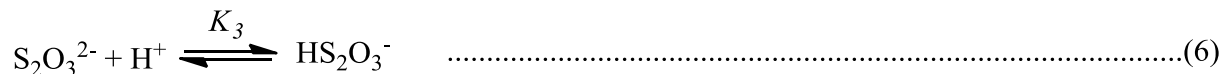
The reaction rate was decreased by Mg^{2+} and increased by NO_3^- ions (Table 3). This inhibitory and catalytic effect is consistent with a reaction following an outer-sphere pathway of electron

transfer. Decreasing the dielectric constant from 80.1–74.01 ($\text{CH}_3\text{COCH}_3/\text{H}_2\text{O}$) has no effect on the rate of reaction.

There was no significant shift in λ_{max} (660 nm) for the spectrum of the reaction mixture as compared with that of $[\text{CoO}_2\text{Co}^{5+}]$ (Fig. 4). Also, Michaelis-Menten plot of $1/k_{\text{obs}}$ versus $1/[\text{S}_2\text{O}_3^{2-}]$ was linear without an intercept (Fig. 5). These suggest that, there is no formation of stable intermediate complex preceding the electron transfer step. The absence of intermediate complex is an evidence that the reaction proceeded by an outer-sphere redox mechanism.

Addition of acrylamide, a known radical scavenger to the reaction mixture in excess methanol produced no precipitate, indicating absence of free radicals in the reaction. The plot of $\ln(k_2/T)$ versus $(1/T)$ is presented in Fig. 6 and the results of temperature dependence of the rate constants and activation parameters for the reaction are presented in Table 4. A large negative value of ΔS^\ddagger ($-249.21\text{Jmol}^{-1}\text{K}^{-1}$) is obtained and that shows that the activated complex formed is more ordered. This further confirms that the reaction proceeded by associative mechanism.

In the end of the reaction, KSCN solution in excess acetone was added to a portion of the final reaction mixture of $\text{CoO}_2\text{Co}^{5+}$ and $\text{S}_2\text{O}_3^{2-}$. A blue colour was obtained which is a qualitative confirmatory test for the presence of Co^{2+} as a product for the reaction under study. A colourless and odourless gas which rekindles a glowing splinter was also evolved. This gas is Oxygen gas. Mercury (I) acetate was added to another portion of the reaction mixture and a yellow precipitate appeared which turned black on heating [41]. This test confirmed the presence of tetrathionate ($\text{S}_4\text{O}_6^{2-}$) as one of the products of the reaction. Furthermore, dilute NaOH solution was added to a portion of the reaction mixture, followed by gentle heating. A colourless gas with a choking smell, which turned damp red litmus paper blue was evolved. The gas is NH_3 from NH_4^+ . This confirmed ammonium ion as one of the product of the reaction under study. Based on the results obtained from this investigation, the following reaction scheme is proposed for this reaction:



$$\text{Rate} = -\frac{d}{dt} \left[\frac{\left\{ \begin{array}{c} [(\text{NH}_3)_5\text{CoO}-\text{OCo}(\text{NH}_3)_5]^{4+} \\ \vdots \\ \text{HS}_2\text{O}_3 \end{array} \right\}}{\left\{ \begin{array}{c} [(\text{NH}_3)_5\text{CoO}-\text{OCo}(\text{NH}_3)_5]^{5+} \\ \vdots \\ \text{HS}_2\text{O}_3 \end{array} \right\}} \right] = k_5 \left[\begin{array}{c} [(\text{NH}_3)_5\text{CoO}-\text{OCo}(\text{NH}_3)_5]^{4+} \\ \vdots \\ \text{HS}_2\text{O}_3 \end{array} \right] \quad \dots\dots\dots(10)$$

from equation (7), we have

$$\begin{array}{c} [(\text{NH}_3)_5\text{CoO}-\text{OCo}(\text{NH}_3)_5]^{4+} \\ \vdots \\ \text{HS}_2\text{O}_3 \end{array} = K_4 [(\text{NH}_3)_5\text{Co}_2\text{O}_2(\text{NH}_3)_5]^{5+} [\text{HS}_2\text{O}_3^-] \quad \dots\dots\dots(11)$$

Substituting equation (11) into (10), we have

$$\text{Rate} = k_5 K_4 \left[\{(\text{NH}_3)_5\text{Co}_2\text{O}_2(\text{NH}_3)_5\}^{5+} \right] [\text{HS}_2\text{O}_3^-] \quad \dots\dots\dots(12)$$

from equation (6), we have

$$[\text{HS}_2\text{O}_3^-] = K_3 [\text{S}_2\text{O}_3^{2-}] [\text{H}^+] \quad \dots\dots\dots(13)$$

Substituting (13) into (12), we have

$$\text{Rate} = k_5 K_4 K_3 \left[\{(\text{NH}_3)_5\text{Co}_2\text{O}_2(\text{NH}_3)_5\}^{5+} \right] [\text{S}_2\text{O}_3^{2-}] [\text{H}^+] \quad \dots\dots\dots(14)$$

Equation (14) is analogous to equation (4)

$$k_2 = k_5 K_4 K_3 [\text{H}^+] = (0.906 \pm 0.03) \times 10^{-1} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

CONCLUSION

The redox reaction of μ -superoxo-bis[pentaamminecobalt(III)] pentachloridemonohydrate complex with thiosulphate ion in aqueous medium showed a stoichiometry of 1:1. The reaction is second-order overall and showed negligible Brønsted-Debye salt effect. The reaction rate changes with varying acid concentration, temperature and dielectric constant. Both spectroscopic and kinetic studies showed no proof of intermediate complex formation. The major redox products of this reaction is Co^{2+} , NH_4^+ and $\text{S}_4\text{O}_6^{2-}$. In general, the results suggest an outer-sphere mechanism as the plausible pathway for the reaction.

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