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Kinetic studies of 1-methyl-2-thiourea with superoxide coordinated to cobalt(III)

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ABSTRACT

At $[H^+] = 0.04$ *mol* dm^{-3}, $\mu = 0.25$ *mol* dm^{-3} $(NaClO_4)$, $T = 31.0 \pm 1.0°C$ *and* $\lambda = 670$ *nm, the bridging superoxide in* $[(NH_3)_5Co(O_2)Co(NH_3)_5]Cl_5.H_2O$, *herein refer to as* $Co(O_2)Co^{5+}$, *quantitatively oxidizes 1-methyl-2-thiourea (MTU) to the corresponding urea derivative, itself being reduced to molecular oxygen and Co(II) in aqueous perchloric acid. The reaction obeys the empirical rate law:*

$$-d[Co(O_2)Co^{5+}]/dt = k_2[Co(O_2)Co^{5+}][MTU]$$

with $k_2 = (2.65 \pm 0.15) \times 10^{-2}$ dm^3 mol^{-1} s^{-1}. *The rate of the reaction increased with increase in ionic strength of reaction medium. There is no evidence for the formation of an intermediate complex of significant stability and free radicals are not detected in the reaction. Added anions catalyzed the reaction. Based on the experimental data obtained, the outer-sphere mechanism is proposed.*

Key words: Kinetics, superoxide, 1-methyl-2- thiourea, oxidation, reaction mechanism.

INTRODUCTION

The binding, transport, and activation of molecular oxygen by metal complexes is a topic of wide, current interest due to the many implications that such metal containing systems have in both biomimetic and abiotic processes involving dioxygen [1]. Peroxo and superoxo complexes, also called dioxygen, complexes are known for most transition metals. They are of considerable interest because of their relevance to the study of biological processes involving uptake and reduction of oxygen [2, 3, 1, 4]. Edward *et al.*, (1974).have reported that a given superoxo complex can show important mechanistic variations with apparently similar reducing agents. We have shown previously, from laboratory investigations, that a synthetic oxygen carrier, a binuclear oxygenated cobalt(III) complex readily oxidizes thiourea to urea and itself being reduced to Co(II) [5]. We herein present the kinetics of the oxidation of 1-methyl-2-thiourea (MTU) - a proximate toxicant and a ring cleavage metabolite [6] - by the same complex. This is our second report in a series of oxidation of the thioureas with $Co(O_2)Co^{5+}$.

EXPERIMENTAL SECTION

The pure chlorate salt of the complex, $[(NH_3)_5Co(O_2)Co(NH_3)_5]Cl_5.H_2O$, was synthesized and characterized as reported earlier [7, 5]. All other materials were of analytical grade reagent and used as received. All solutions were prepared in distilled water. Standard perchloric acid was used as a source of hydrogen ion. Kinetic runs were carried out under subdued light. Absorbances and UV-vis spectra were recorded with a Corning Colorimeter 253 at λ_{max} = 670 nm of the complex. A Shimadzu FTIR-84008 spectrophotometer was used to obtain the infrared spectra.

Stoichiometry

The stoichiometry of the reaction was determined by spectrophotometric titration using the mole ratio method by keeping the concentration of the $Co(O_2)Co^{5+}$ constant at 7.77 x 10^{-4} mol dm^{-3} and varying the concentration of the reductant from 1.94 to 23.32 x 10^{-4} mol dm^{-3} , $[H^+]$ = 0.04mol dm^{-3}, μ = 0.25 mol dm^{-3} ($NaClO_4$), λ_{max} = 670 nm and T = 31.0 ±1.0°C. The absorbances of the reaction mixtures were taken after the reaction had gone to completion as indicated by constant absorbance value obtained over a period of time. The stoichiometry was evaluated from the plot of absorbances versus mole ratio (Figure 1).

Kinetic measurements

All kinetic measurements were made under pseudo-first order condition with the concentration of 1-methyl-2-thiourea at least 30 times greater than that of $Co(O_2)Co^{5+}$. The rates were monitored by following absorbances of the $Co(O_2)Co^{5+}$ at λ_{max} = 670 nm using Corning Spectrophotometer model 253.

The pseudo-first order rate constants in each case were obtained from the plots of log (A_t - A_∞) versus time at various reactant concentrations (A_t and A_∞ are absorbances at time t and at time zero respectively).

The temperature was kept constant at 31.0 ± 1.0°C, $[H^+]$ = 0.04 mol dm^{-3} and the ionic strength of reaction medium was maintained constant at 0.25 mol dm^{-3} ($NaClO_4$) for all runs. A typical pseudo-first order plot is presented in Figure 2.

RESULTS AND DISCUSSION

Stoichiometry

The result of the spectrophotometric titration indicates a 1:1 reaction stoichiometry. The overall reaction is given by equation 1;

$$CoO_2Co^{5+} + CH_3NH(NH_2)C{=}S + 3H_2O \longrightarrow 2Co^{2+} + CH_3NH(NH_2)C{=}O + 3H^+ + SO_4^{2} \qquad (1)$$

A similar stoichiometry was reported for the reduction of CoO_2Co^{5+} by thiourea [5] and for its reaction with VO^{2+}, Sn^{2+}, As^{3+} and $S_2O_3^{2-}$ ions [8, 9].

Product analysis

The reaction products were confirmed by qualitative analysis and infrared spectroscopy.

(1) The Co^{2+} in the product was confirmed by adding 5 drops of 0.50 mol dm^{-3} potassium thiocyanate to 10 drops of the solution. An equal volume of acetone was added and mixed thoroughly. A blue colour was obtained indicating the formation of $[Co(NCS)_4]^{2+}$.

(2) Addition of acidified $BaCl_2$ solution gave a white precipitate- an indication that SO_4^{2-} ion was formed as one of the reaction products.

(3) Infrared spectra of the dioxygen complex and that of 1-methyl-2-thiourea were obtained separately in the region 500 - 4000cm^{-1} prior to the reaction and after the reaction. The υ(C=S) that was at 610-730 cm^{-1} in the pure compound is missing in the reaction product. Meanwhile, a new frequency was observed at 1643.41cm^{-1} in the product and is assigned to the υ(C=O) mode. This compares favourably with literature values of 696-754 cm^{-1} and 1638 – 1668 cm^{-1} respectively [10, 11, 12]. This observation suggests that the 1-methyl-2-thiourea has been oxidized to urea.

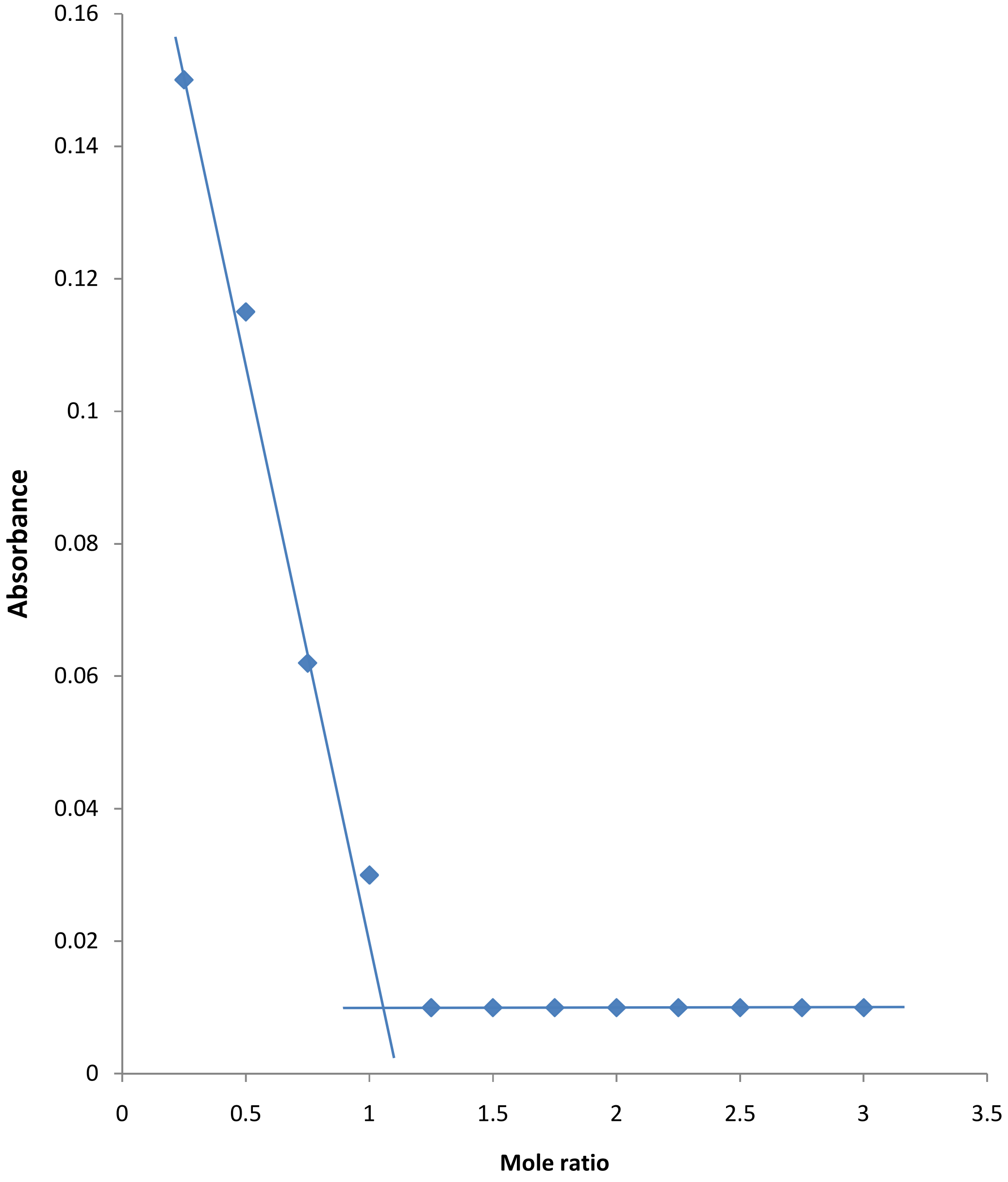

Figure 1: Plot of absorbance versus mole ratio for the determination of the stoichiometry of the oxidation of MTU by CoO_2Co^{5+} at $[CoO_2Co^{5+}]$ = 7.77 x 10^{-4} mol dm^{-3}, [MTU] = (1.94 – 23.32) x 10^{-4} mol dm^{-3}, $[H^+]$ = 0.04 mol dm^{-3}, μ = 0.25 mol dm^{-3} ($NaClO_4$), T = 31.0 ± 1.0°C and λ_{max} = 670 nm

Kinetic measurements

The pseudo-first order plots of log (A_t - A_∞) versus time were linear to more than 90% extent of reaction, indicating that the reaction is first order in $[CoO_2Co^{5+}]$ under the experimental conditions (Figure 2). This is further buttressed by the values of second order rate constant, k_2, which were fairly constant (Table 1). The plot of log k_1 versus log [MTU] was linear with a slope of 1.29 (Figure 3). This suggests a first order dependence on [MTU]. Therefore, the rate equation for the reaction is represented by equation 2;

$$-d[CoO_2Co^{5+}]/dt = k_2[CoO_2Co^{5+}][MTU] \qquad (2)$$

where $k_2 = (2.65 \pm 0.15) \times 10^{-2}\ dm^3\ mol^{-1}\ s^{-1}$

This finding is similar to the one observed by Mishra *et al.*,[13] in the reduction of this complex with hydrogen peroxide and also similar to our earlier work with thiourea [5].

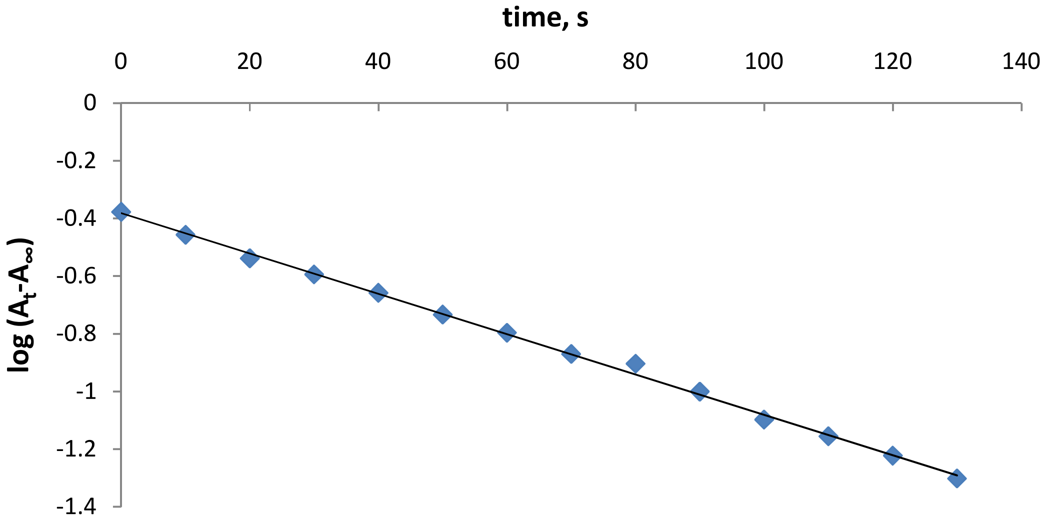

Figure 2: Typical Pseudo-first order plot for the oxidation of MTU by CoO_2Co^{5+} at $[CoO_2Co^{5+}] = 7.77 \times 10^{-4}$ mol dm^{-3}, [MTU] = 9.72×10^{-2} mol dm^{-3}, $[H^+] = 0.04$ mol dm^{-3}, μ = 0.25 mol dm^{-3} ($NaClO_4$), T = 31.0 ± 1.0°C and λ_{max} = 670 nm

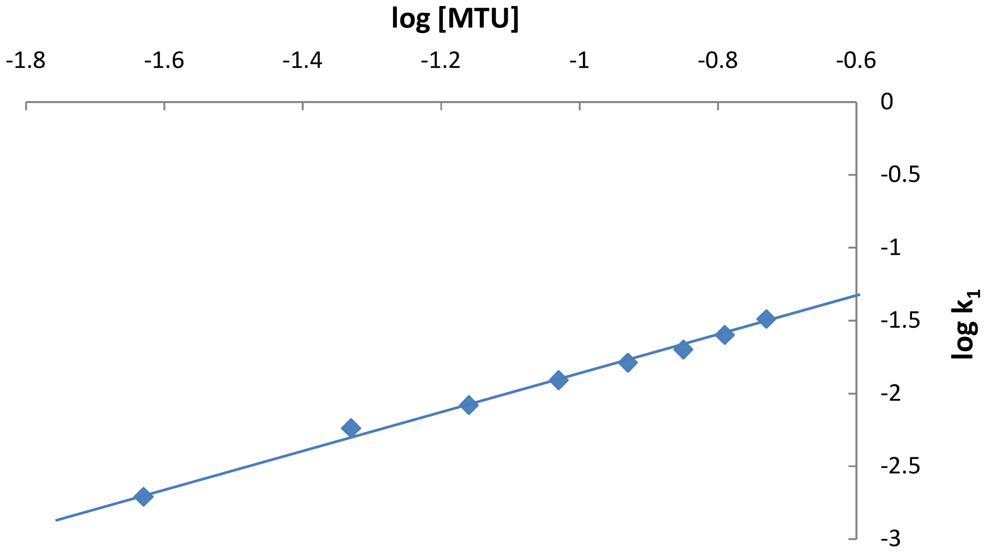

Figure 3: Plot of log k_1 versus log [MTU] for the oxidation of MTU by CoO_2Co^{5+} at $[CoO_2Co^{5+}] = 7.77 \times 10^{-4}$ mol dm^{-3}, [MTU] = (2.33 – 18.65) x 10^{-2} mol dm^{-3}, $[H^+] = 0.04$ mol dm^{-3}, μ = 0.25 mol dm^{-3} ($NaClO_4$), T = 31.0 ± 1.0°C and λ_{max} = 670 nm

Table 1: Pseudo-first order and second order rate constants for the oxidation of MTU by $[CoO_2Co^{5+}]$ at T = 31.0 ± 1.0°C, $[CoO_2Co^{5+}]$ = 7.77×10^{-4} mol dm^{-3} and λ_{max} = 670 nm

10^2[MTU] (mol dm^{-3})	$10^2[H^+]$ (mol dm^{-3})	μ (mol dm^{-3})	10^3k_1 (s^{-1})	$10k_2$ ($dm^3 mol^{-1} s^{-1}$)
2.33	4.0	0.25	1.96	2.60
4.66	4.0	0.25	4.84	2.61
6.99	4.0	0.25	8.29	2.63
9.33	4.0	0.25	12.21	2.66
11.66	4.0	0.25	16.12	2.63
13.99	4.0	0.25	19.81	2.55
16.32	4.0	0.25	25.33	2.67
18.65	4.0	0.25	32.01	2.84
6.99	1.0	0.25	8.17	2.60
6.99	2.0	0.25	8.17	2.60
6.99	4.0	0.25	8.29	2.64
6.99	6.0	0.25	8.40	2.67
6.99	8.0	0.25	9.44	3.00
6.99	10.0	0.25	10.13	3.20
6.99	12.0	0.25	10.36	3.29
6.99	14.0	0.25	9.67	3.07
6.99	16.0	0.25	8.25	2.71
6.99	4.0	0.10	5.30	1.68
6.99	4.0	0.15	6.22	1.98
6.99	4.0	0.20	7.37	2.34
6.99	4.0	0.25	8.29	2.63
6.99	4.0	0.30	9.90	3.14
6.99	4.0	0.35	11.98	3.81
6.99	4.0	0.40	14.97	4.76
6.99	4.0	0.45	17.50	5.56

Acid dependence

The effect of the $[H^+]$ on the rate of reaction within the range (1.0 - 16.0) x 10^{-2} mol dm^{-3} is reported in Table 1. The reaction rate was found to be virtually independent of the change in acid concentration. This result was found to be similar to the effect of hydrogen ions on the oxidation of thiourea by the same complex. This result correlates with some earlier acid dependence studies on this type of dioxygen complex [9, 14]. It has been reported that at pH > 2-3 decomposition of the complex do occur [9]. Furthermore, the observed second-order rate constants, during the course of reactions of the complex with iron(II), have the form

$$k_{obs} = k_1[H^+]^{-1} + k_2 + k_3[H^+] \qquad (3)$$

k_1 is reported to be small and k_3 negligible, and there is essentially no hydrogen ion dependence [119]. Equation 3 fits into the present observed second order rate constants in which $k_{obs} = k_1$. Hence the rate equation is as represented in equation 2.

Effect of added anion on the reaction rate

The effect of added CH_3COOO^- and NO_3^- on the rate was studied and the result is presented in Table 2. There was an increase in the rate of the reaction due to the presence of added anions. The catalysis of this reaction by the anions suggests that the reaction occurs by the outer-sphere mechanism [15, 16]. This result is similar to that reported by Sykes [8].

Effect of ionic strength

The effect of ionic strength on the rate of the reaction was studied over the range of 0.10 – 0.50 mol dm^{-3} ($NaClO_4$) while concentrations of the reactants were kept constant. The results presented in Table 1 show that the rate constants increase with increase in ionic strength of reaction medium indicating a positive Bronsted- Debye salt effect. A plot of log k2 versus $\sqrt{\mu}$ gave a slope of 1.46 (Fig 4). These indicate that there is most likely no bond formation between the reactants at the transition state [17].

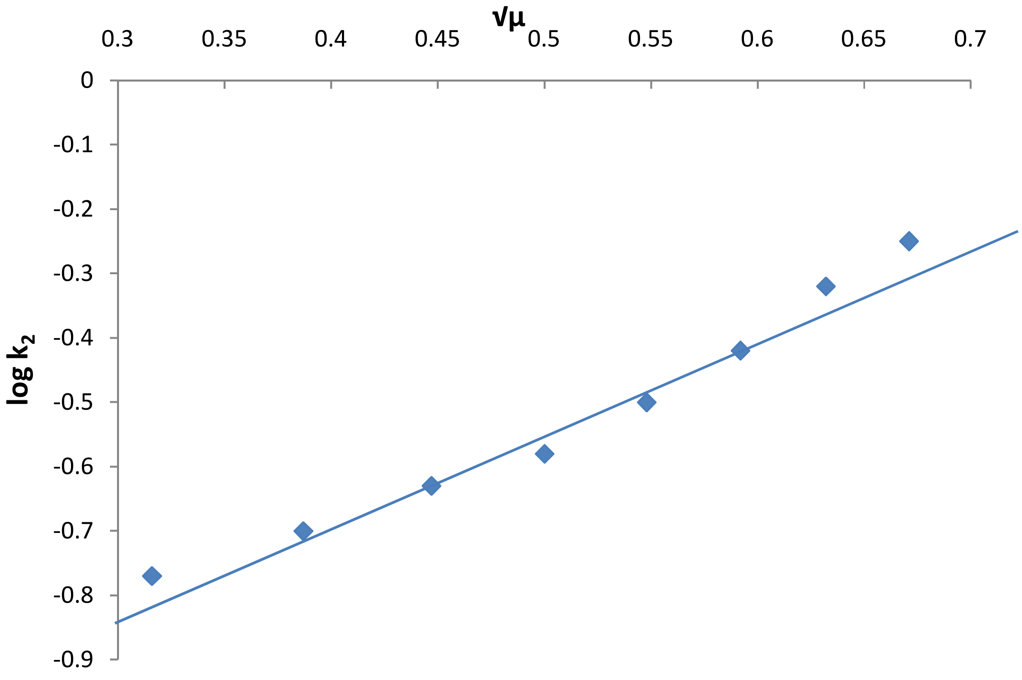

Figure 4: Plot of logk$_2$ versus √μ for the oxidation of MTU by CoO_2Co^{5+} at $[CoO_2Co^{5+}] = 7.77 \times 10^{-4}$ mol dm^{-3}, [MTU] = 6.99×10^{-2} mol dm^{-3}, $[H^+] = 0.04$ mol dm^{-3}, μ = 0.10 - 0.45 mol dm^{-3} ($NaClO_4$), T = 31.0 ± 1.0°C and λ_{max} = 670 nm

Table 2: Dependence of rate constant on anions for the oxidation of 1-methyl-2-thiourea by $[CoO_2Co^{5+}]$ at T = 31.0 ± 1.0°C, λ_{max} = 670 nm, $[CoO_2Co^{5+}] = 7.77 \times 10^{-4}$ mol dm^{-3}, [MTU] = 6.99×10^{-2} mol dm^{-3}, $[H^+] = 0.04$ mol dm^{-3}, μ = 0.25 mol dm^{-3} ($NaClO_4$)

X	10^3[X] (mol dm^{-3})	10^3k_1(s^{-1})	$10k_2$(dm^{3}mol^{-1} s^{-1})
NO_3^-	0	8.29	2.63
	20	8.52	2.71
	40	9.21	2.93
	60	9.67	3.07
	80	10.13	3.22
	100	10.59	3.37
CH_3CHOO^-	0	8.29	2.63
	20	8.75	2.78
	40	9.90	3.15
	60	12.21	3.88
	80	14.51	4.61
	100	17.27	5.49

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 of the reaction medium (Figure 4). The rate was found to increase as a function of 1/D giving positive slopes. According to electron transfer theory, changes in dielectric properties are expected to affect reorganization of a solvent molecule around the reactant and the activated complex [18]. This observation is in support of the influence the ionic strength had on the rate of these reactions which suggests a positive ion – dipole reactions prior to the electron transfer.

Table 3: Dependence of rate constant on anions for the oxidation of 1-methyl-2-thiourea by [CoO_2Co^{5+}] at T = 31.0 ± 1.0°C, λ_{max} = 670 nm, [CoO_2Co^{5+}] = 7.77 x 10^{-4} mol dm^{-3}, [MTU] = 6.99 x 10^{-2} mol dm^{-3}, [H^+] = 0.04 mol dm^{-3}, μ = 0.25 mol dm^{-3} ($NaClO_4$)

D	10^2 1/D	$10^3k_1(s^{-1})$	$10k_2\,(dm^3mol^{-1}s^{-1})$
81.00	1.23	8.29	2.63
79.80	1.25	8.75	2.78
78.60	1.27	9.21	2.93
77.40	1.29	9.44	3.00
76.20	1.31	10.59	3.37
75.00	1.33	11.52	3.66

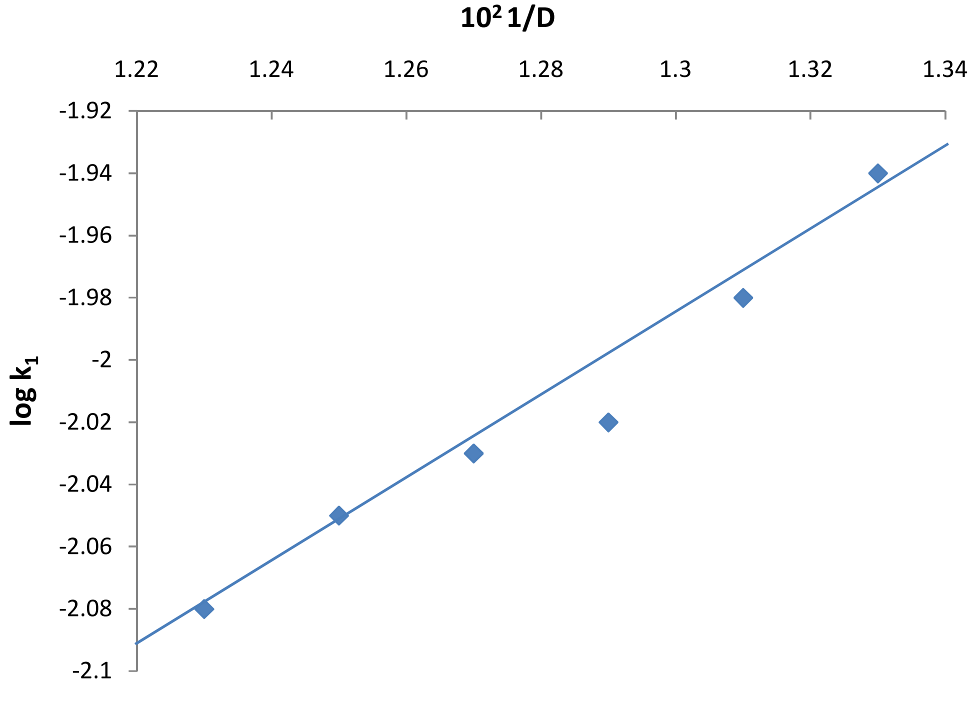

Figure 6: A plot of log k_1 versus 1/D for the oxidation of MTU by CoO_2Co^{5+} at [CoO_2Co^{5+}] = 7.77 x 10^{-4} mol dm^{-3}, [MTU] = 6.99 x 10^{-2} mol dm^{-3}, [H^+] = 0.04 mol dm^{-3}, μ = 0.25 mol dm^{-3} ($NaClO_4$), T = 31.0 ± 1.0°C and λ_{max} = 670 nm

Tests for Intermediate Complex

Spectroscopic studies

The result of spectroscopic studies over a range of wavelength (400 – 700 nm) indicates no significant shifts from the absorption maximum of 670 nm characteristics of CoO_2Co^{5+}. This is suggestive of the absence of the formation of an intermediate complex in the reactions (Figure 7).

Michaelis-Menten plot

Michaelis-Menten plot of $1/k_1$versus 1/MTU was plotted (Figure 9). The plot was linear with a negligible intercept. This is an indication of the absence of an intermediate complex in one of the steps preceding the rate determining step.

Test for free radical

Addition of a solution of acrylamide to partially reacted mixture did not give a gel in the presence of excess methanol, indicating the probable absence of free radicals in the reaction medium.

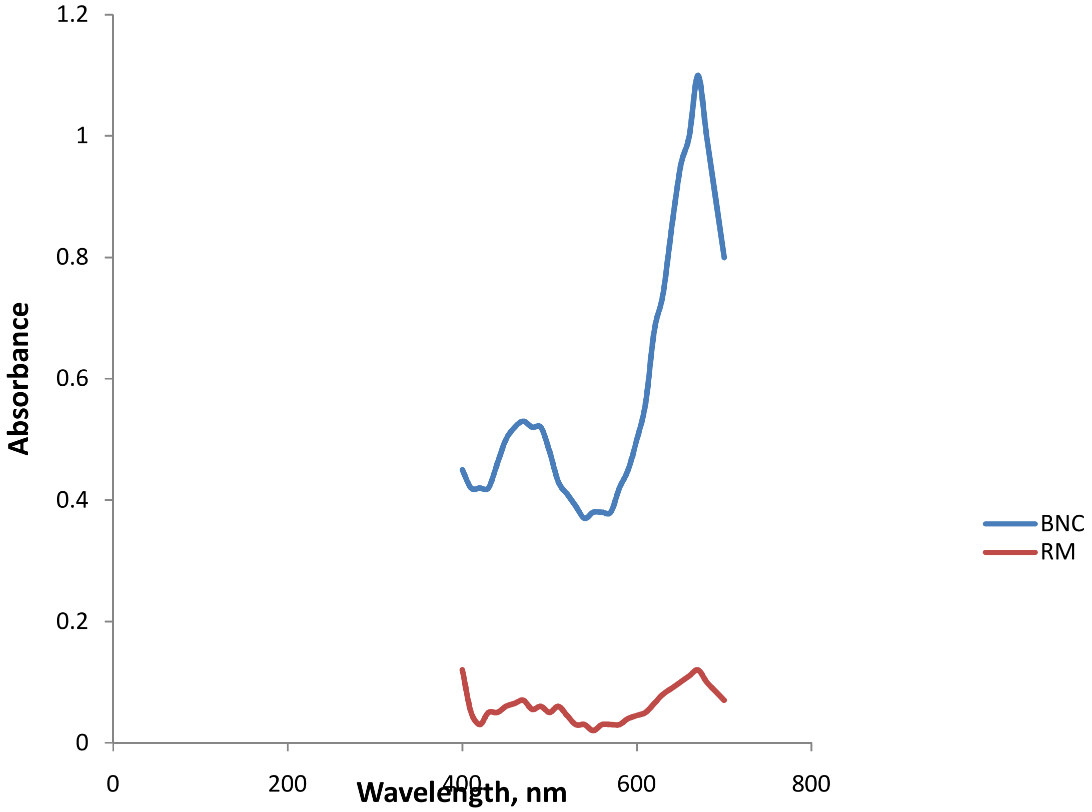

Figure 7: Spectra of CoO_2Co^{5+} and that of reaction mixture (BNC = CoO_2Co^{5+} and RM = reaction mixture)

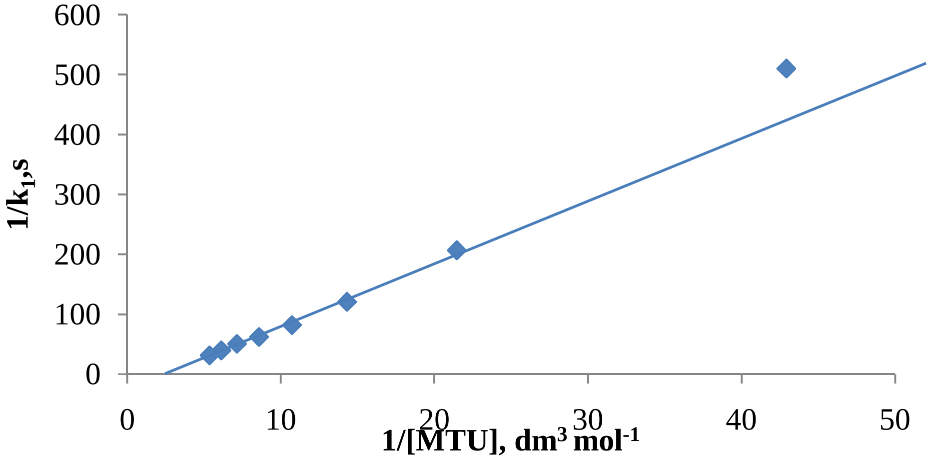

Figure 9: Michaelis-Menten plot of $1/k_1$ versus 1/[MTU] for the oxidation of MTU by CoO_2Co^{5+} at $[CoO_2Co^{5+}] = 7.77 \times 10^{-4}$ mol dm^{-3}, [MTU] = $(2.33 - 18.65) \times 10^{-2}$ mol dm^{-3} $[H^+] = 0.04$ mol dm^{-3}, $\mu = 0.25$ mol dm^{-3} ($NaClO_4$), T = 31.0 ± 1.0°C and $\lambda_{max} = 670$ nm

Reaction mechanism

The kinetic data obtained from this study, and the results of earlier investigations [19, 20, 13, 21], suggest that the mechanism for the present study mimics the dynamics observed in the oxidation of unsubstituted thiourea by CoO_2Co^{5+} which is as follow:

(1). the oxidation of this complex by 1-methyl-2-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 peroxo complex which rapidly decomposes to Co^{2+}, and other products
(3) The O_2 released were scavenged by 1-methyl-2-thiourea and itself oxidized to its urea derivative and sulphate ions.

Hence the following mechanism is proposed:

Let MTU = RS and the superoxo complex = $Co(O_2)Co^{5+}$,

$$Co(O_2)Co^{5+} \underset{H^+}{\overset{K_1}{\rightleftharpoons}} Co(O_2H)Co^{5+} \qquad (3)$$

$$Co(O_2)Co^{5+} + RS \overset{K_2}{\rightleftharpoons} [Co(O_2)Co^{5+}, RS] \qquad (4)$$

$$[Co(O_2)Co^{5+}, RS] \xrightarrow[Slow]{k_3} 2Co^{2+} + -C=O + \text{other products} \qquad \text{r.d.s } (5)$$

From equation (5),

$$Rate = k_3\,[Co(O_2)Co^{5+}, RS] \qquad (6)$$

From equation (3), and (4)

$$Rate = k_3K_2K_1\,[Co(O_2)Co^{5+}][RS] \qquad (7)$$

Let $k_3K_2K_1 = k$, then equation 7 becomes

Rate = $k[Co(O_2)Co^{5+}][RS]$ which conforms to equation 2

with $k = k_2 = (2.65 \pm 0.15) \times 10^{-2}\ dm^3\ mol^{-1}\ s^{-1}$..

A key point of interest is whether this reaction occurs via the inner or outer-sphere mechanism. The mechanism can then be assessed by considering the following points:

(i) The absence of spectroscopic evidence for the formation of an intermediate suggests that a precursor complex is not formed prior to electron transfer and that the redox reaction most probably occurs by the outer-sphere mechanism.
(ii) Michaelis-Menten's plot of $1/k_1$ versus 1/[MTU] (Fig 9) was linear with an insignificant intercept, indicating the absence of a pre-association step.
(iii) The positive salt effects suggests that in the rate determining steps, one or more of such steps involve charged ions of the same charge which is in agreement with our experimental results.
(iv) It was observed that the rate of this reaction was enhanced by added $CH3COO^-$and $NO3^-$ ions, suggesting outer-sphere mechanism.
(v) The absence of gel formation after the addition of a solution of acrylamide to a partially oxidized reaction mixture suggests the absence of free radical in the reactions.
From the above reasoning, it can be inferred that the spectroscopic and kinetic evidence are in support of the occurrence of the outer-sphere mechanism in the titled reaction.

CONCLUSION

The mechanism of MTU oxidation by CoO_2Co^{5+} showed a similar pathway to that of unsubstituted thiourea by the same complex. The reaction rate is independent of changes in hydrogen ion concentrations but is catalyzed by added anions. Mechanism of the reaction showed a two-electron transfer process to the bridging oxygen atom and the Co(III) center in yielding the products that involves the cleavage of the C-S bond.

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