



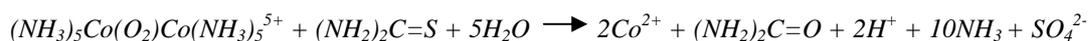
Kinetics and mechanism of thiourea oxidation by oxygenated $[\text{Co}_2(\text{O}_2)(\text{NH}_3)_{10}]^{5+}$ complex

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ABSTRACT

The reaction between thiourea and μ -superoxo-bis[pentaamminecobalt(III)] pentachloride monohydrate, $[(\text{NH}_3)_5\text{Co}(\text{O}_2)\text{Co}(\text{NH}_3)_5]\text{Cl}_5 \cdot \text{H}_2\text{O}$, hereafter referred to as **(I)**, has been studied in aqueous perchloric acid at $[\text{H}^+] = 0.04 \text{ mol dm}^{-3}$, $\mu = 0.25 \text{ mol dm}^{-3}$ (NaClO_4), and $T = 31.0 \pm 1.0^\circ\text{C}$, the reaction conforms to an overall equation:



The experimental data are consistent with a second-order rate law:

$$-d[[\text{Co}(\text{O}_2)\text{Co}^{5+}]/dt = k_2[\text{Co}(\text{O}_2)\text{Co}^{5+}][\text{TU}]$$

with $k_2 = (7.21 \pm 0.09) \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Added NO_3^- and CH_3COO^- catalyzed the reaction. The rate of reaction was dependent on variation in the ionic strength of the reaction medium in the range $0.1 \leq \mu \leq 0.5 \text{ mol dm}^{-3}$, but display a variety of $[\text{H}^+]$ dependences in the acid range $0.01 \leq [\text{H}^+] \leq 0.22 \text{ mol dm}^{-3}$. The absence of both kinetic and spectroscopic evidence of complex formation suggests that the reaction proceeds by the outer-sphere mechanism. This deduction is further supported by the non-conformity of the rate data to the Michaelis-Mentens equation.

Key words: Kinetics, oxidation, dioxygen complex, thiourea,

INTRODUCTION

The chemistry of binuclear metal complexes is a continuously growing field because of their relevance to the function of many metalloenzymes [1], their value as reagents or catalyst in organic chemistry [2], their potential use as artificial oxygen carriers [3], industrial oxidation catalysts [3-7] and as respiratory intermediate [8]. Thus, oxygen coordination and subsequent stepwise reduction at a metal center are key steps in understanding biological systems that uses oxygen. For instance, the active site of biological oxygen carriers hemoglobin and myoglobin are superoxo iron complexes. Both superoxo- and peroxo- metal ions can be seen in the active site of both heme and non-heme of iron-containing oxidase enzymes, as well as being responsible for the antibiotic and antitumor activity of bleomycin [2]. In the heme oxidases, both superoxo- and peroxo-metal ions are important transients in enzymatic activity, either acting as the oxidant for substrates themselves, or being further oxidized to even more powerful terminal oxidants, usually a metal-oxo species in a high oxidation state. The formation, stability, nature of the superoxo-bridge, photochemical decomposition and redox reactions (organic and inorganic substrates) of μ -superoxo-bis[pentaamminecobalt(III)] pentachloride monohydrate, $[(\text{NH}_3)_5\text{Co}(\text{O}_2)\text{Co}(\text{NH}_3)_5]\text{Cl}_5 \cdot \text{H}_2\text{O}$ is well documented in the literature [9]. However, the direct reaction between thiourea (TU) and **(I)**, is hereby reported for the first time. Thiourea has been selected as the reducing agent because of its vast uses in biological and chemical fields. For example, it is a scavenger of peroxide radical and it has been shown to inhibit lipid peroxidation and uv-induced cross-linking of collagen [10]. This is the first in a series of oxidation of the thioureas with **(I)**. Possible stoichiometries and products for the reductions of dicobalt(III) superoxo complexes have been summarized in the

literature [9]. The conformity with or deviation from earlier observations of this complex with similar reductants will present an interesting study.

EXPERIMENTAL SECTION

The superoxo complex (**I**) was prepared by the modifications of a reported procedure [11] as follows: 33.2mmol (8g) of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was dissolved into 80ml of distilled water at 0°C and 40ml of 15 mol dm^{-3} (0.889 specific gravity) ammonia at 0°C was added. 4ml of 30% H_2O_2 was added, one drop per 30 seconds, from a burette with stirring while the reaction is maintained at 0°C . The reaction mixture was left in ice-cold water at 0°C for about 15 minutes while 26.3mmol (6g) of ammonium peroxodisulphate dissolved in about 20ml of ice-cold distilled water was added and stirred gently. The solution was allowed to stand for up to 10minutes. A 20ml of ice-cold concentrated HCl (37%) was slowly added with stirring (the temperature still maintained at 0°C). The solution was kept ice-cold for one hour until precipitation of the product was completed. The blue-green solid was suction-filtered on a sintered glass and washed with 10ml ethanol followed by 5ml ethyl ether. The product was air-dried and then stored in an amber bottle wrapped in aluminum foil in a vacuum desiccator kept in a dark cupboard. The electronic spectra, infrared spectra, colour, light sensitivity and acid stability of the complex are all in agreement with literature results [11, 10]. The uv-visible spectrum of the synthesized complex has a characteristic λ_{max} at 670 nm ($\epsilon = 890 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) (literature: 670 nm) while the infrared spectrum due to ammonia is shifted in the complex. According to Sykes and Weil (1970), the 670 nm peaks is essentially useful as a diagnostic one and for quantitative analysis, since few other cobalt complexes absorb here. The complex is light sensitive but stable in dilute acid.

$3.89 \times 10^{-3} \text{ mol dm}^{-3}$ solution of the dioxygen complex was prepared, stored in an aluminum-foil wrapped container and kept in the dark. Fresh solutions were always prepared after about 12 hours (beyond this time the complex decomposes in-situ into the peroxo-complex). Furthermore, the concentration of the dioxygen complex was generally determined from the absorbance at the maxima and the corresponding extinction coefficient. All other reagents were of analytical grade and were used without further purification. Standard solution of perchloric acid was used as a source of hydrogen ions while the ionic strength of the medium was maintained constant at 0.25 mol dm^{-3} using sodium perchlorate.

Stoichiometric studies

The stoichiometry was determined by spectrophotometric titration using the mole ratio method. The concentration of $[\text{Co}(\text{O}_2)\text{Co}^{5+}]$ was kept constant at $7.77 \times 10^{-4} \text{ mol dm}^{-3}$ and that of thiourea varied from 1.94×10^{-4} to $23.32 \times 10^{-4} \text{ mol dm}^{-3}$ at $[\text{H}^+] = 0.04 \text{ mol dm}^{-3}$, $\mu = 0.25 \text{ mol dm}^{-3}$ (NaClO_4), and $T = 31.0 \pm 1.0^\circ\text{C}$. The reaction mixtures were allowed to undergo complete reaction and the absorbance (A_∞) was plotted against the mole ratio of the reactants. Point of inflection in the plot gave the mole ratio of the reactants (Figure 1).

Kinetic measurements

The rate of reaction was monitored on a Corning Colorimeter 253 by following the decrease in absorbance of the dioxygen complex at $\lambda = 670 \text{ nm}$. The rates were monitored under pseudo-first order conditions with thiourea in at least 50 fold excess over $[\text{Co}(\text{O}_2)\text{Co}^{5+}]$ (Table1). The ionic strength was maintained constant at 0.25 mol dm^{-3} (NaClO_4). Temperature was kept constant at $31.0 \pm 1.0^\circ\text{C}$ for all runs. At the end of the reaction, absorbance at the visible peak (670 nm) of the dioxygen complex was to zero.

Test for intermediate complex formation

Test for the presence of stable, detectable intermediate formed during the course of the reaction was carried out spectrophotometrically. At the visible peak (670 nm), electronic spectra of partially reacted reaction mixtures were recorded at various time intervals. A similar run was made for reactants separately in each case.

Test for free radicals

About 5 cm^3 of $0.015 \text{ mol dm}^{-3}$ acrylamide was added to a partially oxidized reaction mixtures followed by the addition of a large excess of methanol. A control experiment was carried out by adding acrylamide to solutions of the dioxygen complex and thiourea separately at the stated conditions of $[\text{H}^+]$, μ and temperature on Table 1. Absence of gel formation rules out participation of free radicals in the reaction..

Product analysis

The following analyses were carried out:

(1). The infrared spectra of the dioxygen complex and that of thiourea were obtained separately with a Shimadzu FTIR-84008 spectrophotometer in the region $500\text{-}4000 \text{ cm}^{-1}$ prior to the reactions and after the completion of the reaction.

(2). To 10 drops of the solution, 5 drops of 0.50 mol dm^{-3} potassium thiocyanate was added. An equal volume of acetone was added and mixed thoroughly.

(3) The presence of SO_4^{2-} was qualitatively tested for with dilute acidified solution of BaCl_2 and urea derivatives were tested for by the addition of few drops of dilute alkaline CuSO_4 solution.

RESULTS AND DISCUSSION

Stoichiometry

The stoichiometry of the reaction was found to be in the ratio 1:1. The overall equation for the reaction of $\text{Co}(\text{O}_2)\text{Co}^{5+}$ by thiourea can therefore be written as;



This stoichiometry is in accordance with those found for the reduction of this complex with VO^{2+} , Sn^{2+} , As^{3+} and $\text{S}_2\text{O}_3^{2-}$ [12,13].

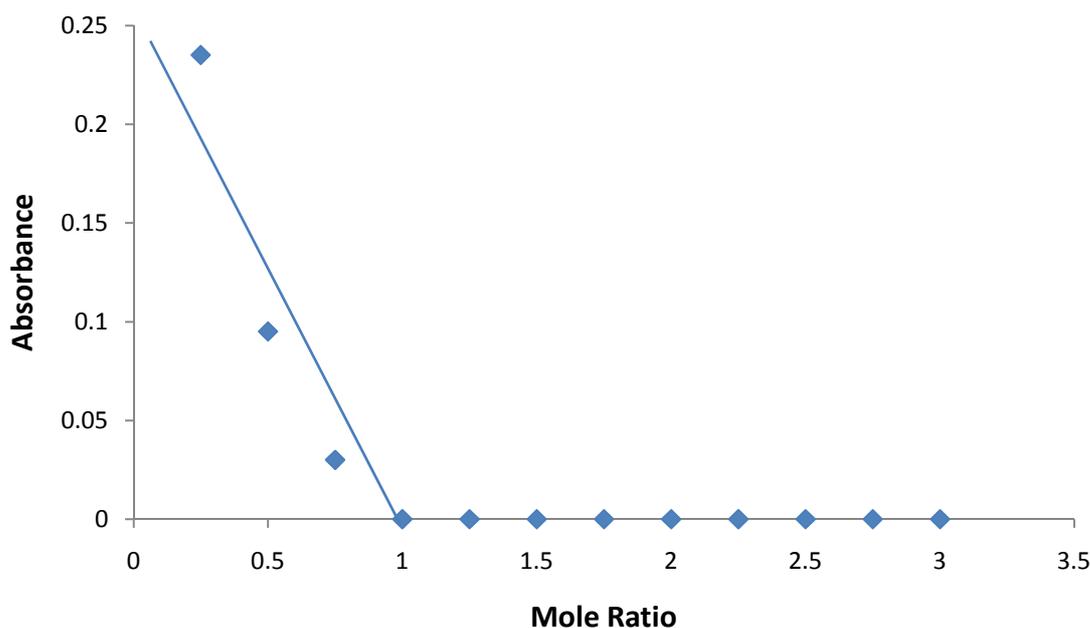


Figure 1: Stoichiometry of the oxidation of TU by $\text{Co}(\text{O}_2)\text{Co}^{5+}$

$[\text{Co}(\text{O}_2)\text{Co}^{5+}] = 7.77 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{TU}] = (1.94 - 23.32) \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{H}^+] = 0.04 \text{ mol dm}^{-3}$, $\mu = 0.25 \text{ mol dm}^{-3}$ (NaClO_4), $T = 31.0 \pm 1.0^\circ\text{C}$ and $\lambda_{\text{max}} = 670 \text{ nm}$

Determination of order of reaction

The pseudo-first order plots obtained from the absorbance-time traces were all linear to more than 90% completion of reaction. A typical plot of these is presented in Figure 2. From the pseudo-first order rate constants, k_1 , second order rate constants, k_2 , were obtained by dividing each first-order rate constant by the appropriate complex concentration. The derived second-order rate constants were fairly constant. This further confirms that the reaction is first order in $[\text{Co}(\text{O}_2)\text{Co}^{5+}]$. The plot of $\log k_1$ versus $\log [\text{TU}]$ was linear with a slope of 1.2 further shows first-order dependence of the rate of reaction on TU (Figure 2). Hence, the rate equation 2 describes the kinetic behavior of the reaction.



Similar order has been observed by Mishra *et al.*, (2009) [14], in the reaction of this complex with hydrogen peroxide.

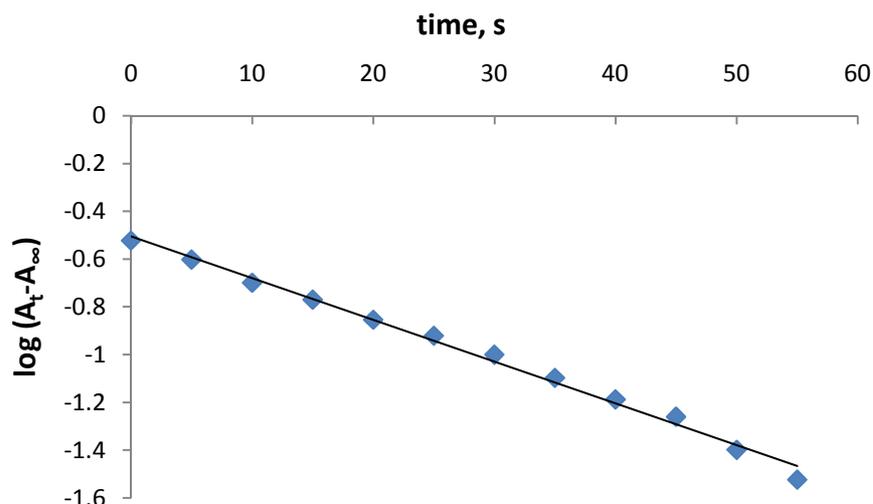


Figure 2: Typical Pseudo-first order plot for the oxidation of TU by $\text{Co}_2(\text{O})_2(\text{NH}_3)_{10}^{5+}$
 $[\text{Co}(\text{O}_2)\text{Co}^{5+}] = 7.77 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{TU}] = (3.89 - 31.09) \times 10^{-2} \text{ mol dm}^{-3}$
 $[\text{H}^+] = 0.04 \text{ mol dm}^{-3}$, $\mu = 0.25 \text{ mol dm}^{-3}$ (NaClO_4), $T = 31.0 \pm 1.0^\circ\text{C}$ and $\lambda_{\text{max}} = 670 \text{ nm}$

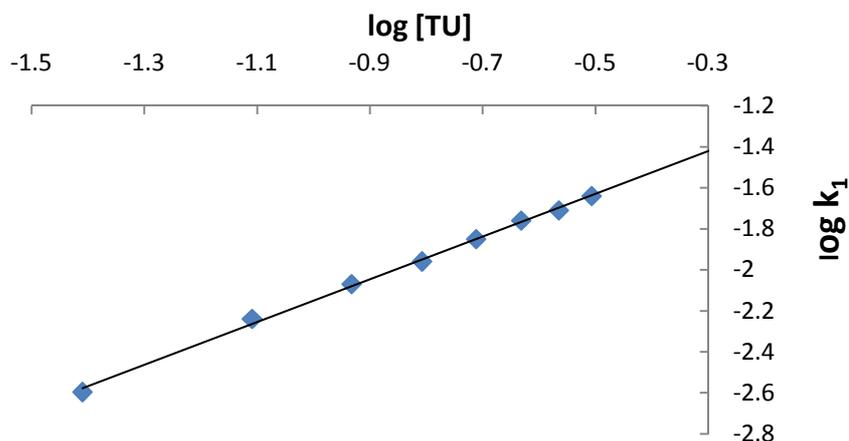


Figure 3: Plot of $\log k_1$ versus $\log [\text{TU}]$ for the oxidation of TU by $[\text{Co}(\text{O})_2\text{Co}^{5+}]$
 $[\text{Co}(\text{O}_2)\text{Co}^{5+}] = 7.77 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{TU}] = (3.89 - 31.09) \times 10^{-2} \text{ mol dm}^{-3}$,
 $[\text{H}^+] = 0.04 \text{ mol dm}^{-3}$, $\mu = 0.25 \text{ mol dm}^{-3}$ (NaClO_4), $T = 31.0 \pm 1.0^\circ\text{C}$ and $\lambda_{\text{max}} = 670 \text{ nm}$

Effect of hydrogen ion concentration

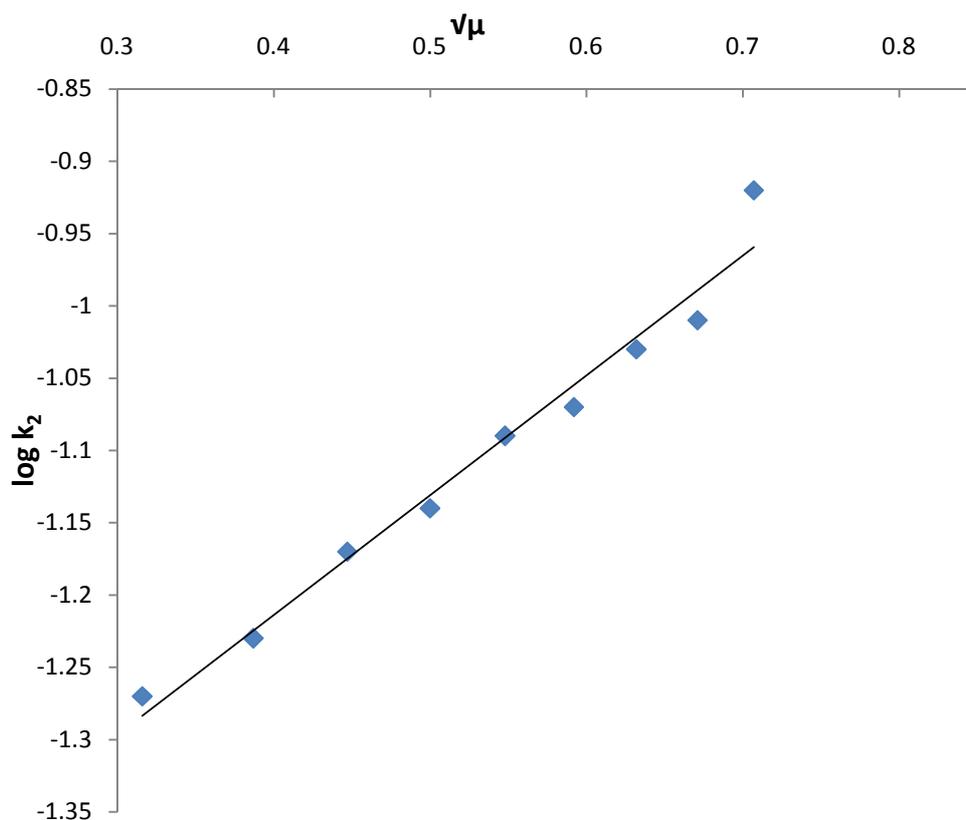
The effect of the $[\text{H}^+]$ on the rate of reaction within the range $(1.0-16.0) \times 10^{-2} \text{ mol dm}^{-3}$ is reported in Table 1. The rates were found to present interesting results: at low $[\text{H}^+]$ of $(1.0-6.0) \times 10^{-2} \text{ mol dm}^{-3}$, the rate constant was insensitive to the change in $[\text{H}^+]$. A little increase in rate was noticed within $(8.0-16.0) \times 10^{-2} \text{ mol dm}^{-3}$ and at higher $[\text{H}^+]$ $(18.0-22.0) \times 10^{-2} \text{ mol dm}^{-3}$, the reaction rates remain unchanged. Plot of $\log [\text{H}^+]$ against $\log k_1$ gave a slope of 0.101 (an indication of zero order hydrogen ion dependence). This result correlates some earlier acid-dependence studies on this type of dioxygen dicobalt(III) complex [15,13,16]. It has also been reported that at $\text{pH} > 2-3$ decomposition of this complex do occurs [9]. Furthermore, the observed second-order rate constants, during the course of reactions of this complex with iron(II), have the form

$$k_{\text{obs}} = k_1[\text{H}^+]^{-1} + k_2 + k_3[\text{H}^+] \quad \text{-----3}$$

k_1 is reported to be small and k_3 negligible, and there is essentially no hydrogen ion dependence [9]. Equation 3 fits into the present observed second-order rate constants in which $k_{\text{obs}} = k_2$. Hence the rate equation is as represented in equation 2.

Table 1: Pseudo-first order and second order rate constants for the oxidation of TU by $[\text{Co}(\text{O}_2)\text{Co}^{5+}]$ at $T = 31.0 \pm 1.0^\circ\text{C}$, $[\text{Co}(\text{O}_2)\text{Co}^{5+}] = 7.77 \times 10^{-4} \text{ mol dm}^{-3}$, $\lambda_{\text{max}} = 670 \text{ nm}$

$10^2[\text{TU}]$ (mol dm^{-3})	$10^3[\text{H}^+]$ (mol dm^{-3})	μ (mol dm^{-3})	10^3k_1 (s^{-1})	10^3k_2 ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)
3.89	4.0	0.25	2.53	6.50
7.78	4.0	0.25	5.76	7.40
11.66	4.0	0.25	8.52	7.31
15.55	4.0	0.25	11.05	7.12
19.43	4.0	0.25	14.28	7.35
23.32	4.0	0.25	17.27	7.41
27.21	4.0	0.25	19.58	7.18
31.09	4.0	0.25	23.03	7.41
11.66	1.0	0.25	8.06	6.91
11.66	2.0	0.25	8.29	7.11
11.66	4.0	0.25	8.52	7.31
11.66	6.0	0.25	8.87	7.61
11.66	8.0	0.25	9.21	7.90
11.66	10.0	0.25	9.90	8.49
11.66	12.0	0.25	10.13	8.69
11.66	14.0	0.25	10.36	8.88
11.66	16.0	0.25	11.28	9.69
11.66	4.0	0.10	6.22	5.33
11.66	4.0	0.15	6.91	5.92
11.66	4.0	0.20	7.83	6.72
11.66	4.0	0.25	8.52	7.31
11.66	4.0	0.30	9.44	8.10
11.66	4.0	0.35	9.90	8.49
11.66	4.0	0.40	10.82	9.28
11.66	4.0	0.45	11.52	9.88
11.66	4.0	0.50	14.04	12.04

**Figure 4:** Plot of $\log k_2$ versus $\sqrt{\mu}$ for the oxidation of TU by $\text{Co}(\text{O}_2)\text{Co}^{5+}$
 $[\text{Co}(\text{O}_2)\text{Co}^{5+}] = 7.77 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{TU}] = 11.66 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{H}^+] = 0.04 \text{ mol dm}^{-3}$, $\mu = 0.10 - 0.50 \text{ mol dm}^{-3}$ (NaClO_4), $T = 31.0 \pm 1.0^\circ\text{C}$
and $\lambda_{\text{max}} = 670 \text{ nm}$

The effect of ionic strength of the medium

The effect of varying ionic strength of the medium on the rate of reaction as the concentrations of other reactants were kept constant was investigated in the range (0.10 – 0.50) mol dm⁻³ (NaClO₄). The relationship of reaction rate with changes in the ionic strength was determined by plotting log *k*₂ against √μ (Figure 4). The rate of reaction was found to increase with increase in ionic strength with a positive slope of 0.83. This is an indication of like charges operating at the rate determining step and in this case, a positively charged TU reacting with Co(O₂)Co⁵⁺.

The effect of added anions

At constant concentration for each of other reactants, the effect of added anions, X, (X = NO₃⁻ or CH₃CHOO⁻) on the rates of the reactions was investigated in the range 20.0 x 10⁻² – 100.0 x 10⁻³ mol dm⁻³. The reaction rate was found to be catalyzed by these anions as shown in Table 2. This result is similar to that reported by Sykes (1963). The anion catalysis suggests that this reaction most probably proceeds by the outer-sphere mechanism Anion catalyzed reaction are thought to be characteristic of outer-sphere reactions [17].

Table 2: Dependence of rate constant on anions for the oxidation of thiourea by [Co(O₂)Co⁵⁺] at T = 31.0 ± 1.0°C, λ_{max} = 670 nm, [Co(O₂)Co⁵⁺] = 7.77 x 10⁻⁴ mol dm⁻³, [TU] = 11.66 x 10⁻² mol dm⁻³, [H⁺] = 0.04 mol dm⁻³, μ = 0.25 mol dm⁻³ (NaClO₄)

X	10 ³ [X] mol dm ⁻³	10 ³ <i>k</i> ₁ (s ⁻¹)	10 ⁴ <i>k</i> ₂ (dm ³ mol ⁻¹ s ⁻¹)
NO ₃ ⁻	0	8.52	7.31
	20	9.21	7.90
	40	9.90	8.49
	60	10.36	8.86
	80	10.82	9.28
	100	11.52	9.88
CH ₃ CHOO ⁻	0	8.52	7.31
	20	11.52	9.88
	40	12.90	11.06
	60	13.35	11.45
	80	16.58	14.22
	100	17.73	15.21

The effect of changes in dielectric constant

The effect of medium dielectric constant on the rate of reaction was investigated by using a binary solvent mixture of water and acetone (2 - 10%) (Table 3). A plot of log *k*₁ against 1/D gave the relationship between the second order rate constant and the total dielectric constant (D) of the reaction medium (Figure 4). The rate was found to be enhanced as a function of 1/D giving a positive slope. This implies the presence of unlike charges at the activated complex during the electron transfer process. However, this dependence cannot be explained in terms of a salt effect, but in terms of a solvation process. As the polarity of the medium decreases, the efficiency of electron transfer is no longer solely dependent on the rearrangement of the solvated molecules. Instead, the activation energy is a function of both the concentration of the solvated molecules around the reactants and deformation of the encounter species [18].

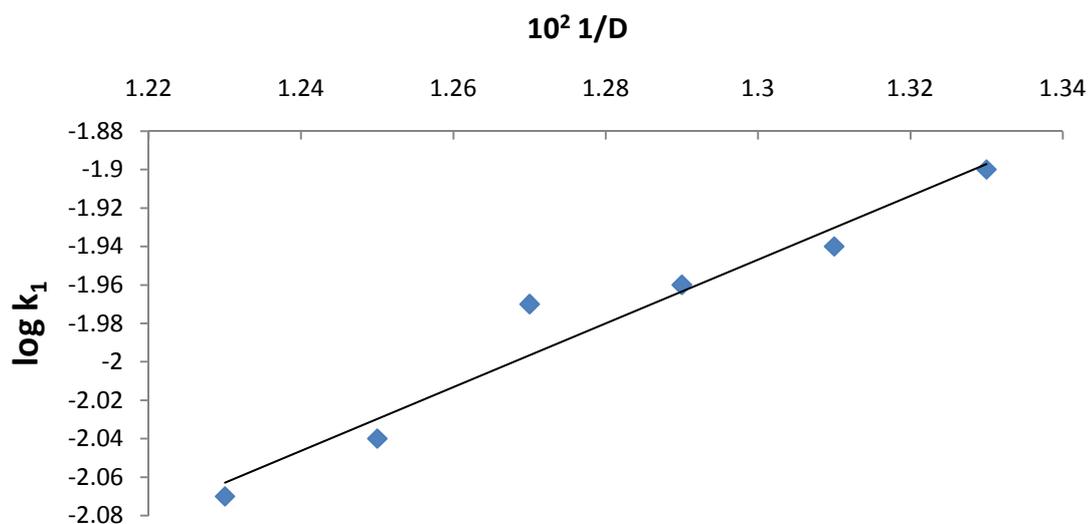


Figure 6: A plot of log *k*₁ versus 1/D for the oxidation of TU by [Co(O₂)Co⁵⁺] [Co(O₂)Co⁵⁺] = 7.77 x 10⁻⁴ mol dm⁻³, [TU] = 11.66 x 10⁻² mol dm⁻³, [H⁺] = 0.04 mol dm⁻³, μ = 0.25 mol dm⁻³ (NaClO₄), T = 31.0 ± 1.0°C and λ_{max} = 670 nm

Table 3: Dependence of rate constant on dielectric constant for the oxidation of thiourea by $\text{Co}(\text{O}_2)\text{Co}^{5+}$ at $T = 31.0 \pm 1.0^\circ\text{C}$, $\lambda_{\text{max}} = 670$ nm, $[\text{Co}(\text{O}_2)\text{Co}^{5+}] = 7.77 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{TU}] = 11.66 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{H}^+] = 0.04 \text{ mol dm}^{-3}$, $\mu = 0.25 \text{ mol dm}^{-3}$ (NaClO_4)

D	$10^2 1/D$	$10^3 k_1 (\text{s}^{-1})$	$10^2 k_2 (\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})$
81.00	1.23	8.52	7.31
79.96	1.25	9.21	7.90
78.32	1.27	10.61	9.09
77.37	1.29	11.05	9.48
76.11	1.31	11.55	9.90
75.00	1.33	12.66	10.86

Tests for intermediate complex formation

Spectroscopic test

The electronic spectra of the reaction mixtures were run over a range of wavelength (400-700nm). The plot of absorbance against wavelength shows that there was no shift in the λ_{max} (Figure 7). This is suggestive of the absence of the formation of intermediate complex in the reaction and thus there is no inner-sphere intermediate complex formation prior to the electron-transfer step. Alternatively, if any such intermediate complex was formed, it must have had a small formation constant [19].

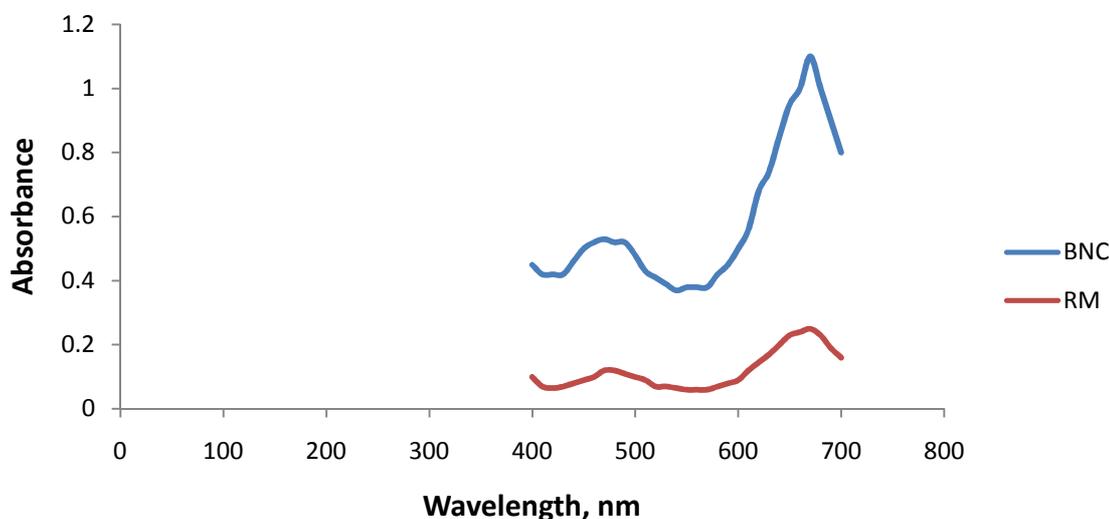


Figure 7: Spectra of $[\text{Co}(\text{O}_2)\text{Co}^{5+}]$ and that of reaction mixture.
BNC = $[\text{Co}(\text{O}_2)\text{Co}^{5+}]$ and RM = reaction mixture

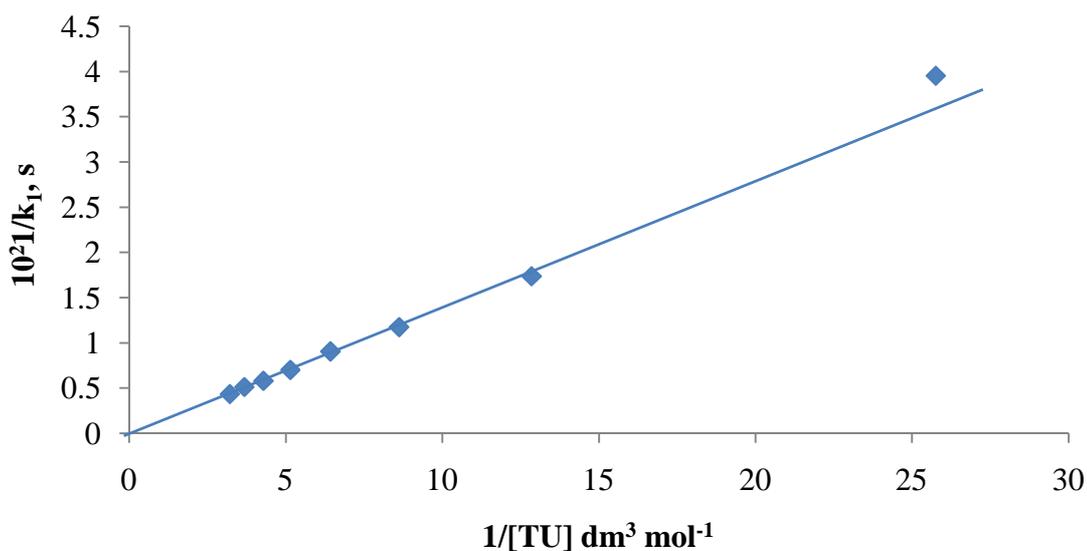


Figure 9: Michaelis-Menten plot of $1/k_1$ versus $1/[\text{TU}]$ for the oxidation of TU by $\text{Co}(\text{O}_2)\text{Co}^{5+}$
 $[\text{Co}(\text{O}_2)\text{Co}^{5+}] = 7.77 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{TU}] = (3.89 - 27.21) \times 10^{-2} \text{ mol dm}^{-3}$,
 $[\text{H}^+] = 0.04 \text{ mol dm}^{-3}$, $\mu = 0.25 \text{ mol dm}^{-3}$ (NaClO_4), $T = 31.0 \pm 1.0^\circ\text{C}$ and $\lambda_{\text{max}} = 670 \text{ nm}$

Michaelis-Menten plot

Michaelis-Menten plot of $1/k_1$ versus $1/TU$ was plotted (Figure 9). The plot was linear with no intercept. This is an indication of absence of an intermediate complex in one of the steps preceding the rate determining step.

Free radical test

Addition of acrylamide to partially oxidized reaction mixture followed by excess methanol showed no gel formation. This is suggestive of absence of free radical formation during the electron transfer.

Product analysis

A blue colour was obtained on the addition of KSCN solution in excess acetone. This is a qualitative confirmatory test for the presence of Co^{2+} as a product for the reaction under study.

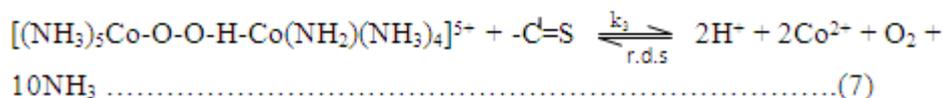
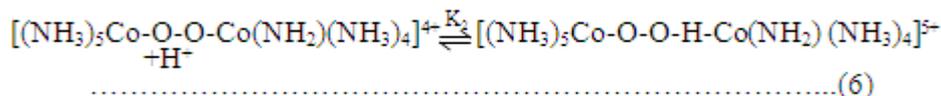
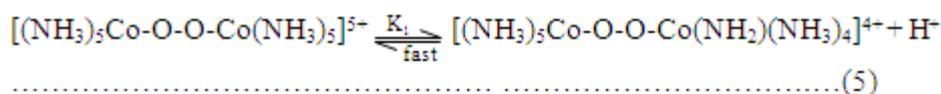
Addition of acidified $BaCl_2$ solution gave a white precipitate, an indication that SO_4^{2-} ion was formed as one of the products. An attempt was made to use infrared spectroscopy to buttress the qualitative tests to analyze the products formed. The center of electron transfer is the C=S functional group in thiourea. Loss of electrons is expected to change the stretching/vibrational frequencies especially the $\nu(C=S)$ mode into the $\nu(C=O)$ mode if thiourea is oxidized into urea. Also, the vibrational frequency due to NH_3 in the complex is compared with the product. The $\nu(C=S)$ that was at $642-754\text{ cm}^{-1}$ in the pure compound is missing in the product. The $\nu(C=O)$ mode is observed at 1643.41 cm^{-1} . This compares favourably with literature values of $696-754\text{ cm}^{-1}$ and $1638-1668\text{ cm}^{-1}$ respectively [20].

Mechanism

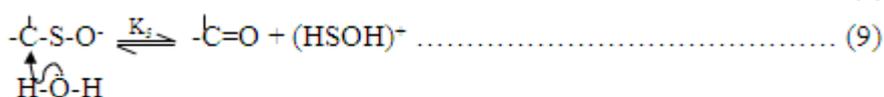
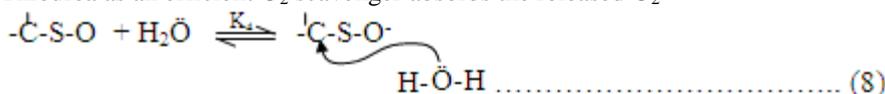
The kinetic data obtained from this study, and the results of earlier investigations [9, 21, 14, 22], suggest that:

- (1). the oxidation of this complex by thiourea is through a two electron reduction process.
- (2). The Co(III) and the dioxygen centers are both reduced through initial conversion of the complex to the hydroperoxo complex which rapidly decomposes to Co^{2+} , NH_3 , e.t.c.
- (3) The O_2 released were scavenged by thiourea and itself oxidized to urea and sulphate ions. Hence the following mechanism is proposed for the oxidation of thiourea by $Co(O_2)Co^{5+}$.

The first step is the conversion of the complex into a hydro-peroxo-type in acidic medium used:



Thiourea as an efficient O_2 scavenger absorbs the released O_2



From equations 5-7, Rate = $k_2 [Co_2(O_2)(NH_3)_{10}][TU]$

where $k_2 = (2.65 \pm 0.15) \times 10^{-2} \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$; $(TU) = -C^I=S$

The pathway for this reaction can be assessed by considering the following points:

- (1). The absence of spectrophotometric evidence suggests that a precursor complex is probably not formed prior to electron transfer and that the redox reaction may occur by the outer-sphere path.

(2). The Michaelis-Mentens plot of $1/k_1$ versus $1/[\text{Co}(\text{O}_2)\text{Co}^{5+}]$ was linear passing through the origin, indicating the absence of a pre-association step. The absence of kinetic evidence for the formation of a precursor complex is not in favour of the inner-sphere path.

(3) The positive salt effects suggests that in the rate determining steps, one or more of such steps involves molecules of similar charges which is in agreement with the experimental results.

(4). It was observed that the rate of this reaction was enhanced by added CH_3COO^- and NO_3^- ions, suggesting outer sphere mechanism.

In view of the above results, the outer-sphere mechanism is the most probable mechanism that best explain the experimental data in this study.

CONCLUSION

The oxidation of thiourea by μ -superoxo-bis[pentaamminecobalt(III)] pentachloride monohydrate has been carried out in aqueous perchloric acid. Kinetic data suggests that the reaction involves successive oxygen additions (from the dioxygen cobalt(III) complex) on the sulphur atom with the cleavage of the sulphur-carbon bond when the sulphur attains the sulphuric acid oxidation state. Major products formed were confirmed to be Co^{2+} and urea.

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