

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

The kinetics of the oxidation of thiocarbamide (thiourea) by diaquotetrakis(2,2'- bipyridine) - μ - oxodiruthenium (III) ion, $[(bpy)_2(H_2O)RuORu(H_2O)(bpy)_2]^{4+}$, in perchloric acid has been investigated 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 $-d[(bpy)_2(H_2O)RuORu(H_2O)(bpy)_2]^{4+}/dt = (a+b \frac{1}{[H^+]})[(bpy)_2(H_2O)RuORu(H_2O)(bpy)_2]^{4+}[RSH]$. Outer sphere mechanism is implicated to operate in this reaction as evidenced by lack of the formation of a stable intermediate complex as suggested by absence of intercept in the Michaelis - Menten plot, lack of shift in λ_{max} of the reaction mixture 1 minute after start of reaction and absence of observable anion catalysis. A plausible mechanism is proposed.

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 TiO_2 (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* $[(bpy)_2(H_2O)RuORu(H_2O)(bpy)_2]^{4+}$ was reported by the Meyer's group in 1982 (17 - 18).

A vast amount of information is available on the oxidation of thiourea and thiourea derivatives by oxidising agents such as hydrogen peroxide (19), bromate (20), nickel (IV) oxime – imine complex (21), chlorine dioxide (22), hydrogen peroxide catalysed by $[Ru^{III}(edta)(H_2O)]$ (23) and 3, 7 – Bis(Dimethylamino) phenazothionium chloride (24).

Studies into the kinetics of the redox behaviour of the ruthenium dimer with some reducing agents such as L – cysteine (25), glutathione (26), iodide (27), sulphite (28), 2 – mercaptoethanol (29), 2 – mercaptoethylamine (29), ascorbic acid (30), bromate (31) and 1 – 4 – benzenediol (32) have been carried out. 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 [33] 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 $NaClO_4$, 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 [33]. The complex had a λ_{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 HClO_4 (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 NaClO_4 obtained from sigma – Aldrich.

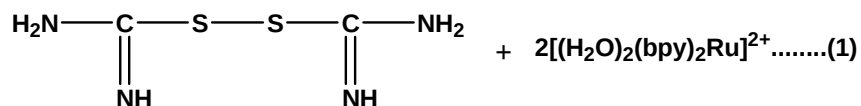
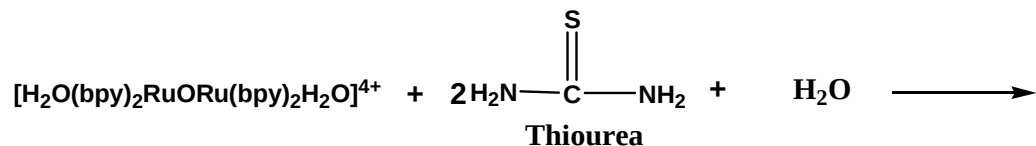
The stoichiometry of the reaction was determined by spectrophotometric titration using the mole ratio method. Reaction rates were determined by observing the decrease in absorbance of the dimer monitored by Seward Biomedical Digital Colorimeter at 660 nm. Test for formation of stable, detectable intermediate complex was carried out spectrophotometrically by comparing the λ_{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 cm^3 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 $[\text{H}^+]$, ionic strength and temperature. Test for the presence of disulphide in the product mixture was carried out according to McAuley and Gomwalk [34,35]). 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 Na_2SO_4 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), suggesting that one mole of the dimer was reduced by two moles of thiourea. Based on this stoichiometry, the reaction of the oxidation of thiourea by $[(\text{bpy})_2(\text{H}_2\text{O})\text{RuORu}(\text{H}_2\text{O})(\text{bpy})_2]^{4+}$ can be given as:

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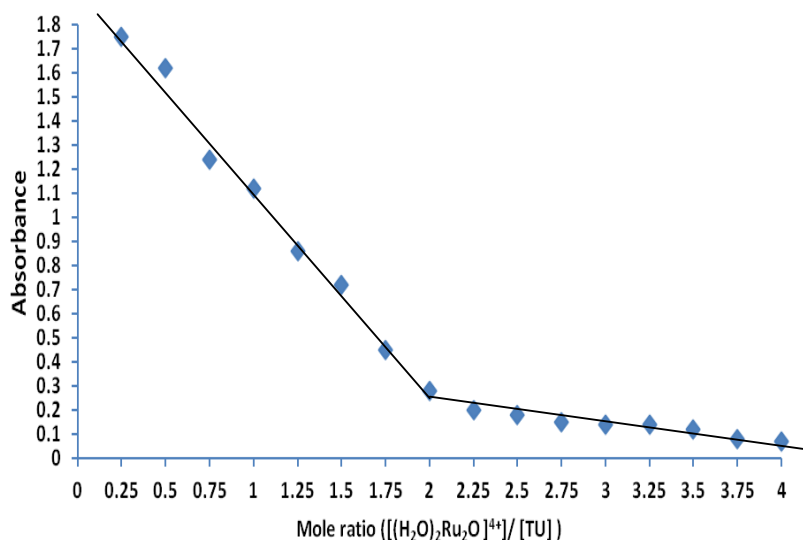


Fig 1 :Stoichiometry of the reaction of $[(\text{H}_2\text{O})_2\text{Ru}_2\text{O}^{4+}]$ and thiourea [TU]
 $[(\text{H}_2\text{O})_2\text{Ru}_2\text{O}^{4+}] = 6.0 \times 10^{-5} \text{ mol dm}^{-3}$; $[\text{TU}] = (1.5 - 24.0) \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{H}^+] = 5.0 \times 10^{-2}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

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84 This stoichiometry is in agreement with that found for the reaction of the ruthenium dimer
 85 and l – cysteine (25) and glutathione (26). However a stoichiometry of 1:1 was found for the
 86 reaction of the ruthenium dimer with iodide [27], sulphite [28], mercaptoethanol and
 87 mercaptoethylamine [29]. Stoichiometry of 2:1 was found for the reaction of the ruthenium
 88 dimer and ascorbic acid [30]. The stoichiometry of the reaction of the ruthenium dimer with
 89 bromate was reported to be 5:1 [31]

90

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).

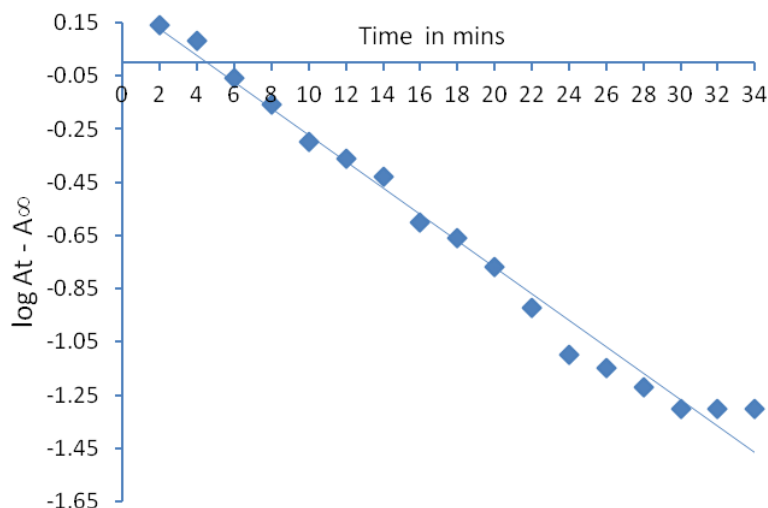


Fig 2 : Typical Pseudo- first order plot for the reaction of $[(H_2O)_2Ru_2O^{4+}]$ and thiourea [TU]. $[(H_2O)_2Ru_2O^{4+}] = 6.0 \times 10^{-5} \text{ mol dm}^{-3}$; $[TU] = 12 \times 10^{-2} \text{ mol dm}^{-3}$; $[H^+] = 5.0 \times 10^{-2} \text{ mol dm}^{-2}$; $I = 0.5 \text{ mol dm}^{-3}$; $\lambda_{\text{max}}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

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Pseudo-first rate constants, k_1 were obtained as the slopes of the latter plots (see Table 1). Obtaining k_1 is significant, as the second order rate constants, k_2 , for the various concentrations of thiourea is calculated from it as $k_1/[TU]$. The second order rate constants, k_2 , for the various concentrations of thiourea obtained 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 plot of $\log k_1$ against $\log [TU]$ was linear with a slope of 0.96 (see Figure 3), suggesting a first order reaction with respect to [TU]. The rate law for this reaction is thus given as:

$$-\frac{d}{dt} [(bpy)_2(H_2O)RuORu(H_2O)(bpy)_2]^{4+} = k_2 [(H_2O)_2Ru_2O]^{4+} [TU] \quad \dots\dots (2)$$

Where $[(H_2O)_2Ru_2O]^{4+} = [H_2O(bpy)_2RuORu(bipy)_2H_2O]^{4+}$ and TU = Thiourea

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Similar second order kinetics have been observed for other reactions of the oxobridged ruthenium dimer with other reducing agents [25 – 32]

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

$10^2 [\text{TU}]$, mol dm^{-3}	$10^3 [\text{H}^+]$, mol dm^{-3}	$10^4 k_1$, s^{-1}	$10^3 k_2$, $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
4.80	50.0	3.57	7.43
7.20	50.0	5.23	7.27
9.60	50.0	7.15	7.45
12.00	50.0	8.83	7.36
14.40	50.0	10.72	7.44
16.80	50.0	12.40	7.38
21.60	50.0	16.03	7.42
12.00	10.0	13.45	11.21
12.00	20.0	12.04	10.03
12.00	30.0	11.11	9.26
12.00	40.0	10.33	8.61
12.00	50.0	8.80	7.33
12.00	60.0	8.15	6.79
12.00	100.0	4.10	3.41

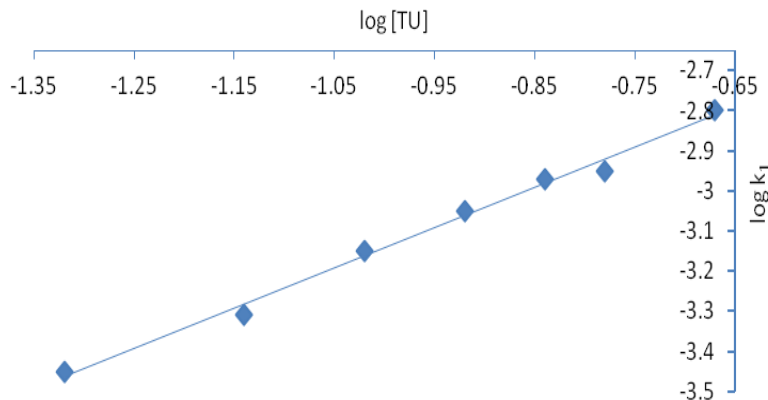


Fig 3 : Plot of $\log k_1$ against $\log [TU]$ for the reaction of $[(H_2O)_2Ru_2O^{4+}]$ and thiourea [TU]. $[(H_2O)_2Ru_2O^{4+}] = 6.0 \times 10^{-5} \text{ mol dm}^{-3}$; $[TU] = 12 \times 10^{-2} \text{ mol dm}^{-3}$; $[H^+] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$; $I = 0.5 \text{ mol dm}^{-3}$;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

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 [28], L- cysteine [25] and 1, 3 – benzenediol [32]. Decrease in rate of reaction with increase in $[H^+]$ had been explained in terms of the deprotonation of the sulphydryl (-SH) groups in thiols prior to electron transfer (35). 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' = $0.882 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$

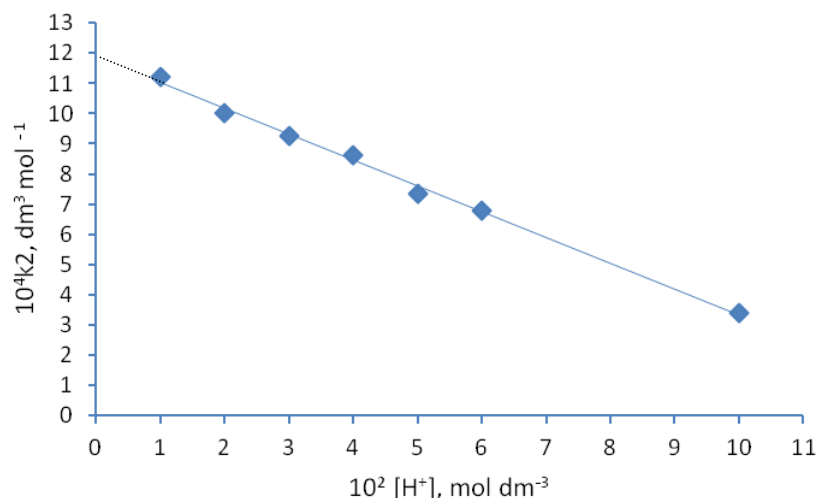


Fig 4 : Plot of k_{H+} against $[H^+]$ for the reaction of $[(H_2O)_2Ru_2O^{4+}]$ and thiourea [TU]. $[(H_2O)_2Ru_2O^{4+}] = 6.0 \times 10^{-5} \text{ mol dm}^{-3}$; $[TU] = 12 \times 10^{-2} \text{ mol dm}^{-3}$; $[H^+] = (1.0 - 10.0) \times 10^{-2} \text{ mol dm}^{-3}$; $I = 0.5 \text{ mol dm}^{-3}$;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

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

147
$$-\frac{d}{dt} [(H_2O)_2Ru_2O^{4+}] = (a + b \frac{1}{[H^+]}) [Ru_2O^{4+}] [TU] \dots\dots\dots(4)$$

148 **3.4 Effect of changes in the ionic strength and dielectric constant of reaction**
149 **medium**

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

152

153 **Table 2 : Effect of changes of ionic strength of the reaction medium for the reaction of**
154 **$[(H_2O)_2Ru_2O]^{4+}$ and thiourea. $[(H_2O)_2Ru_2O]^{4+} = 6.0 \times 10^{-5} \text{ mol dm}^{-3}$; $[TU] = 12 \times 10^{-2} \text{ mol}$**
155 **dm^{-3} ; $[H^+] = 5 \times 10^{-2} \text{ mol dm}^{-3}$; $T = 32 \pm 1^\circ \text{C}$; $\lambda_{\text{max}} = 660 \text{ nm}$**

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157	I,	$10^4 k_1,$	$10^3 k_2,$
158	mol dm^{-3}	s^{-1}	$\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
159	0.10	8.86	7.38
160	0.30	8.90	7.42
161	0.50	8.88	7.40
162	0.70	8.82	7.35
163	0.90	8.86	7.38

164

165 For reactions of ions in aqueous media, the rate of reaction is directly dependent on the
 166 square root of the ionic strength of the media. If ionic strength is varied, the various values of
 167 k_2 obtained could be plotted as $\log k_2$ against $\sqrt{I}$. The magnitude of the slopes of the plots
 168 gives an idea of the product of the charges on the species' reacting in the rate determining
 169 step (37). Non – dependence of rate of reaction on ionic strength will likely be due to no
 170 charge on one of the reactants or both of the reactants. Since ion – pair complex does not
 171 possess a formal charge, the rate of reaction would also not be affected if ion – pairs are
 172 involved in reactions with outer sphere character (32).

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174

175 **Table 3: Effect of changes of dielectric constant of the reaction medium for the**
 176 **reaction of $[(\text{H}_2\text{O})_2\text{Ru}_2\text{O}]^{4+}$ and thiourea.** $[(\text{H}_2\text{O})_2\text{Ru}_2\text{O}]^{4+} = 6.0 \times 10^{-5} \text{ mol dm}^{-3}$; $[\text{TU}] = 12 \times$
 177 $10^{-2} \text{ mol dm}^{-3}$; $[\text{H}^+] = 5 \times 10^{-2} \text{ mol dm}^{-3}$; $I = 0.5 \text{ mol dm}^{-3}$; $T = 32 \pm 1 \text{ }^\circ\text{C}$; $\lambda_{\text{max}} = 660 \text{ nm}$

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179	D	$10^4 k_1,$	$10^3 k_2,$
180		s^{-1}	$\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
181	81.00	8.88	7.40
182	79.80	8.71	7.26
183	78.60	8.87	7.39

184	77.40	8.92	7.43
185	75.00	8.85	7.38
186	72.60	8.89	7.41

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189 3.5 Effect of added anions on the rate constants

190 Added anions did not affect the rate constants of the reaction (Table 4). Absence of
 191 catalysis on added NO_3^- and CH_3COO^- is in line with the formation of ion – pairs in
 192 equations (6) and (12) prior to electron transfer. It is known that the ion – pair complex does
 193 not possess a formal charge, interaction with added ions will not be possible suggesting that
 194 the reaction might have proceeded via the outer – sphere pathway [30]

195

196 **Table 4 : Effect of added anions to reaction medium for the reaction of $[(\text{H}_2\text{O})_2\text{Ru}_2\text{O}]^{4+}$**
 197 **and thiourea.** $[(\text{H}_2\text{O})_2\text{Ru}_2\text{O}]^{4+} = 6.0 \times 10^{-5} \text{ mol dm}^{-3}$; $[\text{TU}] = 12 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{H}^+] = 5 \times$
 198 $10^{-2} \text{ mol dm}^{-3}$; $I = 0.5 \text{ mol dm}^{-3}$; $T = 32 \pm 1 \text{ }^\circ\text{C}$; $\lambda_{\text{max}} = 660 \text{ nm}$

199

200	Ion	$10^3[\text{ion}]$	$10^4k_1,$	$10^3k_2,$
201		mol dm^{-3}	s^{-1}	$\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
202	NO_3^-	1.00	8.89	7.41
203		20.00	8.83	7.36
204		40.00	8.91	7.43
205		100.00	8.88	7.40
206		140.00	8.87	7.39
207				
208	CH_3COO^-	1.00	8.88	7.40
209		20.00	8.85	7.38

210	40.00	8.91	7.43
211	100.00	8.82	7.35
212	140.00	8.87	7.39

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216 3.6 Tests for intermediate complex formation

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

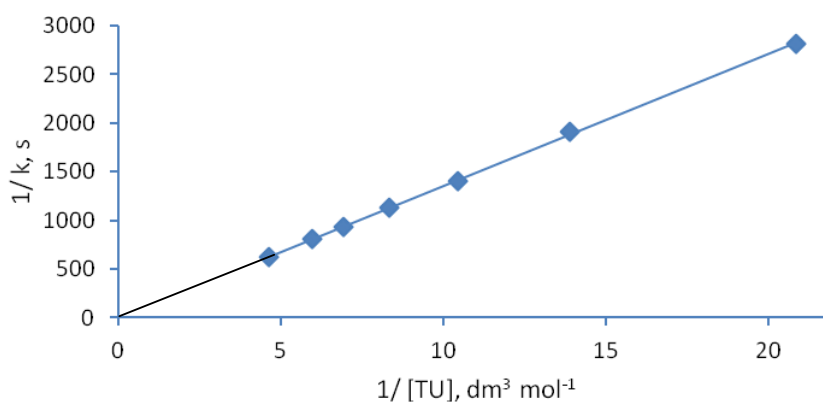


Fig 5 : Plot of $1/k_1$ versus $1/[RSH]$ for the reaction of $[(\text{H}_2\text{O})_2\text{Ru}_2\text{O}^{4+}]$ and thiourea [TU]. $[(\text{H}_2\text{O})_2\text{Ru}_2\text{O}^{4+}] = 6.0 \times 10^{-5} \text{ mol dm}^{-3}$; $[\text{TU}] = (4.8 - 21.60) \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{H}^+]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

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222 3.7 Test for Free radical formation.

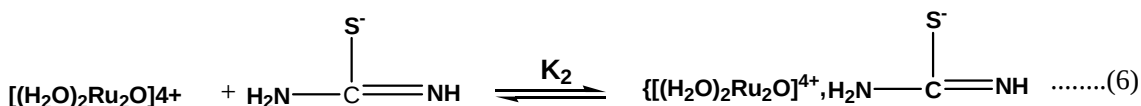
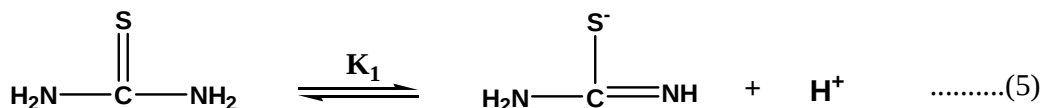
223 On addition of acrylamide to the reaction mixture followed by excess of methanol, a
 224 gelatinous precipitate was formed, suggesting that polymerization has occurred. This
 225 confirms the participation of free radicals during the reaction.

3.8 Product analysis

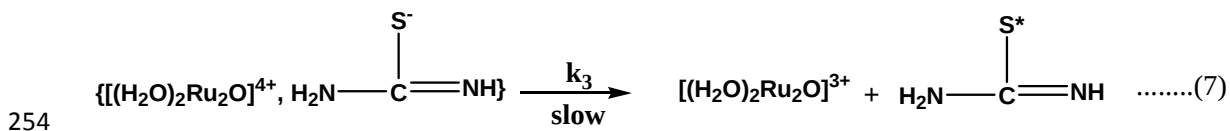
Test for the presence of disulphide was carried out according to McAuley and Gomwalk [34, 35]. The thiourea was reacted with little excess of the oxidant in acid medium and ionic strength of reaction. At the completion of reaction, the mixture was extracted six times with diethyl ether. The combined ether extracts were washed with distilled water and dried with anhydrous Na_2SO_4 and left overnight to dry. Crystals were produced, suggesting that the products of reaction include disulphides.

3.9 Proposed Mechanism of reaction

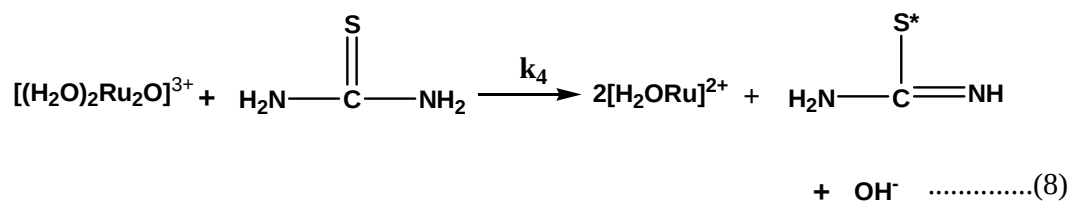
The kinetic data obtained from this study suggest that the reaction involves two parallel pathways, the acid-dependent and the acid independent pathways. The acid dependent pathway exhibits an inverse dependence which results from the deprotonation of the thiourea (equation 5). The deprotonated thiourea forms an ion pair with the dimer (equation 6) prior to a one – electron transfer. Also the neutral thiourea also forms an ion – pair with the dimer (equation 10) prior to another one – electron transfer. Formation and participation of free radicals which later dimerise to form disulphide as an oxidation product of thiourea has been reported by Khan et al (38) in the oxidation of thiourea by Cr (VI) and by Amjad et al (39) in the oxidation of thiourea by vanadium (V). Based on above considerations, a plausible mechanism for the oxidation of thiourea by diaquotetrakis(2,2'- bipyridine) - μ - oxodiruthenium (III) ion has been proposed to accommodate all the kinetic data generated in our work.



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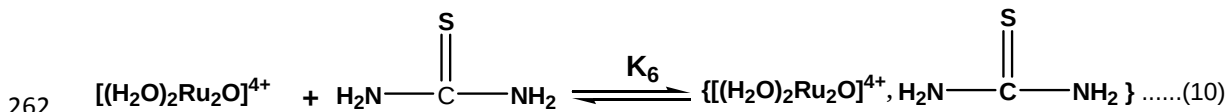
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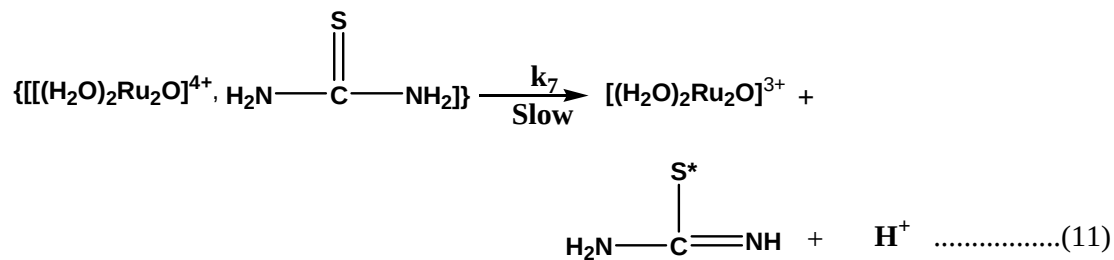


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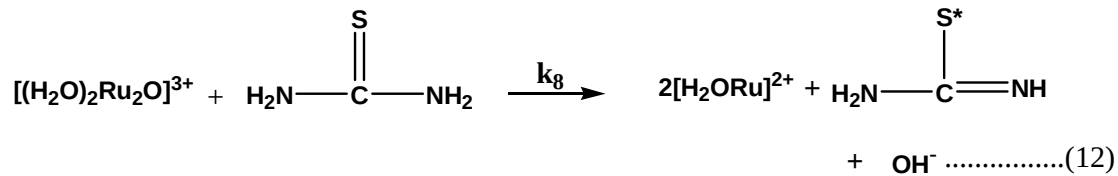


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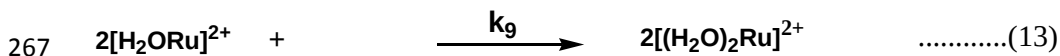


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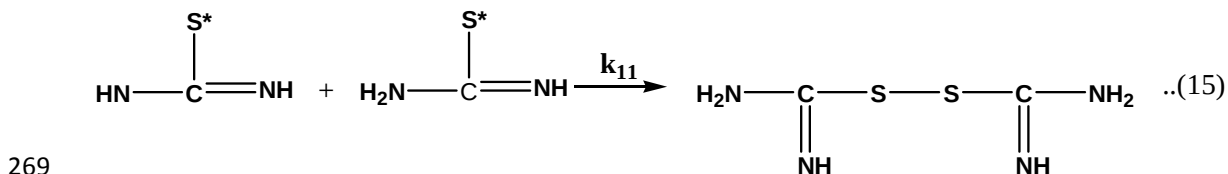
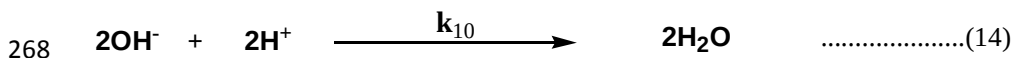
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271 With equations (5) and (11) as the rate determining steps, the rate equation of the reaction
272 can be written as :

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$$-\frac{d}{dt} [(\text{H}_2\text{O})_2\text{Ru}_2\text{O}]^{4+} = k_3[(\text{H}_2\text{O})_2\text{Ru}_2\text{O}^{4+}, \begin{array}{c} \text{S}^- \\ | \\ \text{H}_2\text{N}-\text{C}=\text{NH} \end{array}] + k_7[(\text{H}_2\text{O})_2\text{Ru}_2\text{O}^{4+}, \text{TU}] \dots\dots(16)$$

274 But $[(\text{H}_2\text{O})_2\text{Ru}_2\text{O}^{4+}, \begin{array}{c} \text{S}^- \\ | \\ \text{H}_2\text{N}-\text{C}=\text{NH} \end{array}] = K_2[(\text{H}_2\text{O})_2\text{Ru}_2\text{O}^{4+}][\begin{array}{c} \text{S}^- \\ | \\ \text{H}_2\text{N}-\text{C}=\text{NH} \end{array}] \dots\dots\dots(17)$

275 Putting (17) into (16), we have:

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$$-\frac{d}{dt} [(\text{H}_2\text{O})_2\text{Ru}_2\text{O}]^{4+} = k_3K_2[(\text{H}_2\text{O})_2\text{Ru}_2\text{O}^{4+}][\begin{array}{c} \text{S}^- \\ | \\ \text{H}_2\text{N}-\text{C}=\text{NH} \end{array}] +$$

277
$$k_7[(\text{H}_2\text{O})_2\text{Ru}_2\text{O}^{4+}, \text{TU}] \dots\dots(18)$$

278 Also, $[\begin{array}{c} \text{S}^- \\ | \\ \text{H}_2\text{N}-\text{C}=\text{NH} \end{array}] = K_1 \frac{[\text{TU}]}{[\text{H}^+]} \dots\dots\dots(19)$

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

280
$$-\frac{d}{dt} [(\text{H}_2\text{O})_2\text{Ru}_2\text{O}]^{4+} = k_3K_2K_1[(\text{H}_2\text{O})_2\text{Ru}_2\text{O}^{4+}] \frac{[\text{TU}]}{[\text{H}^+]} +$$

281
$$k_7[(\text{H}_2\text{O})_2\text{Ru}_2\text{O}^{4+}, \text{TU}] \dots\dots\dots(20)$$

282 Remember $[(\text{H}_2\text{O})_2\text{Ru}_2\text{O}]^{4+}, \text{TU} = K_6[(\text{H}_2\text{O})_2\text{Ru}_2\text{O}^{4+}][\text{TU}]$
283
$$\dots\dots\dots(21)$$

284 Putting equation (21) into equation (20), we have :

$$-\frac{d}{dt} [(H_2O)_2Ru_2O]^{4+} = k_3 K_2 K_1 [(H_2O)_2Ru_2O]^{4+} \frac{[TU]}{[H^+]} + k_7 K_6 [(H_2O)_2Ru_2O]^{4+} [TU] \dots (22)$$

$$= (k_7 K_6 + k_3 K_2 K_1 \frac{[1]}{[H^+]}) [(H_2O)_2Ru_2O]^{4+} [TU] \dots \dots \dots (23)$$

Equation (23) agrees with equation (4) where $k_7 K_6 = 'a' = 12.1 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_3 K_2 K_1 = 'b' = 0.882 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$.

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).

4. CONCLUSION

The kinetics of the oxidation of thiocarbamide (thiourea) by diaquotetrakis(2,2'- bipyridine) - μ - oxodiruthenium (III) ion, $[(bpy)_2(H_2O)RuORu(H_2O)(bpy)_2]^{4+}$, in perchloric acid and sodium perchlorate media has been examined. The reaction showed a stoichiometry of 1:2 (oxidant/ thiourea), first order kinetics with respect to the thiourea . 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.

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