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### Reaction of 1, 3-Dimethyl-2-Thiourea with Coordinated Superoxide in $[(\text{NH}_3)_5 \text{Co} (\mu\text{-O}_2)\text{Co}(\text{NH}_3)_5]^{5+}$ : A Mechanistic Study

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The reaction of 1, 3-dimethyl-2-thiourea with coordinated superoxide in  $[(\text{NH}_3)_5\text{CO}(\mu\text{-O}_2)\text{CO}(\text{NH}_3)_5]^{5+}$  has been studied at  $0.01 \leq [\text{H}^+] \leq 0.16 \text{ mol dm}^{-3}$  in aqueous perchloric acid medium under pseudo-first order conditions of an excess [DMTU] at  $\mu = 0.25 \text{ mol dm}^{-3}$  ( $\text{NaClO}_4$ ). The reaction is first order with respect to the oxidant and the reductant and is not hydrogen ion concentration dependent. Simple electron transfer is thought to have occurred leading to the oxygenation of the thiocarbamide. The products were analyzed using conventional methods. The reaction has been rationalized on the basis of the outer-sphere electron transfer mechanism.

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**Keyword:** Kinetics, Stoichiometry, Oxidation, Spectroscopy, 1,3-dimethyl-2-thiourea.

#### 1. Introduction

We recently embarked on a systematic study of the kinetics of dioxygen cobalt (III) complex with the thioureas. In our earlier communications, we examined the oxidation of thiourea by oxygenated  $[\text{Co}_2(\text{O}_2)(\text{NH}_3)_{10}]^{5+}$  complex and the reaction of its 1-methyl substituted analogue<sup>[1,2]</sup>. Dioxygen complexes have been investigated in order to gain insight into the mechanisms of oxygen metabolism such as  $\text{O}_2$  transport, storage and activation, which are essential life phenomena. Superoxo- and peroxo- complexes of the transition metals are important intermediates in autoxidations catalyzed by transition metal<sup>[3]</sup>. The importance of dioxygen species as a gas generant in automobiles<sup>[4]</sup>, in photosynthesis and in combustion of materials, is also well recognized<sup>[5]</sup>. On the other hand, a broad spectrum of reagents has been used to probe the reactivity

of thioureas<sup>[6-11]</sup> in the hope that such reactions might advance the understanding of its function *in vivo* and *in vitro*. The choice of substituted thiourea for this study is 1,3-methyl-2-thiourea (DMTU). DMTU is an extremely diffusible, potent scavenger of hydroxyl radical, hydrogen peroxide, and hypochlorous acid, with a long half-life of 43 hours<sup>[12-16]</sup>, that has been used to test the involvement of  $\text{OH}^\cdot$  in several animal models of human diseases<sup>[17]</sup>. Thus, the present investigation, which examines the reaction of 1, 3-dimethyl-2-thiourea with coordinated superoxide in  $[(\text{NH}_3)_5\text{CO}(\mu\text{-O}_2)\text{CO}(\text{NH}_3)_5]^{5+}$ , was undertaken in the light of the points raised above.

#### 2. Experimental

Analar grade reagents: cobalt(II) chloride, ammonia, sodium acetate, sodium nitrate, sodium perchlorate, hydrogen peroxide, 1,3-dimethyl-2-

thiourea ammonium persulphate and perchloric acid were used as received. The superoxo complex,  $[(\text{NH}_3)_5\text{Co}(\text{O}_2)\text{Co}(\text{NH}_3)_5]\text{Cl}_5 \cdot \text{H}_2\text{O}$ , here after referred to as  $(\text{Co}(\text{O}_2)\text{Co}^{5+})$ , was prepared and characterized by a reported procedure<sup>[18]</sup> with some modifications<sup>[4]</sup>. Stock solutions of reagents were always freshly prepared with distilled water and used immediately. A Shimadzu FTIR-84008 spectrophotometer was used to obtain the infrared spectra.

Changes in absorbances of solutions were monitored on Corning Spectronic 253 Spectrophotometer. Kinetic measurements were conducted at 670 nm which is the  $\lambda_{\text{max}}$  of the dioxygen complex under subdued light because of the sensitivity of the complex to light. All kinetic runs were carried out under pseudo- first order conditions with [DMTU] in at least 20-fold excess over  $[\text{Co}(\text{O}_2)\text{Co}^{5+}]$  while the ionic strength was kept constant.

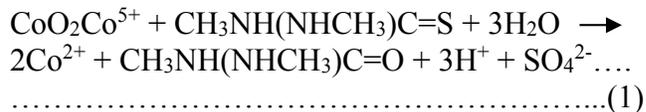
The stoichiometry of the reaction was determined by spectrophotometric titrations as described in literature (Iyun *et al.*, 1995).  $[\text{Co}(\text{O}_2)\text{Co}^{5+}]$  was kept constant at  $7.77 \times 10^{-4} \text{ mol dm}^{-3}$  and [DMTU] varied from  $1.94$  to  $23.32 \times 10^{-4} \text{ mol dm}^{-3}$  at  $[\text{H}^+] = 0.04 \text{ mol dm}^{-3}$ ,  $\mu = 0.25 \text{ mol dm}^{-3}$  ( $\text{NaClO}_4$ ),  $T = 31.0 \pm 1.0 \text{ }^\circ\text{C}$  and the absorbances were measured at 670 nm. A point of inflection (i.e. point at which repeated measurement of absorbance over time showed no change in absorbance) on a curve of absorbance ( $A_\infty$ ) versus mole ratio plot gave the mole ratio corresponding to the reaction stoichiometry.

Plots of  $\log(A_t - A_\infty)$  against time,  $t$  (where  $A_t$  and  $A_\infty$  are the absorbances at time  $t$  and at the end of the reaction respectively) were linear for about 90% extent of reaction. Pseudo-first order rate constants,  $k_1$ , were determined as the slopes of above plots. Second order rate constants,  $k_2$ , were obtained from  $k_1/[\text{DMTU}]$ .

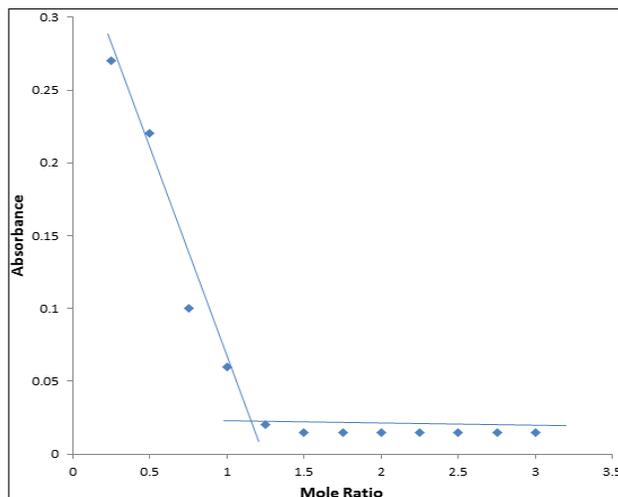
### 3. Results and discussion

#### 3.1 Stoichiometry and product analysis

Stoichiometric studies (Figure 1) indicated a 1:1 stoichiometry as given by equation 1;



This is consistent with what has been reported in our earlier works<sup>[1, 2]</sup> and with  $\text{VO}^{2+}$ ,  $\text{Sn}^{2+}$ ,  $\text{As}^{3+}$  and  $\text{S}_2\text{O}_3^{2-}$  ions<sup>[19, 20]</sup>.



**Fig 1:** Plot of absorbance versus mole ratio for the determination of the stoichiometry of the oxidation of DMTU by  $\text{CoO}_2\text{Co}^{5+}$  at  $[\text{CoO}_2\text{Co}^{5+}] = 7.77 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{DMTU}] = (1.94 - 23.32) \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{H}^+] = 0.04 \text{ mol dm}^{-3}$ ,  $\mu = 0.25 \text{ mol dm}^{-3}$  ( $\text{NaClO}_4$ ),  $T = 31.0 \pm 1.0 \text{ }^\circ\text{C}$  and  $\lambda_{\text{max}} = 670 \text{ nm}$

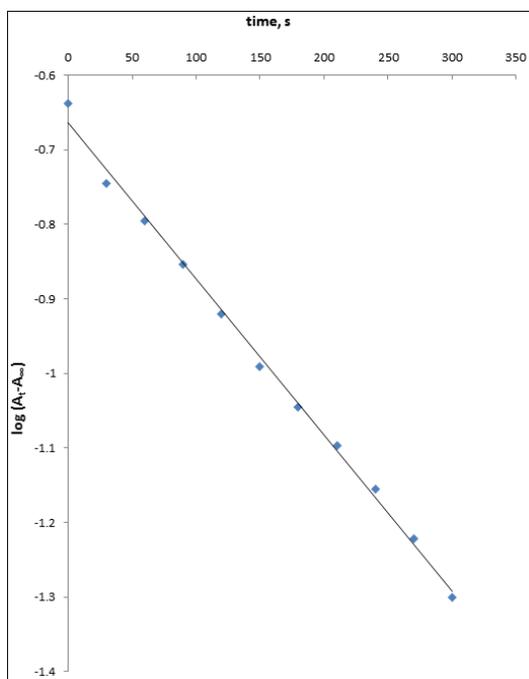
The products in the above reaction represented in equation (1) were confirmed as follows:

- (1) The  $\text{Co}^{2+}$  in the product was confirmed by adding 5 drops of  $0.50 \text{ mol dm}^{-3}$  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  $[\text{Co}(\text{NCS})_4]^{2+}$ .
- (2) Addition of acidified  $\text{BaCl}_2$  solution gave a white precipitate which is an indication that  $\text{SO}_4^{2-}$  ion was formed as one of the products.
- (3) Infrared spectra of the dioxygen complex and that of 1,3-dimethyl-2-thiourea were obtained separately in the region  $500-4000 \text{ cm}^{-1}$  prior to the reaction and after the reaction. The  $\nu(\text{C}=\text{S})$  that was at  $624-713 \text{ cm}^{-1}$  in the pure compound is missing

in the product. Meanwhile, a new frequency was observed at  $1645.33\text{cm}^{-1}$  in the product and is assigned to the  $\nu(\text{C}=\text{O})$  mode. This compares favourably with literature values of  $696\text{--}754\text{ cm}^{-1}$  and  $1638\text{--}1668\text{ cm}^{-1}$  respectively<sup>[21-23]</sup>. This observation suggests that the 1,3-dimethyl-2-thiourea has been oxidized to the urea analogue.

### 3.2 Kinetic measurements

The pseudo-first order plots of  $\log(A_t - A_\infty)$  versus time were linear to more than 90% extent of reaction (Figure 2).



**Fig 2:** Typical pseudo-first order plot for the oxidation of DMTU by  $\text{CoO}_2\text{Co}^{5+}$  [ $\text{CoO}_2\text{Co}^{5+}$ ] =  $7.77 \times 10^{-4}\text{ mol dm}^{-3}$ , [ $\text{DMTU}$ ] =  $9.32 \times 10^{-2}\text{ mol dm}^{-3}$  [ $\text{H}^+$ ] =  $0.04\text{ mol dm}^{-3}$ ,  $\mu = 0.25\text{ mol dm}^{-3}$  ( $\text{NaClO}_4$ ),  $T = 31.0 \pm 1.0\text{ }^\circ\text{C}$  and  $\lambda_{\text{max}} = 670\text{ nm}$

This suggests that there is no product inhibition and the reaction is first order in [ $\text{CoO}_2\text{Co}^{5+}$ ]. Plot of  $\log k_1$  versus  $\log [\text{DMTU}]$  was also linear with a gradient of 1.0 (Figure 3) which is indicative of first order in [ $\text{DMTU}$ ].

In the range  $0.01 \leq [\text{H}^+] \leq 0.16\text{ mol dm}^{-3}$ ,  $k_2$  remains virtually unchanged as shown in Table 1.

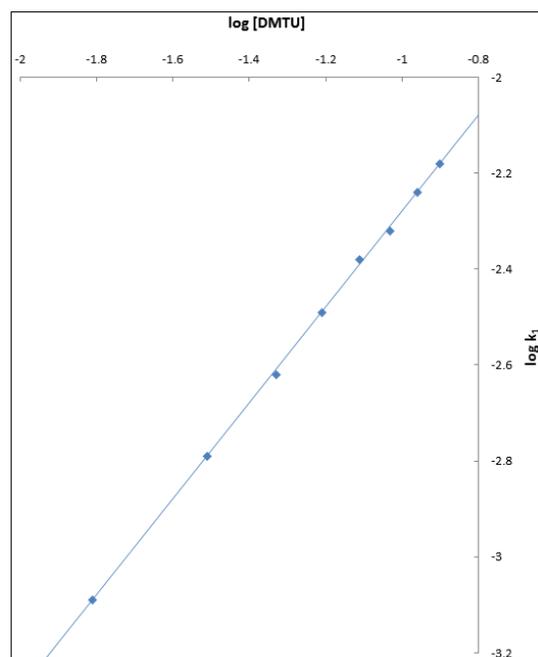
Therefore, the rate equation for the reaction can be represented as in equation 2;

$$-\frac{d[\text{CoO}_2\text{Co}^{5+}]}{dt} = k_2[\text{CoO}_2\text{Co}^{5+}][\text{DMTU}] \quad (2)$$

Where

$$k_2 = (5.24 \pm 0.0689) \times 10^{-2}\text{ dm}^3\text{ mol}^{-1}\text{ s}^{-1}$$

Hydrogen-ion concentration independence is a common feature in redox reactions involving this dioxygen complex as observed by Sykes and Weil<sup>[24]</sup>; Mishra *et al.*,<sup>[25]</sup> in the reduction of this complex with hydrogen peroxide and to our earlier work with thiourea and 1-methyl-2-thiourea<sup>[1,2]</sup>.



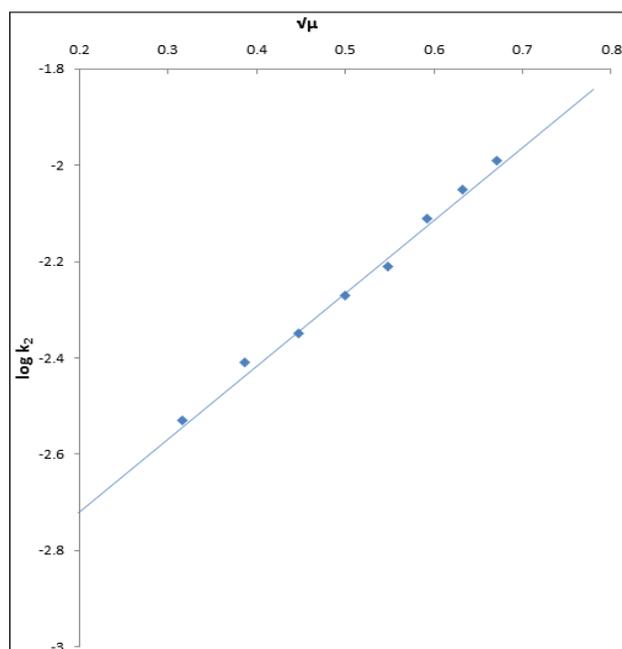
**Fig 3:** Plot of  $\log k_1$  versus  $\log [\text{DMTU}]$  for the oxidation of DMTU by  $\text{CoO}_2\text{Co}^{5+}$  at [ $\text{CoO}_2\text{Co}^{5+}$ ] =  $7.77 \times 10^{-4}\text{ mol dm}^{-3}$ , [ $\text{DMTU}$ ] =  $(1.55\text{--}12.40) \times 10^{-2}\text{ mol dm}^{-3}$  [ $\text{H}^+$ ] =  $0.04\text{ mol dm}^{-3}$ ,  $\mu = 0.25\text{ mol dm}^{-3}$  ( $\text{NaClO}_4$ ),  $T = 31.0 \pm 1.0\text{ }^\circ\text{C}$  and  $\lambda_{\text{max}} = 670\text{ nm}$

Table 1 show that increase in ionic strength of the reaction medium increases the rate of reaction and a plot of  $\log k_2$  versus  $\sqrt{\mu}$  is positive (Fig. 4). This is suggesting the presence of anion-anion or cation-cation interaction in the activated complex and in this reaction it is the interaction of  $\text{CoO}_2\text{Co}^{5+}$  and  $\text{DMTU}^+$ . This is corroborated by

the increase of the reaction rate as the dielectric constant,  $D$ , of the reaction medium (Table 3) decreases.

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

$10^2[\text{DMTU}]$ ( $\text{mol dm}^{-3}$ )	$10^2[\text{H}^+]$ ( $\text{mol dm}^{-3}$ )	$\mu$ ( $\text{mol dm}^{-3}$ )	$10^3k_1$ ( $\text{s}^{-1}$ )	$10^2k_2$ ( $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ )
1.55	4.0	0.25	0.81	5.20
3.11	4.0	0.25	1.61	5.18
4.66	4.0	0.25	2.42	5.19
6.22	4.0	0.25	3.22	5.18
7.77	4.0	0.25	4.15	5.34
9.32	4.0	0.25	4.84	5.19
10.88	4.0	0.25	5.76	5.29
12.40	4.0	0.25	6.68	5.38
7.77	1.0	0.25	4.15	5.34
7.77	2.0	0.25	4.15	5.34
7.77	4.0	0.25	4.15	5.34
7.77	6.0	0.25	4.15	5.34
7.77	8.0	0.25	4.15	5.34
7.77	10.0	0.25	4.19	5.39
7.77	12.0	0.25	4.16	5.36
7.77	14.0	0.25	4.19	5.39
7.77	4.0	0.10	2.30	2.96
7.77	4.0	0.15	2.99	3.85
7.77	4.0	0.20	3.45	4.45
7.77	4.0	0.25	4.14	5.33
7.77	4.0	0.30	4.84	6.22
7.77	4.0	0.35	5.99	7.77
7.77	4.0	0.40	6.91	8.89
7.77	4.0	0.45	7.83	10.08



**Fig 4:** Plot of  $\log k_2$  versus  $\sqrt{\mu}$  for the oxidation of DMTU by  $\text{CoO}_2\text{Co}^{5+}$  at  $[\text{CoO}_2\text{Co}^{5+}] = 7.77 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{DMTU}] = 7.77 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[\text{H}^+] = 0.04 \text{ mol dm}^{-3}$ ,  $\mu = 0.10 - 0.45 \text{ mol dm}^{-3}$  ( $\text{NaClO}_4$ ),  $T = 31.0 \pm 1.0 \text{ }^\circ\text{C}$  and  $\lambda_{\text{max}} = 670 \text{ nm}$

Figure 5 shows the plot of  $\log k_1$  and  $1/D$  with a positive slope. Also, the rate of reaction increased with the addition of  $\text{CH}_3\text{COO}^-$

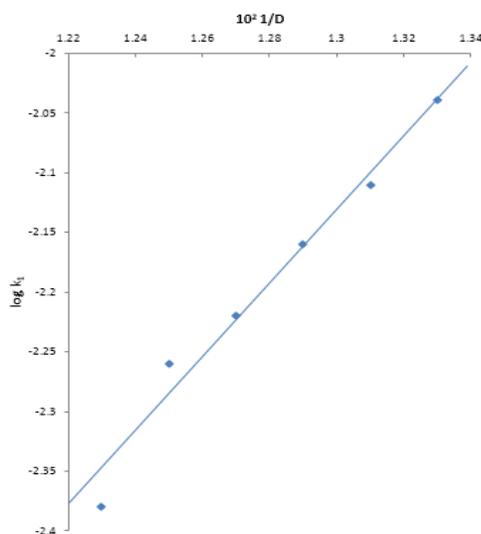
and  $\text{NO}_3^-$  ions. This observation points to the outer-sphere mechanism<sup>[26,27]</sup>. This result is similar to that reported by Sykes<sup>[19]</sup>.

**Table 2:** Dependence of rate constant on anions for the oxidation of 1,3-dimethyl-2-thiourea by  $[\text{CoO}_2\text{Co}^{5+}]$  at  $T = 31.0 \pm 1.0^\circ\text{C}$ ,  $\lambda_{\text{max}} = 670 \text{ nm}$ ,  $[\text{CoO}_2\text{Co}^{5+}] = 7.77 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{DMTU}] = 7.77 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[\text{H}^+] = 0.04 \text{ mol dm}^{-3}$  and  $\mu = 0.25 \text{ mol dm}^{-3}$  ( $\text{NaClO}_4$ )

X	$10^3[\text{X}] (\text{mol dm}^{-3})$	$10^3k_1 (\text{s}^{-1})$	$10^2k_2 (\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})$
$\text{NO}_3^-$	0	4.15	5.34
	20	4.61	5.93
	40	5.53	7.11
	60	5.76	7.41
	80	6.45	8.30
	100	6.91	8.59
$\text{CH}_3\text{COO}^-$	0	4.15	5.34
	20	5.53	7.11
	40	6.91	8.89
	60	10.36	13.33
	80	13.82	17.78
	100	17.27	22.29

**Table 3:** Dependence of rate constant on dielectric constant for the oxidation of 1,3-dimethyl-2-thiourea by  $[\text{CoO}_2\text{Co}^{5+}]$  at  $T = 31.0 \pm 1.0^\circ\text{C}$ ,  $\lambda_{\text{max}} = 670 \text{ nm}$ ,  $[\text{CoO}_2\text{Co}^{5+}] = 7.77 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{DMTU}] = 7.77 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[\text{H}^+] = 0.04 \text{ mol dm}^{-3}$  and  $\mu = 0.25 \text{ mol dm}^{-3}$  ( $\text{NaClO}_4$ )

D	$10^2 1/D$	$10^3k_1 (\text{s}^{-1})$	$10^2k_2 (\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})$
81.00	1.23	4.15	5.34
79.80	1.25	5.53	7.11
78.60	1.27	5.99	7.71
77.40	1.29	6.91	8.89
76.20	1.31	7.60	9.78
75.00	1.33	9.21	11.86

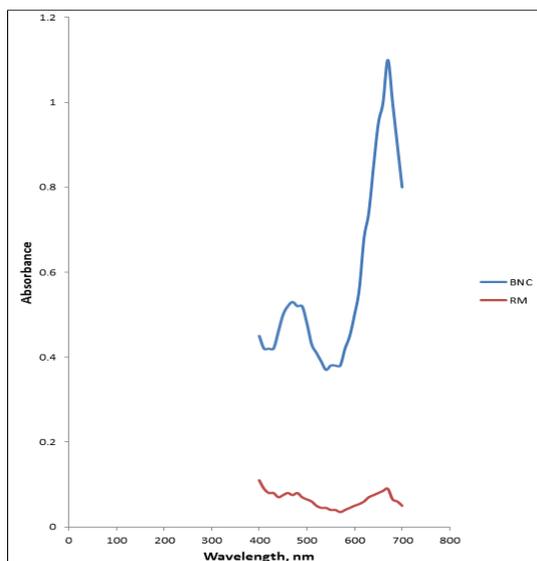


**Fig 5:** A plot of  $\log k_1$  versus  $1/D$  for the oxidation of DMTU by  $\text{CoO}_2\text{Co}^{5+}$  at  $[\text{CoO}_2\text{Co}^{5+}] = 7.77 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{DMTU}] = 7.77 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[\text{H}^+] = 0.04 \text{ mol dm}^{-3}$ ,  $\mu = 0.25 \text{ mol dm}^{-3}$  ( $\text{NaClO}_4$ ),  $T = 31.0 \pm 1.0^\circ\text{C}$  and  $\lambda_{\text{max}} = 670 \text{ nm}$

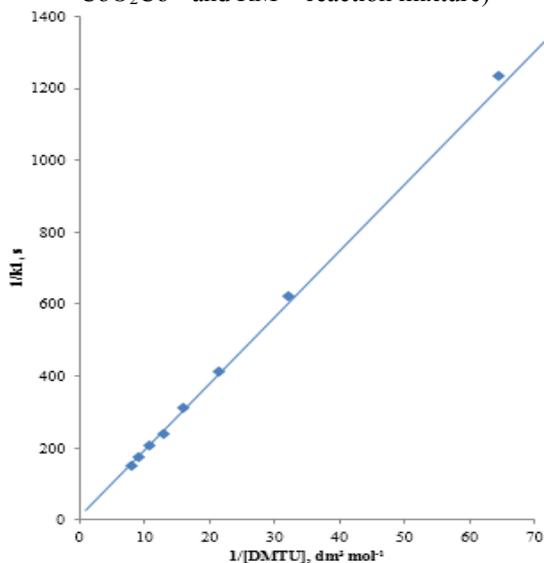
### 3.3 Tests for Intermediate Complex

#### 3.3.1 Spectroscopic studies

The electronic spectra of partly reacted solutions containing  $[\text{CoO}_2\text{Co}^{5+}] = 7.77 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{DMTU}] = 7.77 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[\text{H}^+] = 0.04 \text{ mol dm}^{-3}$  and  $\mu = 0.25 \text{ mol dm}^{-3}$  ( $\text{NaClO}_4$ ) were compared with those of  $[\text{CoO}_2\text{Co}^{5+}] = 7.77 \times 10^{-4} \text{ mol dm}^{-3}$  in  $[\text{H}^+] = 0.04 \text{ mol dm}^{-3}$ . There was an isosbestic point at 670 nm (Figure 6), suggesting that there was no intermediate complex formed of any appreciable formation constant between  $\text{CoO}_2\text{Co}^{5+}$  and DMTU [27].



**Fig 6:** Spectra of  $\text{CoO}_2\text{Co}^{5+}$  and that of reaction mixture (BNC =  $\text{CoO}_2\text{Co}^{5+}$  and RM = reaction mixture)



**Fig 7:** Michaelis-Menten plot of  $1/k_1$  versus  $1/[\text{DMTU}]$  for the oxidation of DMTU by  $\text{CoO}_2\text{Co}^{5+}$  at  $[\text{CoO}_2\text{Co}^{5+}] = 7.77 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{DMTU}] = (1.55-12.40) \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[\text{H}^+] = 0.04 \text{ mol dm}^{-3}$ ,  $\mu = 0.25 \text{ mol dm}^{-3}$  ( $\text{NaClO}_4$ ),  $T = 31.0 \pm 1.0^\circ\text{C}$  and  $\lambda_{\text{max}} = 670 \text{ nm}$ .

#### 3.3.2 Michaelis-Menten plot

Michaelis-Menten plot of  $1/k_1$  versus  $1/[\text{DMTU}]$  was plotted (Figure 9). The plot was linear without intercept. This is an indication of absence of an intermediate complex in one of the steps preceding the rate determining step.

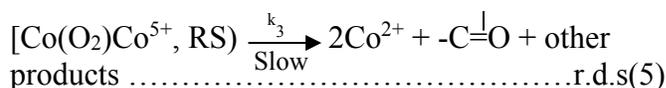
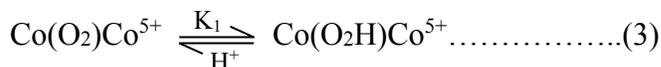
#### 3.3.3 Test for free radicals

Tests for the polymerization of acrylamide by partly reacted reaction solutions, performed as described elsewhere [28,29] were negative. This is indicative of the probable absence of free radicals in the reaction medium [30].

#### 3.4 Reaction mechanism

The reaction pathway exhibited by the reaction of  $\text{Co}(\text{O}_2)\text{Co}^{5+}$  with DMTU follows closely the mechanism that was observed for the earlier work on thiourea and 1-methyl-2-thiourea. However, the kinetics of the rate of reaction is of this order  $\text{TU} < \text{MTU} < \text{DMTU}$ , nevertheless the route to the products formation are similar and is summarized as follows:

Let  $\text{DMTU} = \text{RS}$  and the superoxo complex =  $\text{Co}(\text{O}_2)\text{Co}^{5+}$ ,



From equation (5),

$$\text{Rate} = k_3 [\text{Co}(\text{O}_2)\text{Co}^{5+}, \text{RS}] \dots \dots \dots (6)$$

From equation (3), and (4)

$$\text{Rate} = k_3 K_2 K_1 [\text{Co}(\text{O}_2)\text{Co}^{5+}] [\text{RS}] \dots \dots \dots (7)$$

Let  $k_3 K_2 K_1 = k$ , then equation 7 becomes

$$\text{Rate} = k [\text{Co}(\text{O}_2)\text{Co}^{5+}] [\text{RS}] \text{ which conforms to equation 2 with } k = k_2 = (5.24 \pm 0.0689) \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$$

The proposed reaction mechanism most probable follows the outer-sphere mechanism on the ground that:

- (i) Spectrophotometric evidence did not show any shift in wavelength maxima of the

complex as reaction progressed thereby ruling out formation of a stable intermediate.

- (ii) Added  $\text{CH}_3\text{COO}^-$  and  $\text{NO}_3^-$  increased the rate of reaction indicating that the reaction most probably occurs by the outer-sphere mechanism.
- (iii) The views above are supported by the Michaelis-Menten plot of  $1/k_1$  versus  $1/[\text{DMTU}]$  which was linear and without intercept indicating the absence of a pre-electron transfer association step.
- (iv) The absence of gel formation after the addition of a solution of acrylamide to a partially oxidized reaction mixture suggests the probable absence of free radicals in the reaction medium.

#### 4. Conclusion

The oxidation mechanism of DMTU by  $\text{CoO}_2\text{Co}^{5+}$  showed a similar pathway to that of the oxidation of thiourea and 1-methyl-2-thiourea respectively by the same complex. The reaction rate is independent of changes in hydrogen ion concentrations but is catalyzed by added anions. The suggested mechanism for this reaction involves a two-electron process transfer to the bridging oxygen atom and Co (III) center in yielding the products that involves the cleavage of the C-S bond as earlier reported [1,2].

#### 5. Acknowledgements

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#### 6. References

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