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INVESTIGATIONS INTO THE KINETICS AND MECHANISM OF THE ELECTRON TRANSFER REACTIONS OF N- METHYL THIOUREA AND DIAQUOTETRAKIS(2,2'- BIPYRIDINE) - µ - OXODIRUTHENIUM (III) ION, IN AQUEOUS ACIDIC MEDIUM

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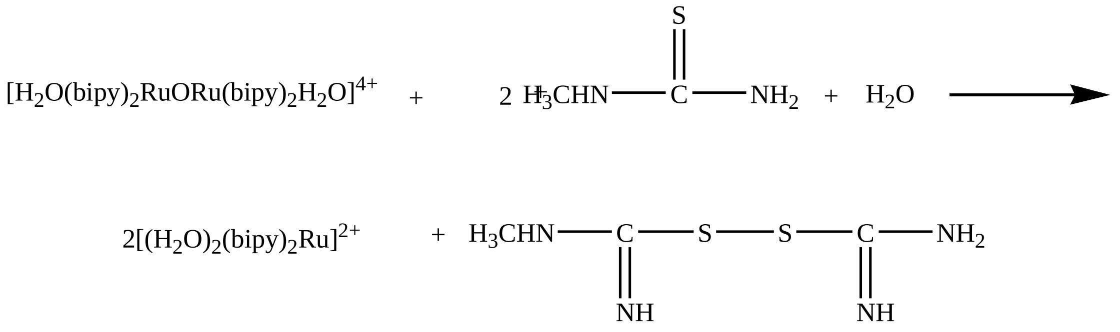
ABSTRACT

The kinetics of the oxidation of n- Methyl thiourea (MTU) by diaquotetrakis (2,2'- bipyridine) - µ - oxodiruthenium (III) ion, $[(bipy)_4(H_2O)_2Ru_2O]^{4+}$, in an $HClO_4$ medium has been studied spectrophotometrically at a temperature, $T = 30 \pm 1°C$, ionic strength, $I = 0.5$ mol dm^{-3} ($NaClO_4$) and hydrogen ion concentration, $[H^+] = 5.0 \times 10^{-2}$ mol dm^{-3}. The stoichiometry of the reaction conformed to an overall equation :



$$\mathrm{[H_2O(bipy)_2RuORu(bipy)_2H_2O]^{4+}} + 2\,\mathrm{H_3CHN}-\overset{\overset{\displaystyle \mathrm{S}}{\|}}{\mathrm{C}}-\mathrm{NH_2} + \mathrm{H_2O} \longrightarrow 2\mathrm{[(H_2O)_2(bipy)_2Ru]^{2+}} + \mathrm{H_3CHN}-\underset{\underset{\displaystyle \mathrm{NH}}{\|}}{\mathrm{C}}-\mathrm{S}-\mathrm{S}-\underset{\underset{\displaystyle \mathrm{NH}}{\|}}{\mathrm{C}}-\mathrm{NH_2}$$

The reaction showed first order kinetics with respect to the dimer and [MTU], respectively, $k_2 = (3.14 \pm 0.05) \times 10^{-2}$ $dm^3\ mol^{-1}\ s^{-1}$, and was inversely affected by changes in $[H^+]$. Changes in ionic strength and dielectric constant of reaction medium and addition of ions to the reaction medium had no or little effect on the rate constants of the reaction. The reaction has been found to conform to the rate equation:

$$-d[[(H_2O)_2Ru_2O^{4+}]/\,dt = (a+b\,\frac{1}{[H+]})[[(H_2O)_2Ru_2O^{4+}][MTU]$$

The reaction is considered to proceed through the formation of ion – pairs which go on to decompose at the rate determining steps to give rise to free radicals which diamerise to form *the reaction products. The reduction product was found to be disulfides and the reaction is considered to proceed through the outer sphere pathway. A plausible mechanism is proposed.*

Keywords: kinetics; oxidation; anion catalysis; salt effect; rate constants

Introduction

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 and 1985 (Gersten et al., 1982; Gilbert et al., 1985). Consequent upon T.J. Meyers *et al* report of the catalytic activity of the *blue dime*r, many studies have been carried out on the mechanism of this catalysis with Ce^{IV} and Co^{III} as oxidants (Nagoshi et al., 1999; Meyer and Huynh, 2003; Yamada et al., 2001; Binstead et al., 2000.Quite a lot of work has been done on the redox behaviour of the ruthenium dimer with some reducing agents such as l – cysteine, glutathione, iodide, sulphite, 2 – mercaptoethanol and 2 – mercaptoethylamine, ascorbic acid, bromate and 1, 4- benzenediol. (Iyun et al., 1996; Ayoko et al., 1993; Iyun et al., 1992a, 1992b, 1995a, 1995b, 1992c, 1992d). Further work on the redox behaviour of diaquotetrakis (2,2'- bipyridine) - µ - oxodiruthenium (III) ion is important due to the versatility of the ruthenium dimer for their potential use in diverse areas such as photosensitizers for photochemical conversion of solar energy (Kalyanasundaram and Gratzel, 1998; Juris et al., 1998; Meyer, 1990, Balzani et al., 1996; Hammerstrom et al., 2000; Islam et al., 2003), molecular electronic devices (Newkome et al., 2004; Mishra et al., 2003; Barigelleti and Flamigni, 2000; El-Ghayoury et al., 2000). Thioureas, containing sulphur and nitrogen atoms are susceptible to oxidation by a large number of oxidants giving rise to various products including ureas, sulphides, oxides of sulphur, and nitrogen (Sahu et al., 2011)[27]. A vast amount of information available on the reaction of thiourea and thiourea derivatives. with oxidizing agents such as 3,7-Bis(Dimethylamino)phenazothionium chloride, hydrogen peroxide, bromate, chlorine dioxide and H_2O_2 catalysed by $[Ru^{III}(edta)(H_2O)]$ (Osunlaja et al., 2013; Hoffman and Edwards, 1997; Simoyi et al., 1994; Rabai et al, 2004; Chatterjee et al., 2013) have been documented. This work is done to investigate the redox behaviour of a thiourea derivative with the ruthenium dimer, diaquotetrakis (2,2'- bipyridine) - µ - oxodiruthenium (III) ion

Material and methods

Materials

Diaquotetrakis (2, 2’bipyridine) -µ - oxodiruthenium (III) perchlorate , was prepared according to literature (Weaver et al., 1975). 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 (Iyun et al, 1992). The complex had a λ_{max} of 660 nm, which agreed with literature and a molar extinction coefficient, ε = 21, 167 dm^3 mol^{-I} cm^{-1} (literature: ε = 25, 000 dm^3 mol^{-I} cm^{-1} . Solutions of N - methylthiourea) (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.

Methods.

Stoichiometric studies

The stoichiometry of the reaction was determined by spectrophotometric titration using the mole ratio method. The concentration of the dimer is maintained at while the concentrations of the dimethyl thiourea was varied between maintaining the hydrogen ion concentration, [H^+] and the ionic strength at respectively. The reaction is allowed to go to completion. The absorbances of the individual product mixtures were recorded. A plot of absorbance against mole ratio was done and point of inflexion was obtained.

Kinetic measurements

All kinetic measurements were carried out under pseudo- first order conditions with respect to [MTU] over [$[(bipy)_4(H_2O)_2Ru_2O]^{4+}$]. The rate of reaction was monitored by following the decrease in absorbance of the dimer using Seward Biomedical Digital Colorimeter at 660 nm, the λ_{max} of the ruthenium dimer. The products of the reaction had no appreciable absorbance at this wavelength. The ionic strength and the hydrogen ion concentration were maintained constant at 0.5 mol dm^{-3} ($NaClO_4$) and 5 x 10^{-2} ($HClO_4$) mol dm^{-3} , respectively and Temp. = 30.0 ± 1 °C.

Pseudo – first order plots of log (A_t - A_∞) against time were made and the slopes of the plots gave the pseudo-first order rate constants, k_1. The second order rate constants, k_2, were obtained from k_1 as k_1/ [[MTU].

Reaction rate dependence on changes in $[H^+]$ was investigated by keeping [MTU] and $[[(bipy)_4(H_2O)_2Ru_2O]^{4+}]$ constant, while varying $[H^+]$ from (0.1– 10.0) x 10^{-4} mol dm^{-3}, maintaining ionic strength constant at 0.5 mol dm^{-3} and the temperature of reaction was maintained at 30 ± 1°C. Variation of acid dependent second order rate constant with $[H^+]$ was obtained from the plot of k_{H+} versus $[H^+]$, while order of reaction with respect to $[H^+]$ was obtained as the slope of the plot of log k_{obs} versus log $[H^+]$.

Dependence of reaction rates on changes of ionic strength of reaction medium

Effect of changes in ionic strength of reaction medium on rates of reaction was studied by varying the ionic strength, I, from 0.05 – 0.8 mol dm^{-3} (NaCl), while maintaining [MTU], $[[(bipy)_4(H_2O)_2Ru_2O]^{4+}]$ and $[H^+]$ constant at 1.1 x 10^{-5} mol dm^{-3}, 9.9 x 10^{-3} mol dm^{-3}, and 1.0 x 10^{-4} mol dm^{-3}, respectively. Reaction temperature was maintained at 30 ± 1°C.

Dependence of reaction rates on changes in dielectric constant of reaction medium

Effect of changes of dielectric constant of reaction medium on reaction rates was studied by adding various quantities of acetone to adjust the dielectric constants, D, from 81.0 to 73.8, keeping [MTU], $[[(bipy)_4(H_2O)_2Ru_2O]^{4+}]$, $[H^+]$, μ and temperature constant. Plot of log k_2 versus 1/ D was done to appreciate the effect of the variation of dielectric constant on the rate constants.

Test for formation of intermediate complex prior to electron transfer

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 free radicals' participation in the reaction

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 $[H^+]$, ionic strength and temperature. Appearance of a gelatinous precipitate indicates he participation of free radicals.

Product analysis

Test for the presence of disulphide in the product mixture was carried out according to McAuley and Gomwalk (1969). 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. Appearance of crystals would suggest the presence of disulphides in the product

Results and discussion

Stoichiometric studies

The stoichiometry of the reaction was found to be in the ratio 1:2 (dimer/ thiourea) (Fig 1).

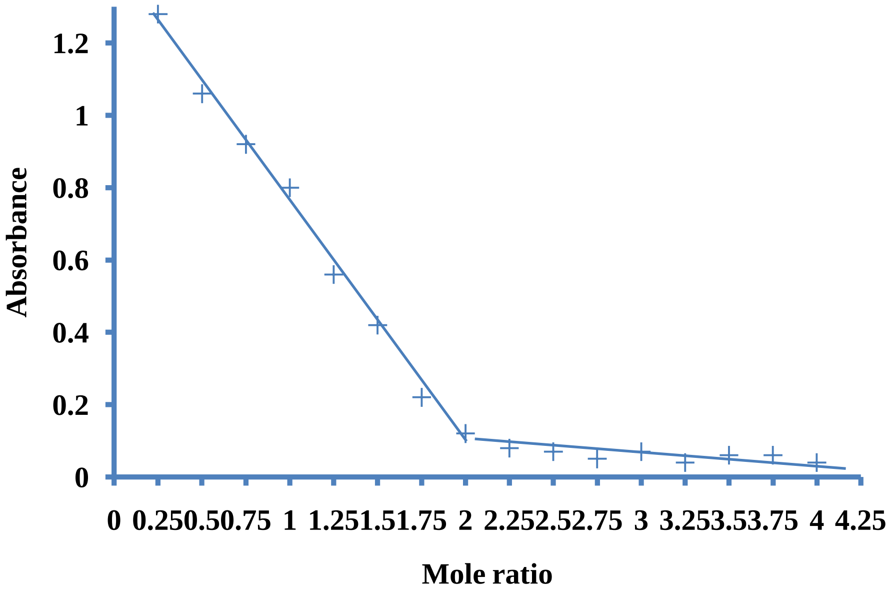
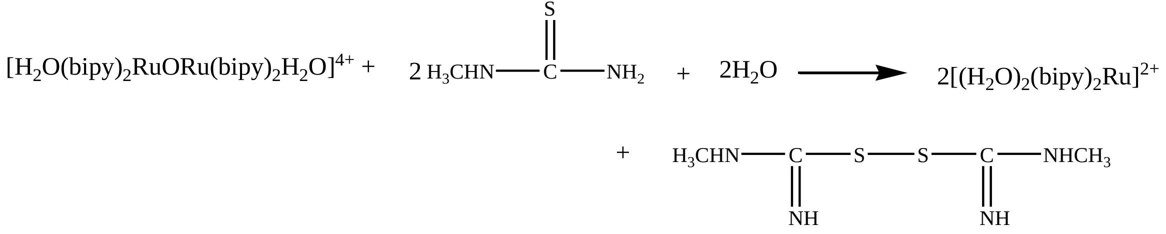


Figure 1 : Stoichiometry of the reaction of $[(H_2O)_2Ru_2O^{4+}]$ and N - methyl thiourea [MTU] . $[(H_2O)_2Ru_2O^{4+}]$ = 6.5 x 10^{-5} mol dm^{-3}; [MTU] = (1.63 - 26.0) x 10^{-5} mol dm^{-}; $[H^+]$ = 5.0 x 10^{-2} mol dm^{-3} ; I = 0.5 mol dm^{-3} ; λ_{max} = 660 nm

This finding conforms to the equation:



........(1)

$$[H_2O(bipy)_2RuORu(bipy)_2H_2O]^{4+} + 2\,H_3CHN{-}\overset{\overset{\displaystyle S}{\|}}{C}{-}NH_2 + 2H_2O \longrightarrow 2[(H_2O)_2(bipy)_2Ru]^{2+} + H_3CHN{-}\underset{\underset{\displaystyle NH}{\|}}{C}{-}S{-}S{-}\underset{\underset{\displaystyle NH}{\|}}{C}{-}NHCH_3 \quad ....(1)$$

Investigations by Iyun et al (1996) and Ayoko et al (1993) revealed the same stoichiometry for the reaction of the ruthenium dimer and l – cysteine and glutathione, respectively. On the other hand, investigations by Iyun et al (1992, 1995) revealed a stoichiometry of 1:1 in the reaction of the ruthenium dimer with iodide, sulphite and mercaptoethanol and mercaptoethylamine, respectively. While in the reaction of the dimer with ascorbic acid and bromate, Iyun et al. (1995, 1992) reported a stoichiometry of 5:1 and 2:1, respectively.

Order of reaction

Linearity of the pseudo first order plots of log (A_t - A_∞) versus time suggests that the reaction is first order in Ru_2O^{4+} (see a typical plot in Figure 2). Values representing the findings of the kobs obtained at different [MTU], [H^+] and I and are summarised in Table 1. The second order rate constants, k_2, for the various [MTU] were constant. Plots of log k_{obs} as a function of log [MTU] and constant [H^+] and I was linear with a slope of 0.98 (Figure 3), indicating that the kinetic order for [MTU] is one. This sums up to second order overall, suggesting the rate law for the reaction as:

$$-\frac{d}{dt}[[(bipy)_4(H_2O)_2Ru_2O]^{4+}] \quad = \quad k_2\,[[(bipy)_4(H_2O)_2Ru_2O]^{4+}][MTU]\ldots\ldots(2)$$

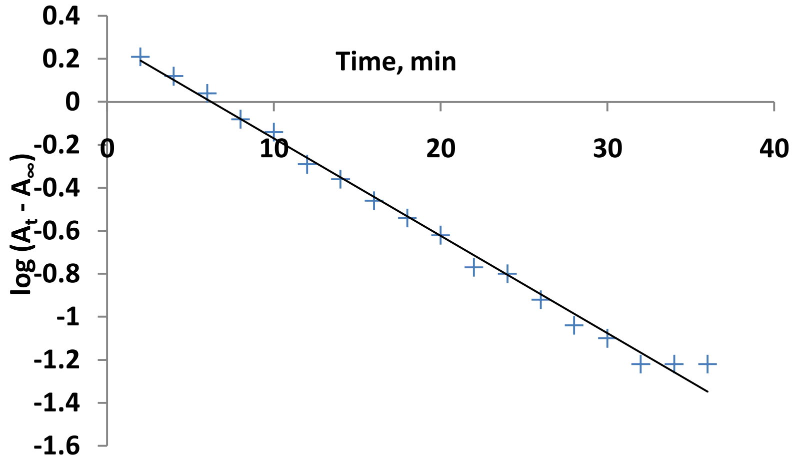


Figure 2 : Typical Pseudo- first order plot for the reaction of $[(H_2O)_2Ru_2O^{4+}]$ and N - methyl thiourea [MTU]. $[(H_2O)_2Ru_2O^{4+}]$ = 6.5 x 10^{-5} mol dm^{-3}; [MTU] = 2.6 x 10^{-2} mol dm^{-3} ; $[H^+]$ = 5.0 x 10^{-2} mol dm^{-2}; I = 0.5 mol dm^{-3} ; λ_{max} = 660 nm ; T = 32 ± 1°C

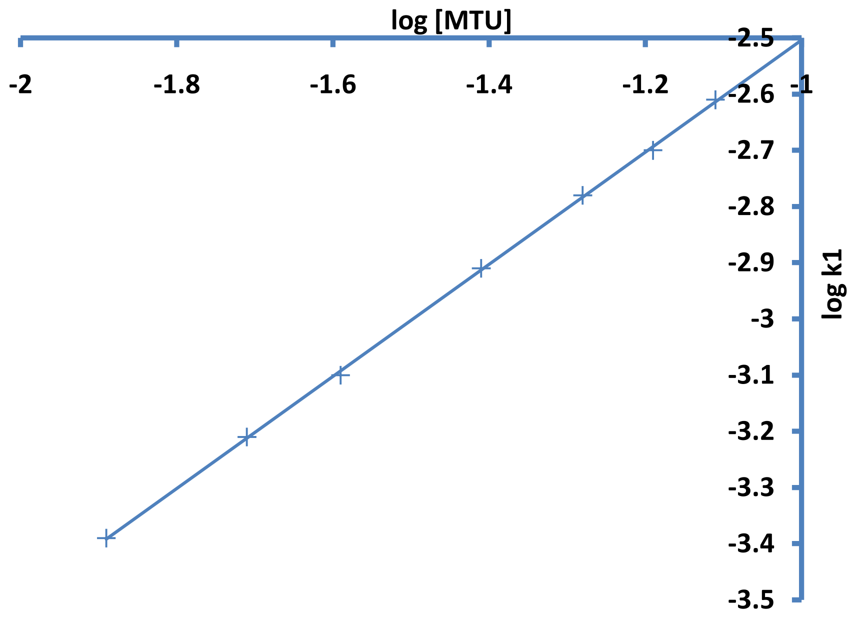


Figure 3 : Plot of log k_1 against log [MTU] for the reaction of $[(H_2O)_2Ru_2O^{4+}]$ and N - methylthiourea [MTU]. $[(H_2O)_2Ru_2O^{4+}]$ = 6.0 x 10^{-5} mol dm^{-3}; [MTU] = 12 x 10^{-2} mol dm^{-3}; $[H^+]$ = 5.0 x 10^{-2} mol dm^{-3} ; I = 0.5 mol dm^{-3} ; λ_{max} = 660 nm ; T = 32 ± 1°C

Table 1: Values of the pseudo-first order and second order rate constants with different variables for the oxidation of MTU by $[(bipy)_4(H_2O)_2Ru_2O]^{4+}$. $[[(bipy)_4(H_2O)_2Ru_2O]^{4+}]$ = 6.50×10^{-5} mol dm $^{-3}$; λ_{max} = 660 nm and Temp = 30 ± 1 °C

10^2[MTU] (mol dm^{-3})	$10^2[H^+]$ (mol dm^{-3})	I (mol dm^{-3})	10^4k_{obs} (s^{-1})	10^2k_2, (dm^3, mol $^{-1}$ s^{-1})
H^+				
1.30	5.00	0.50	4.12	3.17
1.95			6.22	3.19
2.60			7.92	3.04
3.90			12.35	3.17
5.20			16.67	3.20
6.50			19.94	3.07
7.80			24.54	3.14
5.20	2.00	0.50	19.76	3.80
	3.00		18.20	3.50
	4.00		17.42	3.35
	5.00		16.38	3.15
	7.00		14.04	2.70
	10.00		11.40	2.20
	20.00		5.20	0.10
	5.00	0.10	16.28	3.13
		0.20	16.02	3.08
		0.50	16.41	3.16
		0.60	16.33	3.14
		0.70	16.07	3.09
		0.90	16.17	3.11

Similar order has been observed for other reactions of the oxobridged dimer and l – cysteine (Iyu et al., 1996), glutathione (Ayoko et al., 1993), iodide (Iyun et al., 1992), sulphite (Iyun et al., 1992), 2- mercaptoethylamine and 2 – mercaptoethanol (Iyun et al., 1995), ascorbic acid (Iyun et al., 1995), bromate (Iyun et al., 1992), and 1 – 4 benzenediol (Iyun et al., 1992).

H^+ dependence on reaction rates

Changes of [H^+] affected the reaction rates inversely in the acid range used i.e $10^{-3} \leq [H^+] \leq 10^{-2}$ mol dm^{-3} (Table 1). Such inverse acid dependence was observed in the reaction of the ruthenium dimer and L– cysteine (Iyun et al., 1996), sulphite (Iyun et al., 1992) and 1, 3 – benzenediol (Iyun et al., 1992). Decrease in rate of reaction with increase in [H^+] had been explained in terms of the deprotonation of the sulphyhydryl (- SH) groups in thiols prior to electron transfer (Zueva et al., 1990). A plot of acid dependent second order rate constant, k_{H+}, against [H^+] was linear with a slope = 2.01 dm^6 mol^{-2} s^{-1} and intercept = 3.92 x 10^{-2} dm^3 mol^{-1} 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

$$k_{H+} = a + b\frac{1}{[H+]} \quad …….. \quad .(3)$$

where 'a' = 3.92 x 10^{-2} dm^3 mol^{-1} s^{-1} and 'b' = 2.01 dm^6 mol^{-2} s^{-1}

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

$$-\frac{d}{dt}[[(H_2O)_2Ru_2O]^{4+}] = \left(a + b\frac{1}{[H+]}\right)[Ru_2O^{4+}][MTU] \quad ………(4)$$

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

Changes in the ionic strength and dielectric constant of reaction medium had no significant effect on the rate constants (Tables 1 and 2).

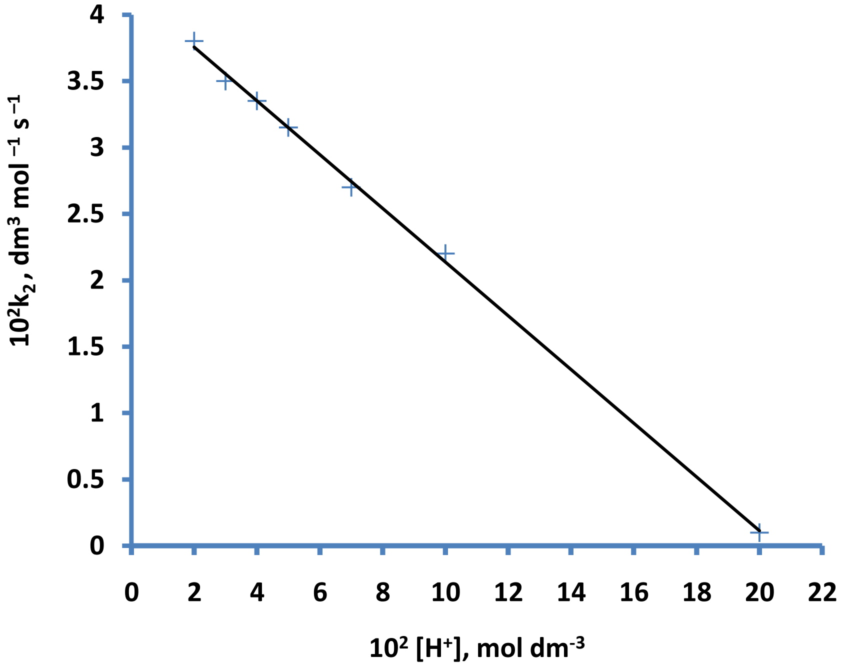


Figure 4 : Plot of k_{H+} against [H$^+$] for the reaction of [$(H_2O)_2Ru_2O^{4+}$] and thiourea [MTU]. [$(H_2O)_2Ru_2O^{4+}$] = 6.5 x 10^{-5} mol dm^{-3}; [MTU] = 5.2 x 10^{-2} mol dm$^{-;}$ [H$^+$] = (2.0 - 20.0) x 10^{-2} mol dm^{-3}; I = 0.5 mol dm^{-3} ; λ_{max} = 660 nm ; T = 32 ± 1°C

Table 2: Effects of changing the dielectric constant of reaction medium on the pseudo-first order rate constants for the oxidation of MTU by [$(bipy)_4(H_2O)_2Ru_2O]^{4+}$.
[[$(bipy)_4(H_2O)_2Ru_2O]^{4+}$]= 6.50 x 10^{-5} mol dm^{-3}. [MTU] = 5.2 x 10^{-2} mol dm^{-3}; [H$^+$] = 5.00 x 10^{-2} mol dm^{-3}, I = 0.50 mol dm^{-3}, λ_{max} = 660 nm and Temp. = 30±1°C

D	10^4k_{obs}, (s^{-1})	10^2k_2, (dm^3, mol^{-1} s^{-1})
81.00	16.30	3.14
79.80	16.43	3.16
78.60	16.07	3.09
77.40	16.38	3.15
75.00	16.28	3.13
72.66	15.86	3.05

Effect of added ions on the rate constants

Added ions did not affect the rate constants of the reaction (Tables 3 and 4). Absence of catalysis on added NO_3^- and CH_3COO^- and Mg^{2+} 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 (Iyun et al., 1995)

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Tests for intermediate complex formation

A plot $1/k_1$ against 1/[MTU] (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 λ_{max}. These are suggestive of absence of formation of intermediate complex.

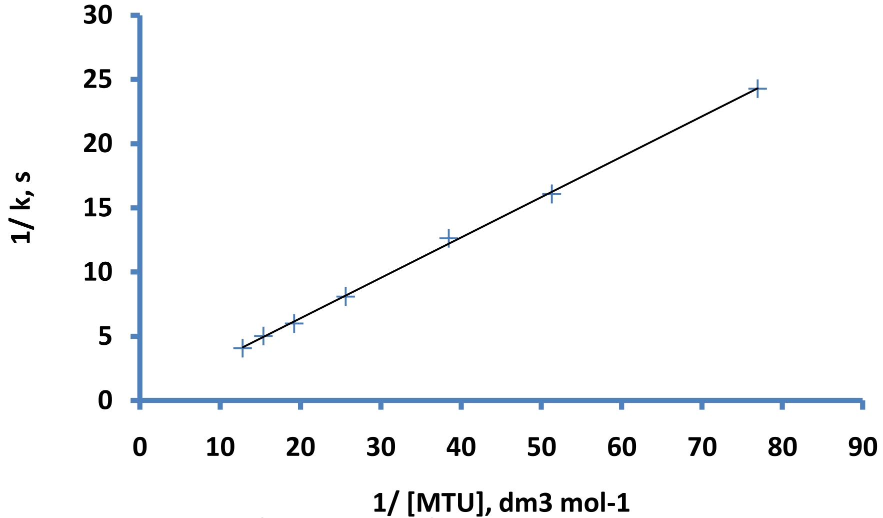


Figure 5 : Plot of 1/ k_1 versus 1/ [MTU] for the reaction of $[(H_2O)_2Ru_2O^{4+}]$ and N - methylthiourea [MTU]. $[(H_2O)_2Ru_2O^{4+}]$ = 6.5 x 10^{-5} mol dm^{-3}; [MTU] = (1.3- 7.80) x 10^{-2} mol $dm^{-;}$ $[H^+]$ = 5.0 x 10^{-2} mol dm^{-3} ; I = 0.5 mol dm^{-3} ; λmax = 660 nm ; T = 32 ± 1°C

Table 3: Effects of added anions on the pseudo-first and second order rate constants for the oxidation of MTU by $[(bipy)_4(H_2O)_2Ru_2O]^{4+}$. $[[(bipy)_4(H_2O)_2Ru_2O]^{4+}]$= 6.50 x 10^{-5} mol dm $^{-3}$. [MTU] = 5.2 x 10^{-2} mol dm^{-3}; [H^+] = 5.00 x 10^{-2} mol dm^{-3}, I = 0.50 mol dm^{-3}, λ_{max} = 660 nm and Temp. = 30±1°C .

10^3 [ion] (mol dm^{-3})	**10^4k_{obs},** (s^{-1})	**10^2k_2,** (dm^3, mol $^{-1}$ s^{-1})
Ion = NO_3^-		
0.00	16.54	3.18
1.00	16.07	3.09
20.00	16.38	3.15
60.00	16.22	3.12
100.00	15.86	3.05
200.00	16.28	3.13
Ion = CH_3COO^-		
0.00	16.11	3.10
1.00	16.38	3.15
20.00	16.25	3.13
60.00	16.12	3.10
100.00	15.97	3.07
200.00	16.38	3.15

Table 4: Effects of added cations on the pseudo-first and second order rate constants for the oxidation of MTU by $[(bipy)_4(H_2O)_2Ru_2O]^{4+}$. $[[(bipy)_4(H_2O)_2Ru_2O]^{4+}]$= 6.50 x 10^{-5} mol dm $^{-3}$. [MTU] = 5.2 x 10^{-2} mol dm^{-3}; $[H^+]$ = 5.00 x 10^{-2} mol dm $^{-3}$, I = 0.50 mol dm^{-3}, λ_{max} = 660 nm and Temp. = 30±1°C

10^3 [ion] (mol dm^{-3})	10^4k_{obs}, (s^{-1})	10^2k_2, (dm^3, mol $^{-1}$ s^{-1})
Ion = Mg^{2+}		
0.00	16.25	3.13
1.00	16.41	3.16
20.00	16.08	3.09
60.00	16.38	3.15
100.00	16.11	3.10

Test for free radicals' formation.

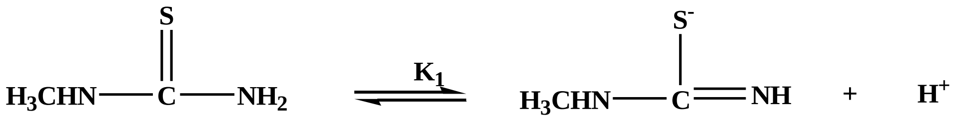
On addition of acrylamide to the reaction mixture followed by excess of methanol, a gelatinous precipitate was formed, suggesting that polymerization has occurred. This confirms the participation of free radicals during the reaction.

Product analysis

Test for the presence of disulphide was carried out according to McAuley and Gomwalk (1969a, 1969b). 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.

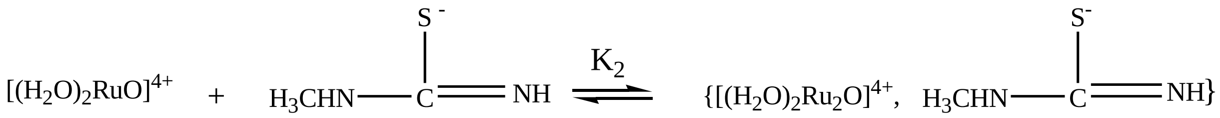
Proposed Mechanism

From the kinetic data obtained in this study there is evidence that the reaction involves two parallel pathways, the acid-dependent and the acid independent pathways. The deprotonation of the N - methylthiourea (equation 5), which is the acid dependent pathway, exhibits an inverse dependence. The deprotonated N- methylthiourea forms an ion pair with the dimer (equation 6) prior to a one – electron transfer. Also the neutral N - methylthiourea 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 N- dimethylthiourea has been reported by Khan et al (2004) in the oxidation of thiourea by Cr (VI) and by Amjad and McAuley (1977) in the oxidation of thiourea by vanadium (V). Based on above considerations, a plausible mechanism for the oxidation of N - methylthiourea by diaquotetrakis(2,2'-bipyridine) - µ - oxodiruthenium (III) ion has been proposed to accommodate all the kinetic data generated in our work.



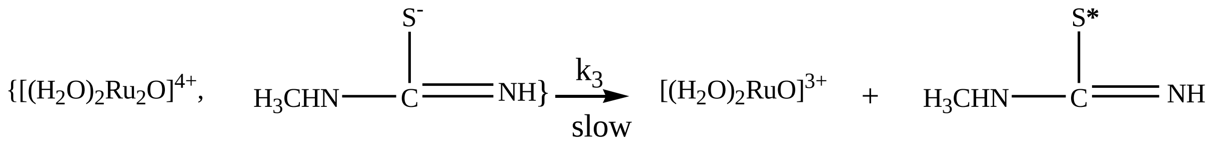
$$\mathbf{H_3CHN{-}\overset{\overset{S}{\|}}{C}{-}NH_2 \overset{K_1}{\rightleftharpoons} H_3CHN{-}\overset{\overset{S^-}{|}}{C}{=}NH + H^+}$$

....................(5)



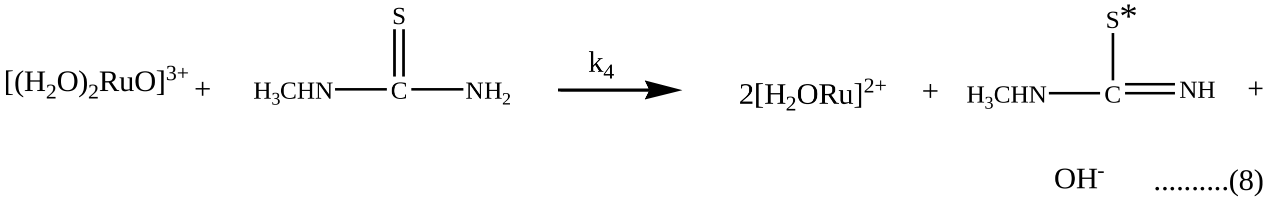
$$[(H_2O)_2RuO]^{4+} + H_3CHN{-}\overset{\overset{S^-}{|}}{C}{=}NH \overset{K_2}{\rightleftharpoons} \{[(H_2O)_2Ru_2O]^{4+},\ H_3CHN{-}\overset{\overset{S^-}{|}}{C}{=}NH\}$$

............................(6)



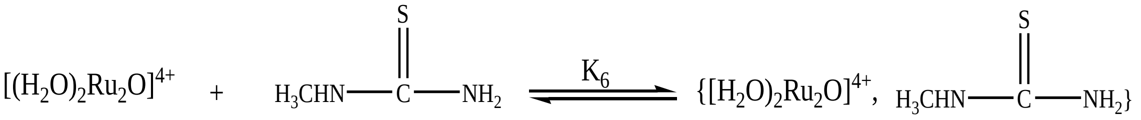
$$\{[(H_2O)_2Ru_2O]^{4+},\ H_3CHN{-}\overset{\overset{S^-}{|}}{C}{=}NH\} \xrightarrow[\text{slow}]{k_3} [(H_2O)_2RuO]^{3+} + H_3CHN{-}\overset{\overset{S^*}{|}}{C}{=}NH$$

...............................(7)

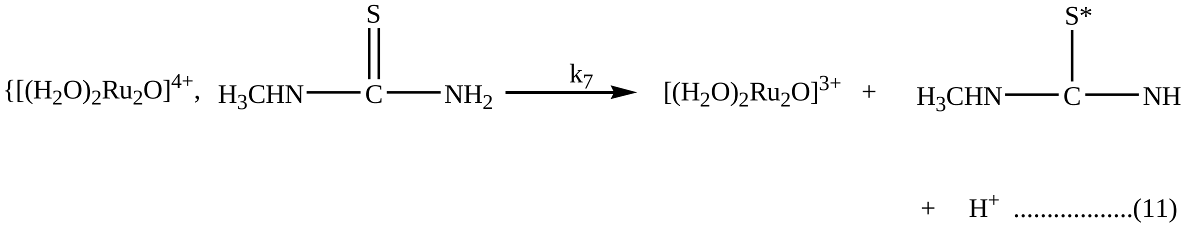


$$[(H_2O)_2RuO]^{3+} + H_3CHN-\overset{\overset{S}{\|}}{C}-NH_2 \xrightarrow{k_4} 2[H_2ORu]^{2+} + H_3CHN-\overset{\overset{S^*}{|}}{C}=NH + OH^- \quad ....(8)$$

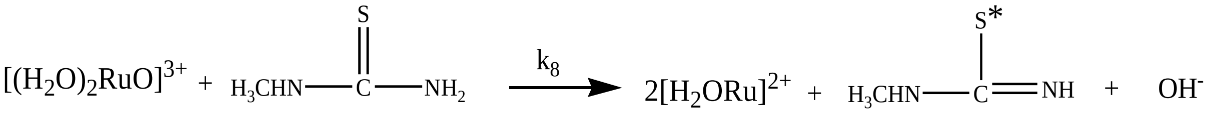
$$2[H_2ORu]^{2+} + 2H_2O \xrightarrow{k_5} 2[H_2O]_2Ru]^{2+} \quad ....(9)$$



$$[(H_2O)_2Ru_2O]^{4+} + H_3CHN-\overset{\overset{S}{\|}}{C}-NH_2 \xrightleftharpoons{K_6} \{[(H_2O)_2Ru_2O]^{4+}, H_3CHN-\overset{\overset{S}{\|}}{C}-NH_2\} \quad ....(10)$$



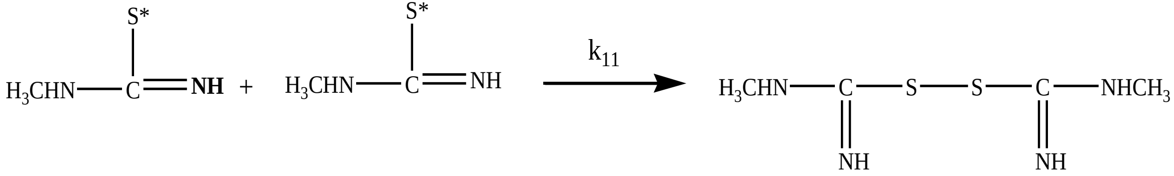
$$\{[(H_2O)_2Ru_2O]^{4+}, H_3CHN-\overset{\overset{S}{\|}}{C}-NH_2 \xrightarrow{k_7} [(H_2O)_2Ru_2O]^{3+} + H_3CHN-\overset{\overset{S^*}{|}}{C}-NH + H^+ \quad ....(11)$$



$$[(H_2O)_2RuO]^{3+} + H_3CHN-\overset{\overset{S}{\|}}{C}-NH_2 \xrightarrow{k_8} 2[H_2ORu]^{2+} + H_3CHN-\overset{\overset{S^*}{|}}{C}=NH + OH^- \quad ....(12)$$

$$2[H_2ORu]^{2+} + 2H_2O \xrightarrow{k_9} 2[H_2O]_2Ru]^{2+} \quad ....(13)$$

$$2OH^- + 2H^+ \xrightarrow{k_{10}} 2H_2O \quad .... (14)$$



$$H_3CHN-\overset{S^*}{\overset{|}{C}}=NH + H_3CHN-\overset{S^*}{\overset{|}{C}}=NH \xrightarrow{k_{11}} H_3CHN-\underset{NH}{\underset{\|}{C}}-S-S-\underset{NH}{\underset{\|}{C}}-NHCH_3 \ldots\ldots.(15)$$

The pathway to this reaction can be assessed as follows:

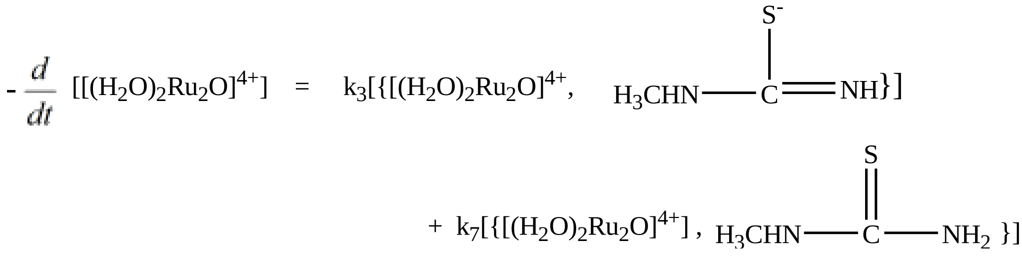
a) Absence of spectroscopic evidence suggests that a precursor complex is probably not formed prior to the act of electron transfer and that the electron transfer may occur by the outer-sphere path.

b) Michaelis-Menten’s plot of $1/k_1$ versus 1/[MTU] was found to be linear without positive intercept suggesting the absence of a preassociation step. This also favours an outer - sphere mechanism.

c) Lack of ion catalysis is in line with the formation of ion pairs in equations (6) and (10) .

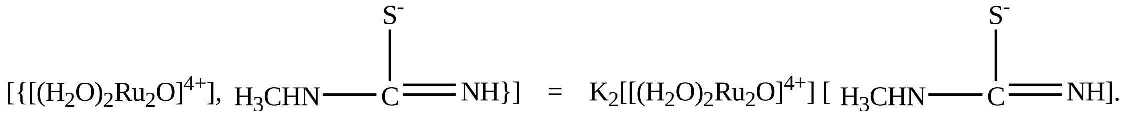
d) The positive result of polymerization test suggests the formation and participation of free radical intermediates in the reaction in equations (7), (8), (11), (12) and (15).Based on the above evidences, an outer sphere mechanistic pathway is proposed for the reaction.

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



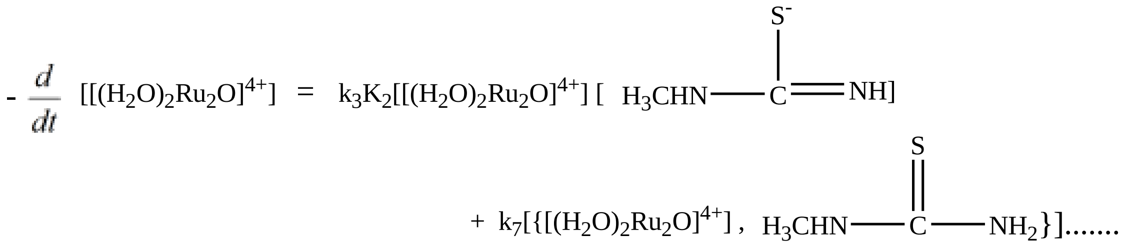
$$-\frac{d}{dt}[[(H_2O)_2Ru_2O]^{4+}] = k_3[\{[(H_2O)_2Ru_2O]^{4+}, H_3CHN-\overset{S^-}{\overset{|}{C}}=NH\}] + k_7[\{[(H_2O)_2Ru_2O]^{4+}], H_3CHN-\overset{S}{\overset{\|}{C}}-NH_2\}]\ldots\ldots\ldots.(16)$$

But from equation (6),



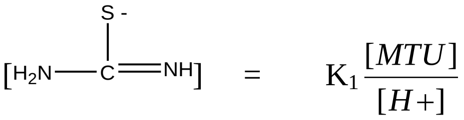
$$[\{[(H_2O)_2Ru_2O]^{4+}], H_3CHN-\overset{S^-}{\overset{|}{C}}=NH\}] = K_2[[(H_2O)_2Ru_2O]^{4+}][H_3CHN-\overset{S^-}{\overset{|}{C}}=NH]\ldots\ldots\ldots.(17)$$

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



$$-\frac{d}{dt}[[(H_2O)_2Ru_2O]^{4+}] = k_3K_2[[(H_2O)_2Ru_2O]^{4+}][\ H_3CHN-\overset{\overset{S^-}{|}}{C}=NH] + k_7[\{[(H_2O)_2Ru_2O]^{4+}],\ H_3CHN-\overset{\overset{S}{\|}}{C}-NH_2\}]\ldots\ldots.(18)$$

Also, from equation (1),

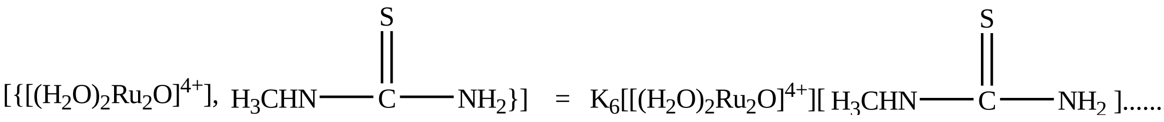


$$[H_2N-\overset{\overset{S\,-}{|}}{C}=NH] = K_1\frac{[MTU]}{[H+]} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(19)$$

Putting equation (19) into equation (18), we have:

$$-\frac{d}{dt}[[(H_2O)_2Ru_2O]^{4+} = k_3K_2K_1[(H_2O)_2Ru_2O^{4+}]\frac{[MTU]}{[H+]} + k_7[(H_2O)_2Ru_2O^{4+}, MTU]\ldots\ldots(20)$$

From equation (10),



$$[\{[(H_2O)_2Ru_2O]^{4+}],\ H_3CHN-\overset{\overset{S}{\|}}{C}-NH_2\}] = K_6[[(H_2O)_2Ru_2O]^{4+}][\ H_3CHN-\overset{\overset{S}{\|}}{C}-NH_2\ ].......(21)$$

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

$$-\frac{d}{dt}[[(H_2O)_2Ru_2O]^{4+}] = k_3\mathbf{K}_2\mathbf{K}_1[[(H_2O)_2Ru_2O]^{4+}]\frac{[MTU]}{[H+]} + k_7\mathbf{K}_6[[(H_2O)_2Ru_2O]^{4+}][MTU]\ldots.(22)$$

$$= (k_7\mathbf{K}_6 + k_3\mathbf{K}_2\mathbf{K}_1\frac{[1]}{[H+]})[[(H_2O)_2Ru_2O]^{4+}][MTU] \ldots\ldots\ldots.(23)$$

Equation (23) agrees with equation (4) where $k_7\mathbf{K}_6$ = 'a' = 3.92 x 10^{-2} dm^3 mol^{-1} s^{-1} and $k_3\mathbf{K}_2\mathbf{K}_1$ = 'b' = 2.01 dm^6 mol^{-2} 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).

3 CONCLUSION

The kinetics of the oxidation of N – methyl 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/ N- methylthiourea), first order kinetics with respect to the ruthenium dimer and methylthiourea and inverse acid dependence. Evidence of the formation of intermediate complex based on absence of intercept in the Michaelis - Menten plot and shift in λ_{max} of the reaction mixture 1 minute after start of reaction was lacking. Coupled with absence of observable anion catalysis, it is proposed that the reaction most probably proceeded through the outer sphere mechanism.

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