

Original Research Article

REDOX KINETICS AND MECHANISM OF THE OXIDATION OF THIOUREA BY

DIAQUOTETRAKIS(2,2'- BIPYRIDINE) - μ - OXODIRUTHENIUM (III) ION, IN AQUEOUS PERCHLORIC ACID

ABSTRACT

Investigations of the kinetics of the oxidation of thiocarbamide (thiourea) by diaquotetrakis(2,2'- bipyridine) - μ - oxodiruthenium (III) ion, $[(H_2O)_2Ru_2O]^{4+}$, in perchloric acid has been done at a temperature, $T = 30 \pm 1^\circ C$, ionic strength, $I = 0.5 \text{ mol dm}^{-3}$ ($NaClO_4$) and hydrogen ion concentration, $[H^+] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$. The reaction showed a stoichiometry of 1:2 (oxidant/ thiourea), first order kinetics with respect to the thiourea (RSH), $k_2 = (7.39 \pm 0.05) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, inverse $[H^+]$ dependence and zero salt effect. The rate equation for the reaction has been proposed $-d[(H_2O)_2Ru_2O^{4+}]/dt = (a+b \frac{1}{[H^+]})[(H_2O)_2Ru_2O^{4+}][RSH]$. Based on the lack of evidence of the formation of intermediate complex from absence of intercept in the Michaelis - Menten plot and lack of shift in λ_{max} of the reaction mixture 1 minute after start of reaction from that of the dimer and lack of observable anion catalysis, it is proposed that the reaction most probably proceeded through the outer sphere mechanism.

Keywords: kinetics; oxidation; anion catalysis; salt effect

1. INTRODUCTION

Ruthenium complexes with polypyridyl ligands have received much attention owing to their interesting spectroscopic, photophysical, photochemical and electrochemical properties, which is responsible for

their potential uses in diverse areas such as photosensitizers for photochemical conversion of solar energy (1 – 7), molecular electronic devices (8 - 11). Ruthenium bipyridyl complexes have been used as efficient sensitizers for photochemical cells based on non-porous films of TiO₂ (12). These polypyridylic complexes have been used as photoactive DNA cleavage agents for therapeutic purposes (13 - 16). They are also known to perform a variety of inorganic and organic transformations. Their synthetic versatility, high catalytic performance under relatively mild reaction conditions and high selectivity make these complexes particularly well suited for this purpose. The catalytic oxidation of water and chloride with a binuclear ruthenium complex known as the *blue dimer* [(bpy)₂(H₂O)RuORu(H₂O)(bpy)₂]⁴⁺ was reported by the .Meyer's group in 1982 (17 – 18)

Studies into the kinetics of the redox behaviour of the ruthenium dimer with some reducing agents have been carried out (19 - 26). A further investigation into the redox behaviour of the dimer with other reducing agents is necessary knowing the importance of this versatile dimer.

2. MATERIALS AND METHODS

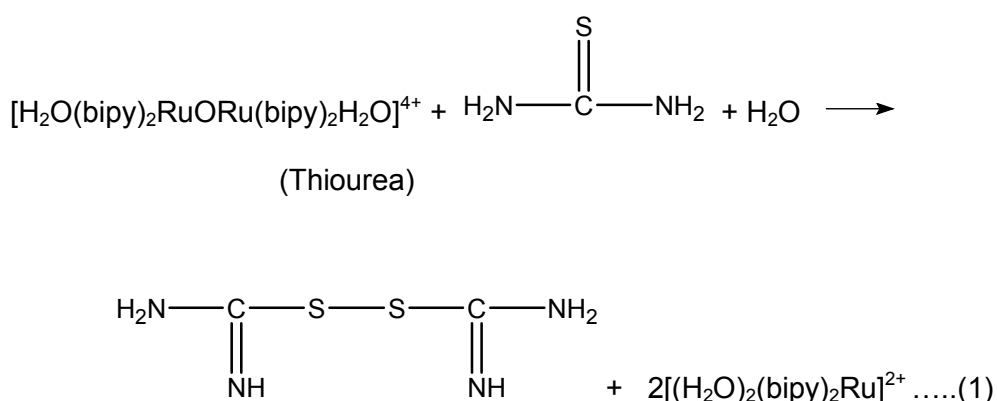
Diaquotetrakis (2, 2'bipyridine) - - oxodiruthenium (III) perchlorate , was prepared according to literature [27] as follows: 2.00 g (4.13 mmol) *cis*-Dichlorobis(2, 2'bipyridine)ruthenium (II) (Sigma - Aldrich) was suspended in 80 ml of water containing 1.76 g or 10.36 mmol silver nitrate. The mixture was heated to reflux for 8 hr, then cooled to room temperature and centrifuged. The supernatant liquid filtered by suction onto a fine frit to remove silver chloride and silver metal. The filtrate was heated on a steam bath and treated with a saturated solution of sodium perchlorate until precipitation began to occur. Slow cooling to 0° produced the desired material, which was collected by suction filtration, washed with a small portion of cold water, and air dried. The salt was recrystallized from hot water containing small amounts of NaClO₄, giving a dark micro-crystalline solid and a deep green solution in water. The yield was 1.243 g or 47.1% of theoretical (literature 56%). Stability of complex in water and in the presence of acid and added anions agreed to literature [27]. The complex had a $\lambda_{\max}$ of 660 nm, which agreed with literature and a molar extinction coefficient, $\epsilon = 21,167 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ (literature: $\epsilon = 25,000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. Solutions of thiocarbamide(thiourea) (M&B) were prepared by dissolving accurate quantities of the reagent in known amount of distilled water. Analar grade HClO₄ (Sigma Aldrich) was used to furnish H⁺, while the ionic strength of the reaction medium was maintained at 0.5 mol dm⁻³ by using NaClO₄ obtained from sigma – Aldrich.

The stoichiometry of the reaction was determined by spectrophotometric titration using the mole ratio method. Reaction rates were determined by observing the decrease in absorbance of the dimer monitored by Seward Biomedical Digital Colorimeter at 660 nm. Test for formation of stable, detectable intermediate complex was carried out spectrophotometrically by comparing the $\lambda_{\max}$ of the dimer and that of the partially reacted reaction mixture. Michaelis – Menten plot also gave an idea on the presence or not of intermediate complex. Test for the presence of free radicals in the course of the reaction was carried out by the addition of 5 cm³ acrylamide to a partially oxidised reaction mixture, followed by the addition of a large excess of methanol. Observation and comparison with a control made up by adding acrylamide to a solution of the dimer at the same condition of [H⁺], ionic strength and temperature. Test for the presence of disulphide in the product mixture was carried out according to McAuley and Gomwalk [28,29]). The thiourea was reacted with little excess of the oxidant in acid medium and ionic strength of reaction. At the completion of reaction, the mixture was extracted six times with diethyl ether. The combined ether extracts were washed with distilled water and dried with anhydrous Na₂SO₄ and left overnight to dry.

3. RESULTS AND DISCUSSION

3.1 Stoichiometry

The stoichiometry of the reaction was found to be in the ratio 1:2 (dimer/ thiourea) (Fig 1). Based on this stoichiometry, the reaction of the oxidation of thiourea by Ru₂O⁴⁺ can be given as:



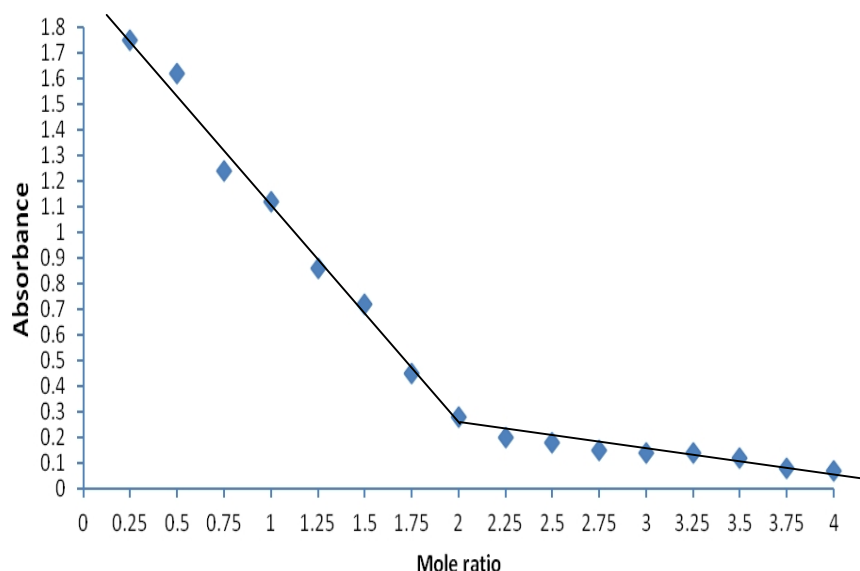


Fig 1 :Stoichiometry of the reaction of $[(\text{H}_2\text{O})_2\text{Ru}_2\text{O}^{4+}]$ and thiourea [TU]
 $[(\text{H}_2\text{O})_2\text{Ru}_2\text{O}^{4+}] = 6.0 \times 10^{-5} \text{ mol dm}^{-3}$; $[\text{TU}] = (1.5 - 24.0) \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{H}^+] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$; $l = 0.5 \text{ mol dm}^{-3}$; $\lambda_{\text{max}} = 660 \text{ nm}$

This stoichiometry is in agreement with that found for the reaction of the ruthenium dimer and l – cysteine (19) and glutathione (20). However a stoichiometry of 1:1 was found for the reaction of the ruthenium dimer with iodide [21], sulphite [22], mercaptoethanol and mercaptoethylamine [23]. Stoichiometry of 2:1 was found for the reaction of the ruthenium dimer and ascorbic acid [24]. The stoichiometry of the reaction of the ruthenium dimer with bromate was reported to be 5:1 [25]

3.2 Order of reaction

Pseudo first order plots of $\log (A_t - A_\infty)$ against time were all linear to more than 90% completion of reaction (where A_t and A_∞ are the absorbances at time 't' and at infinity, respectively) confirming that the reaction is first-order with respect to [dimer] (see a typical plot on Fig 2).

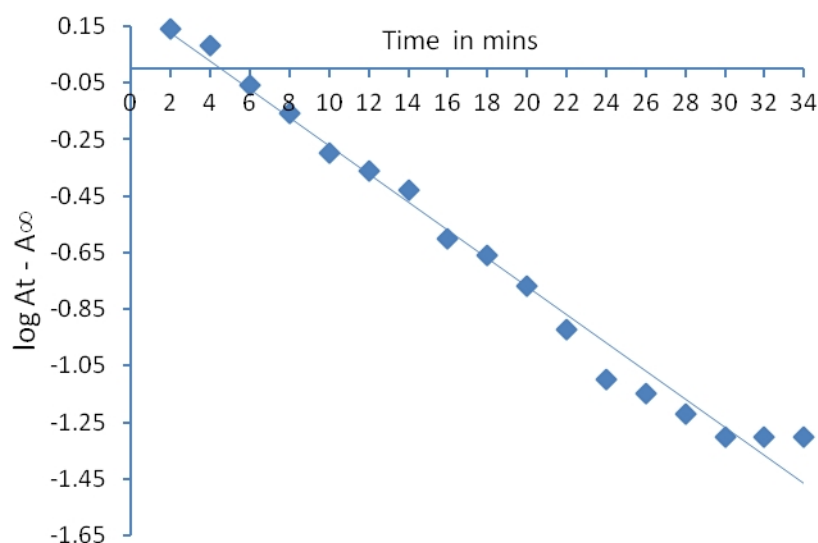


Fig 2 : Typical Pseudo- first order plot for the reaction of $[(\text{H}_2\text{O})_2\text{Ru}_2\text{O}^{4+}]$ and thiourea [TU]. $[(\text{H}_2\text{O})_2\text{Ru}_2\text{O}^{4+}] = 6.0 \times 10^{-5} \text{ mol dm}^{-3}$; $[\text{TU}] = 12 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{H}^+] = 5.0 \times 10^{-2} \text{ mol dm}^{-2}$; $I = 0.5 \text{ mol dm}^{-3}$; $\lambda_{\text{max}} = 660 \text{ nm}$; $T = 32 \pm 1^\circ\text{C}$

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95 Pseudo-first rate constants, k_1 were obtained as the slopes of the latter plots (see Table 1).

96 The second order rate constants, k_2 , for the various concentrations of thiourea obtained from

97 $k_1 / [\text{RSH}]$ were fairly constant (Table 1) and given as $(7.39 \pm 0.05) \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. A

98 plot of $\log k_1$ against $\log [\text{TU}]$ was linear with a slope of 0.96 (see Figure 3), suggesting a

99 first order reaction with respect to [TU]. The rate law for this reaction is thus given as:

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$$-\frac{d}{dt} [(\text{H}_2\text{O})_2\text{Ru}_2\text{O}^{4+}] = k_2 [(\text{H}_2\text{O})_2\text{Ru}_2\text{O}^{4+}][\text{TU}] \quad \dots\dots (2)$$

101 Where $[(\text{H}_2\text{O})_2\text{Ru}_2\text{O}^{4+}] = [\text{H}_2\text{O}(\text{bpy})_2\text{RuORu}(\text{bipy})_2\text{H}_2\text{O}]^{4+}$ and TU = Thiourea

102 Similar second order kinetics have been observed for other reactions of the oxobridged

103 ruthenium dimer [19 – 25]

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105 **Table 1 : Pseudo – first order and second order rate constants for the reaction of**
 106 **$[(\text{H}_2\text{O})_2\text{Ru}_2\text{O}]^{4+}$ and thiourea.** $[(\text{H}_2\text{O})_2\text{Ru}_2\text{O}]^{4+} = 6.0 \times 10^{-5} \text{ mol dm}^{-3}$; $I = 0.5 \text{ mol dm}^{-3}$
 107 (NaClO_4) ; $T = 32^\circ\text{C}$; $\lambda_{\text{max}} = 660 \text{ nm}$

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109	$10^2 [\text{TU}]$,	$10^3 [\text{H}^+]$,	$10^4 k_1$,	$10^3 k_2$,
110	mol dm^{-3}	mol dm^{-3}	s^{-1}	$\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$

111	4.80	50.0	3.57	7.43
112	7.20	50.0	5.23	7.27
113	9.60	50.0	7.15	7.45
114	12.00	50.0	8.83	7.36
115	14.40	50.0	10.72	7.44
116	16.80	50.0	12.40	7.38
117	21.60	50.0	16.03	7.42
118	12.00	10.0	13.45	11.21
119	12.00	20.0	12.04	10.03
120	12.00	30.0	11.11	9.26
121	12.00	40.0	10.33	8.61
122	12.00	50.0	8.80	7.33
123	12.00	60.0	8.15	6.79
124	12.00	100.0	4.10	3.41

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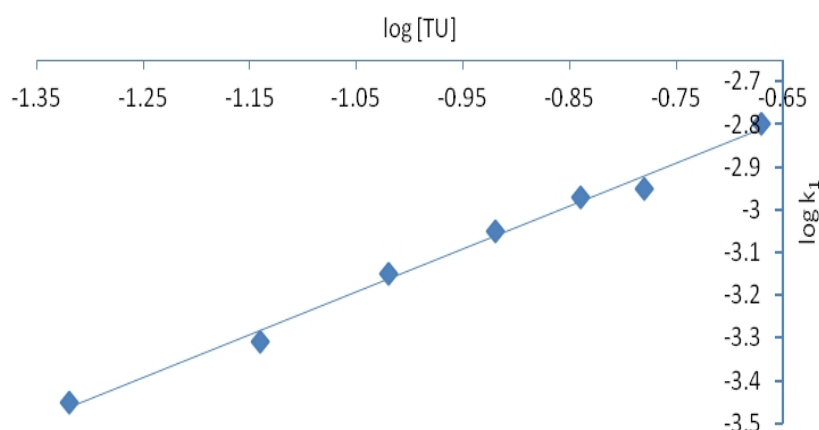


Fig3 : Plot of $\log k_1$ against $\log [TU]$ for the reaction of $[(H_2O)_2Ru_2O^{4+}]$ and thiourea [TU]. $[(H_2O)_2Ru_2O^{4+}] = 6.0 \times 10^{-5} \text{ mol dm}^{-3}$; $[TU] = 12 \times 10^{-2} \text{ mol dm}^{-3}$; $[H^+] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$; $I = 0.5 \text{ mol dm}^{-3}$; $\lambda_{\text{max}} = 660 \text{ nm}$; $T = 32 \pm 1^\circ\text{C}$

3.3 H^+ dependence on reaction rates

Changes of $[H^+]$ affected the reaction rates inversely in the acid range used i.e. $10^{-3} \leq [H^+] \leq 10^{-2} \text{ mol dm}^{-3}$ (Table 1). Such inverse acid dependence was observed in the reaction of the ruthenium dimer and sulphite [22], L- cysteine [19] and 1, 3 – benzenediol [26]. A plot of acid dependent second order rate constant, k_{H^+} , against $[H^+]$ was linear with a slope = 0.882 $\text{dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ and intercept = $12.1 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (see Figure 4), suggesting that this reaction occurs by two parallel pathways. One of the pathways is inverse acid- dependent and the other acid - independent. This result obeys the equation

$$k_{H^+} = a + b \frac{1}{[H^+]} \dots\dots\dots (3)$$

where 'a' = $12.1 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and 'b' = $0.882 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$

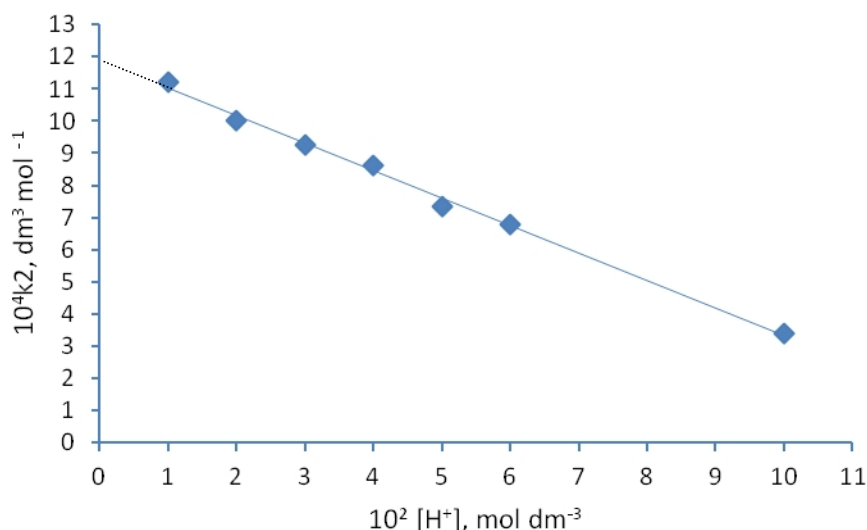


Fig 4 : Plot of k_{H+} against $[H^+]$ for the reaction of $[(H_2O)_2Ru_2O^{4+}]$ and thiourea [TU]. $[(H_2O)_2Ru_2O^{4+}] = 6.0 \times 10^{-5} \text{ mol dm}^{-3}$; $[TU] = 12 \times 10^{-2} \text{ mol dm}^{-3}$; $[H^+] = (1.0 - 10.0) \times 10^{-2} \text{ mol dm}^{-3}$; $I = 0.5 \text{ mol dm}^{-3}$; $\lambda_{\text{max}} = 660 \text{ nm}$; $T = 32 \pm 1^\circ\text{C}$

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142 The rate equation for the reaction of Diaquotetrakis (2, 2'bipyridine) - μ - oxodiruthenium (III)
143 ion and thiourea can now be written as:

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$$-\frac{d}{dt} [(H_2O)_2Ru_2O^{4+}] = (a + b \frac{1}{[H^+]}) [Ru_2O^{4+}] [TU] \dots\dots\dots(4)$$

145 3.4 Effect of changes in the ionic strength and dielectric constant of reaction 146 medium

147 Changes in the ionic strength and dielectric constant of reaction medium had no significant
148 effect on the rate constants (Tables 2 and 3)

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Table 2 : Effect of changes of ionic strength of the reaction medium for the reaction of $[(\text{H}_2\text{O})_2\text{Ru}_2\text{O}]^{4+}$ and thiourea. $[(\text{H}_2\text{O})_2\text{Ru}_2\text{O}]^{4+} = 6.0 \times 10^{-5} \text{ mol dm}^{-3}$; $[\text{TU}] = 12 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{H}^+] = 5 \times 10^{-2} \text{ mol dm}^{-3}$; $T = 32 \pm 1 \text{ }^\circ\text{C}$; $\lambda_{\text{max}} = 660 \text{ nm}$

I,	$10^4 k_1,$	$10^3 k_2,$
mol dm^{-3}	s^{-1}	$\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
0.10	8.86	7.38
0.30	8.90	7.42
0.50	8.88	7.40
0.70	8.82	7.35
0.90	8.86	7.38

Table 3: Effect of changes of dielectric constant of the reaction medium for the reaction of $[(\text{H}_2\text{O})_2\text{Ru}_2\text{O}]^{4+}$ and thiourea. $[(\text{H}_2\text{O})_2\text{Ru}_2\text{O}]^{4+} = 6.0 \times 10^{-5} \text{ mol dm}^{-3}$; $[\text{TU}] = 12 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{H}^+] = 5 \times 10^{-2} \text{ mol dm}^{-3}$; $I = 0.5 \text{ mol dm}^{-3}$; $T = 32 \pm 1 \text{ }^\circ\text{C}$; $\lambda_{\text{max}} = 660 \text{ nm}$

D	$10^4 k_1,$	$10^3 k_2,$
	s^{-1}	$\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
81.00	8.88	7.40
79.80	8.71	7.26
78.60	8.87	7.39
77.40	8.92	7.43
75.00	8.85	7.38
72.60	8.89	7.41

3.5 Effect of added anions on the rate constants

Added anions did not affect the rate constants of the reaction (Table 4). Absence of catalysis on added NO_3^- and CH_3COOH^- is in line with the formation of ion – pairs in equations (6) and (12) prior to electron transfer. It is known that the ion – pair complex does not possess a formal charge, interaction with added ions will not be possible suggesting that the reaction might have proceeded via the outer – sphere pathway [24]

Table 4 : Effect of added anions to reaction medium for the reaction of $[(\text{H}_2\text{O})_2\text{Ru}_2\text{O}]^{4+}$ and thiourea. $[(\text{H}_2\text{O})_2\text{Ru}_2\text{O}]^{4+} = 6.0 \times 10^{-5} \text{ mol dm}^{-3}$; $[\text{TU}] = 12 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{H}^+] = 5 \times 10^{-2} \text{ mol dm}^{-3}$; $I = 0.5 \text{ mol dm}^{-3}$; $T = 32 \pm 1 \text{ }^\circ\text{C}$; $\lambda_{\text{max}} = 660 \text{ nm}$

Ion	$10^3[\text{ion}]$ mol dm^{-3}	$10^4k_1,$ s^{-1}	$10^3k_2,$ $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
NO_3^-	1.00	8.89	7.41
	20.00	8.83	7.36
	40.00	8.91	7.43
	100.00	8.88	7.40
	140.00	8.87	7.39
CH_3COO^-	1.00	8.88	7.40
	20.00	8.85	7.38
	40.00	8.91	7.43
	100.00	8.82	7.35
	140.00	8.87	7.39

3.6 Tests for intermediate complex formation

A plot $1/k_1$ against $1/[TU]$ (Michaelis Menten plot) was linear passing through the origin (Figure 5). Also, comparison of the electronic spectrum of the reaction mixture run a minute after start of reaction, with that of the dimer showed no shift in $\lambda_{\max}$. These are suggestive of absence of formation of intermediate complex.

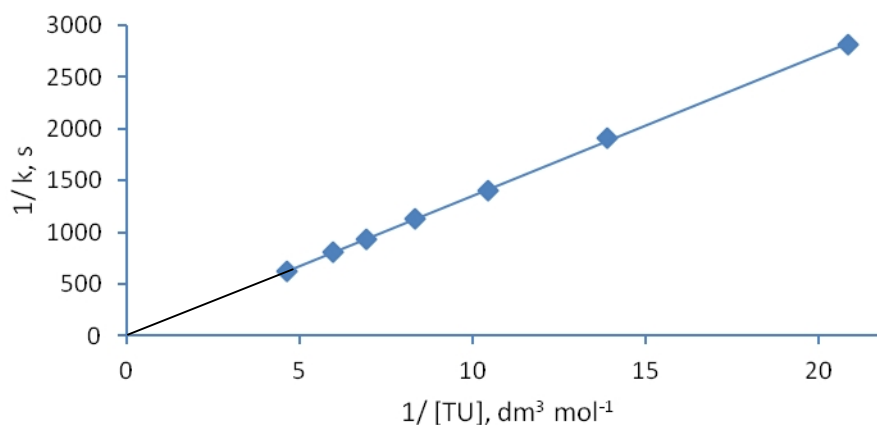


Fig 5 : Plot of $1/k_1$ versus $1/[RSH]$ for the reaction of $[(\text{H}_2\text{O})_2\text{Ru}_2\text{O}^{4+}]$ and thiourea [TU]. $[(\text{H}_2\text{O})_2\text{Ru}_2\text{O}^{4+}] = 6.0 \times 10^{-5} \text{ mol dm}^{-3}$; $[TU] = (4.8 - 21.60) \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{H}^+] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$; $I = 0.5 \text{ mol dm}^{-3}$; $\lambda_{\max} = 660 \text{ nm}$; $T = 32 \pm 1^\circ\text{C}$

3.7 Test for Free radical formation.

Gel was formed, confirming the participation of free radicals during the reaction.

3.8 Product analysis

Test for the presence of disulphide was carried out according to McAuley and Gomwalk [28, 29]. Crystals were produced, suggesting that the products of reaction include disulphides.

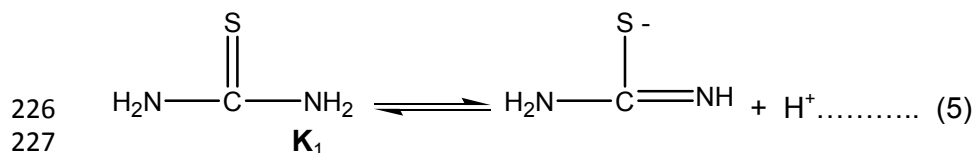
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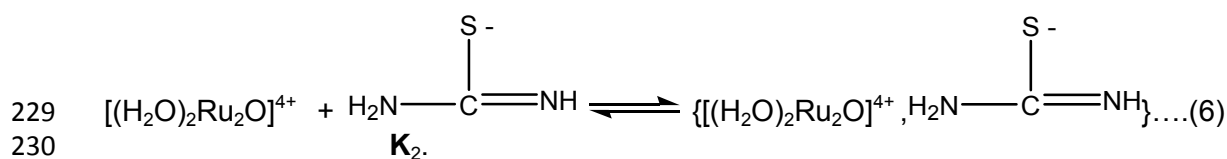
224 3.9 Proposed Mechanism of reaction

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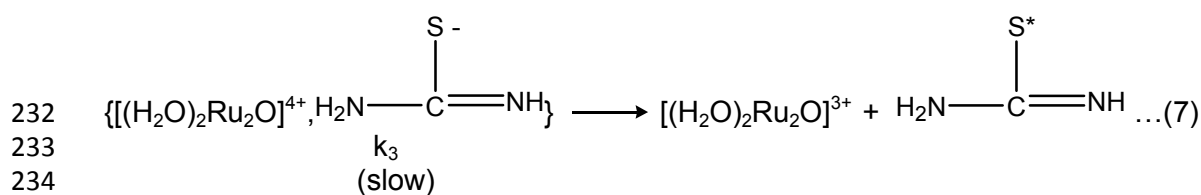
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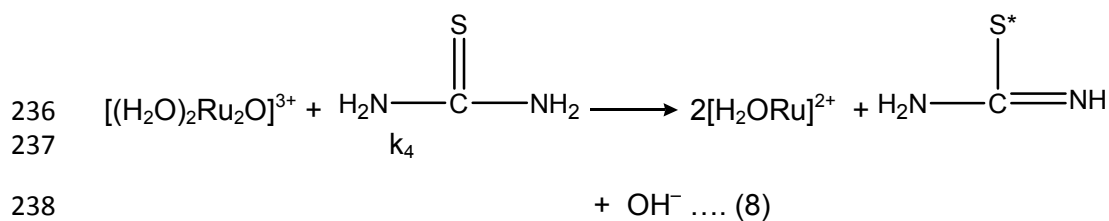


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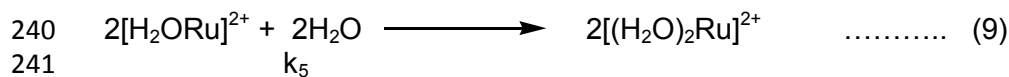
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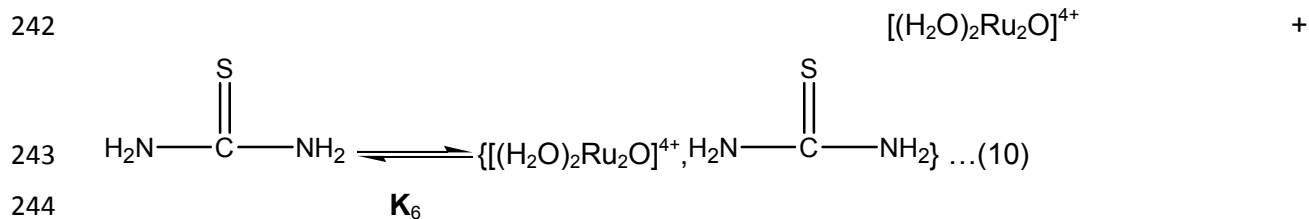
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268 Putting (20) into (19), we have:

$$-\frac{d}{dt} [(H_2O)_2Ru_2O]^{4+} = k_3K_2[(H_2O)_2Ru_2O^{4+}][H_2N-\overset{\overset{S^-}{|}}{C}=NH] + k_7[(H_2O)_2Ru_2O^{4+}, TU] \dots (21)$$

$$\text{Also, } [H_2N-\overset{\overset{S^-}{|}}{C}=NH] = K_1 \frac{[TU]}{[H^+]} \dots (22)$$

Putting (22) into (21), we have:

$$-\frac{d}{dt} [(H_2O)_2Ru_2O]^{4+} = k_3K_2K_1[(H_2O)_2Ru_2O^{4+}] \frac{[TU]}{[H^+]} + k_7[(H_2O)_2Ru_2O^{4+}, TU] \dots (23)$$

$$\text{Remember } [(H_2O)_2Ru_2O^{4+}, TU] = K_6[(H_2O)_2Ru_2O^{4+}][TU]$$

$$\dots (24)$$

Putting equation (24) into equation (23), we have :

$$-\frac{d}{dt} [(H_2O)_2Ru_2O]^{4+} = k_3K_2K_1[(H_2O)_2Ru_2O^{4+}] \frac{[TU]}{[H^+]} + k_7K_6[(H_2O)_2Ru_2O^{4+}][TU] \dots (25)$$

$$= (k_7K_6 + k_3K_2K_1 \frac{[1]}{[H^+]}) [(H_2O)_2Ru_2O^{4+}][TU] \dots (26)$$

Equation (26) agrees with equation (4) where $k_7K_6 = 'a' = 12.1 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and

$k_3K_2K_1 = 'b' = 0.882 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$.

The inverse H^+ dependence is consistent with the deprotonation of the thiourea in equation (5). Positive polymerization test is rationalized by the formation and participation of free radicals in equations (7), (8), (11), (12), and (15). Lack of anion catalysis is in line with the formation of ion – pairs in equation (6) and (10)

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289 4. CONCLUSION

290 Investigations of the kinetics of the oxidation of thiocarbamide (thiourea) by
 291 diaquotetrakis(2,2'- bipyridine) - μ - oxodiruthenium (III) ion, $[(H_2O)_2Ru_2O]^{4+}$, in perchloric
 292 acid and sodium perchlorate media has been carried out. The reaction showed a
 293 stoichiometry of 1:2 (oxidant/ thiourea), first order kinetics with respect to the thiourea .
 294 Based on the lack of evidence of the formation of intermediate complex from absence of
 295 intercept in the Michaelis - Menten plot and lack of shift in λ_{max} of the reaction mixture 1
 296 minute after start of reaction from that of the dimer and lack of observable anion catalysis, it
 297 is proposed that the reaction most probably proceeded through the outer sphere
 298 mechanism.

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