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Oxidation Of *N*, *N*-Dimethylthiourea By Diaquotetrakis(2,2'-BIPYRIDINE) - µ - Oxodiruthenium (III) Ion In Aqueous Acid Medium: A Kinetic Approach To Mechanism Of Reaction

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Abstract

Background: *Electron transfer (redox) reactions play very important roles in many biological processes including collagen synthesis, steroid metabolism, the immune response, drug activation, neurotransmitter metabolism, nitrogen fixation, respiration and photosynthesis. Ruthenium complexes with polypyridyl ligands have received much attention owing to their interesting spectroscopic, photophysical, photochemical and electrochemical properties, which are responsible for their potential uses in diverse areas such as photosensitizers for photochemical conversion of solar energy. Thiourea and its derivatives, of which DMTU is one, can be oxidised by a wide variety of oxidising agents and the reaction pathways and final products of the oxidation reaction depend on the reagents used and condition of the reaction mixtures.*

Materials and Methods: *Kinetic and mechanistic studies of the oxidation of N,N-dimethyl thiourea (DMTU) by diaquotetrakis(2,2'-bipyridine) - µ - oxodiruthenium (III) ion, hitherto referred to as* Ru_2O^{4+}*, has been carried out in hydrogen ion concentration,* $[H^+] = 5.0 \times 10^{-2}$ *mol* dm^{-3} *(*$HClO_4$*), ionic strength,* $I = 0.5$ *mol* dm^{-3} *(*$NaClO_4$*) and at a temperature,* $T = 30\pm1°C$*.*

Results*: The reaction revealed that a stoichiometry of 2:1 (DMTU/* Ru_2O^{4+}*, first order dependence with respect to [DMTU], an acid – independent and inverse acid dependent pathways. The reaction rates were not affected by changes in ionic strength and dielectric constant of the reaction medium. Addition of ions to the reaction medium had little or no effect on the reaction rates. There was evidence of the participation of free radicals in the reaction. There was no shift in* λ_{max} *of the reaction mixture 1 minute after start of reaction. Michaelis Menten plot revealed no appreciable intercept.*

Conclusion: *Based on the findings, an outersphere mechanism is implicated to operate in the reaction and a plausible mechanism is proposed.*

Keywords*: Kinetics; oxidation; anion catalysis; salt effect.*

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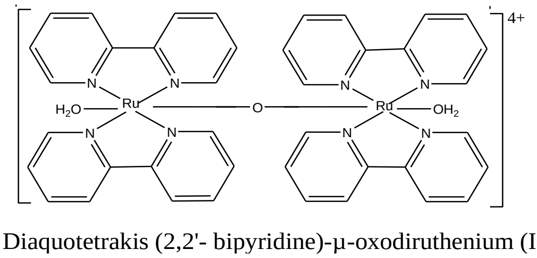
I. Introduction

Ruthenium complexes with polypyridyl ligands are of great interest due to their potential to be used in diverse areas such as photo sensitizers for photochemical conversion of solar energy[1-4], molecular electronic devices[5] and as photoactive DNA cleavage agents for therapeutic purposes[6].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 $[(bpy)_2(H_2O)RuORu(H_2O)(bpy)_2]^{4+}$ (scheme 1) was reported by the Meyers group in 1982[7,8] .



Scheme 1: Diaquotetrakis (2,2'- bipyridine)-µ-oxodiruthenium (III) ion

Thiourea and its derivatives, including DMTU, have been used as effective scavenger of reactive oxygen intermediates[9]. Due to their reducing properties, they have been used in the textile industry[10], as corrosion inhibitors[11] and in industrial equipment such as boilers which develop scales due to corrosion. Besides these, several thiourea derivatives have various agricultural uses as fungicides, herbicides and rodenticides and industrial uses which include applications in rubber industries as accelerators, and in photography as fixing agents and to remove stains from negatives. A vast amount of information is available on the oxidation of thiourea and thiourea derivatives by oxidising agents such as hydrogen peroxide[12], bromate[13], nickel (IV)oxime – imine complex[14], chlorine dioxide[15], hydrogen peroxide catalysed by$[Ru^{III}(EDTA)(H_2O)]$[16] and 3,7–Bis(Dimethylamin phenazothionium chloride[17]. It is our intention to study the oxidation of this thiourea derivative by this versatile ruthenium dimer.

II. Materials And Methods

Materials: Diaquotetrakis(2,2'bipyridine)-µ- oxodiruthenium(III) perchlorate, was prepared according to literature[18]. A 3.0 x 10^{-4} mol dm^{-3} standard solution of the synthesised ruthenium dimer was prepared by dissolving 3.83 x 10^{-2} g of the synthesised complex in a 100 cm^3 volumetric flask and made up to the mark. Solutions of N,N-dimethylthiourea (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 $NaClO_4$ (Sigma – Aldrich)

Methods: The stoichiometry of the reaction was determined by spectrophotometric titration using the mole ratio method. $[Ru_2O^{4+}]$ was kept constant at 6.0 x 10^{-5} mol dm^{-3} while [DMTU] was varied between (1.5 – 24.0) x 10^{-5} mol dm^{-3} (mole ratio 1:0.25 to 1:4) (oxidant /reductant). The rates of reactions of Ru_2O^{4+} and DMTU were studied by monitoring the decrease in absorbance of the dimer at its λ_{max} (660 nm) using Seward Biomedical Digital Colorimeter. All kinetic measurements were carried out under pseudo–first order conditions with respective reductant concentrations in excess of the oxidant concentration at stated temperature. Ionic strength as well as $[H^+]$ were maintained constant throughout the study unless otherwise stated. The pseudo – first order rate constants, k_{obs},were obtained as the slopes of the pseudo – first order plots of log $(A_t - A_\infty)$ against time. The second order rate constants, k_2 , were determined from k_{obs} as k_{obs}/ [reductant]. The effect of changes in $[H^+]$ on the reaction rate was investigated by keeping $[Ru_2O^{4+}]$ and [DMTU] constant, while $[H^+]$ was varied. Ionic strength, I, was maintained constant at 0.50 mol dm^{-3} [salt] and at the stated temperature the reaction was carried out. Order of reaction with respect to $[H^+]$ was obtained as the slope of the plot of log k_{obs} against log $[H^+]$. Relationship between acid-dependent second order rate constant, $k_2(H^+)$ with $[H^+]$ was obtained by plotting $k_2(H^+)$ against $[H^+]$. Effect of change in dielectric constant of the reaction medium on the reaction rate was investigated by adding various amounts of acetone to the reaction mixture while maintaining $[Ru_2O^{4+}]$, [DMTU], $[H^+]$ as well as I constant. The effect of added ions on the reaction rate was observed by the addition of various amounts of ions (NO_3^-, CH_3COO^-) while maintaining the dimer, reductant and hydrogen ion concentrations constant. The ionic strength and temperature were maintained constant, also. Test for formation of stable and 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 [H+], ionic strength and temperature. Test for the presence of disulphide in the product mixture was carried out according to McAuley and Gomwalk[19].

III. Results And Discussion

Stoichiometry

Plot of absorbance against mole ratio of the reaction (Figure 1) suggested that two moles of DMTU was oxidised by one mole of Ru_2O^{4+}. This is consistent with the stoichiometric Equation 1.

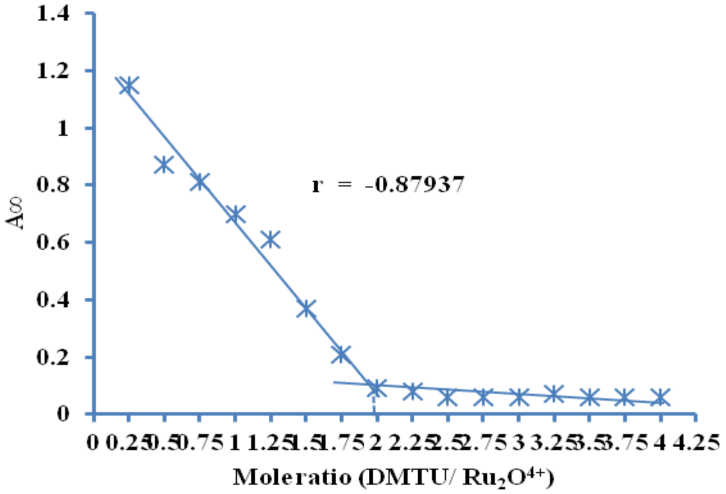
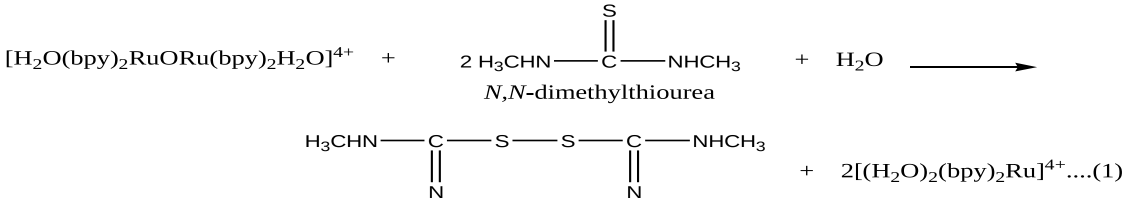


Figure 1: Plot of Absorbance versus Mole Ratio for the Reaction of $[(H_2O)_2Ru_2O]^{4+}$ and *N, N'*-dimethylthiourea (DMTU) at $[(H_2O)_2Ru_2O^{4+}]$ = 6.0 x 10^{-5} mol dm^{-3}, [DMTU] = (1.5 - 24.0) x 10^{-5} mol dm^{-3}, $[H^+] = 5.0 \times 10^{-2}$ mol dm^{-3}, I = 0.5 mol dm^{-3} and λ_{max} = 660 nm



$$[H_2O(bpy)_2RuORu(bpy)_2H_2O]^{4+} + \underset{N,N\text{-dimethylthiourea}}{2\,H_3CHN-\overset{\overset{S}{\|}}{C}-NHCH_3} + H_2O \longrightarrow H_3CHN-\underset{\underset{N}{\|}}{C}-S-S-\underset{\underset{N}{\|}}{C}-NHCH_3 + 2[(H_2O)_2(bpy)_2Ru]^{4+}....(1)$$

This agrees with the stoichiometry found for the reaction of Ru_2O^{4+} and l – cysteine[20] and glutathione[21], while in disagreement with the stoichiometry of 1:1 found for the reaction of the Ru_2O^{4+} and iodide[22], sulphite[23], mercaptoethanol and mercaptoethylamine[24]. Also, a stoichiometry of 2:1 was found for the reaction of $Ru_2O^{4+}$and ascorbic acid[25] and that of the reaction of Ru_2O^{4+} and bromate was reported to be 5:1[26].

Rate Constants and Order of Reaction

There was a linearity to more than 90% completion of reaction of all of the pseudo first order plots of log (A_t - A_∞) against time (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 $[Ru_2O^{4+}]$ (see a typical plot on Figure 2). Slopes of the pseudo-first order plots gave the pseudo-first order rate constants, k_{obs}, and are depicted in Table 1.The second order rate constants, k_2, for the various [DMTU] calculated from k_{obs} as k_{obs}/ [DMTU] were found to be fairly constant i.e (8.12 ± 0.04) x 10^{-2} dm^3 mol^{-1} s^{-1} and also presented in Table 1. A plot of log k_{obs} against log [DMTU] was linear with a slope of 0.97 (Figure 3), suggesting a first order reaction with respect to [DMTU]. The rate law for this reaction is thus given as Equation 2.

$$-\frac{d}{dt}[Ru_2O^{4+}] = k_2[Ru_2O^{4+}][DMTU] \qquad \ldots \quad (2)$$

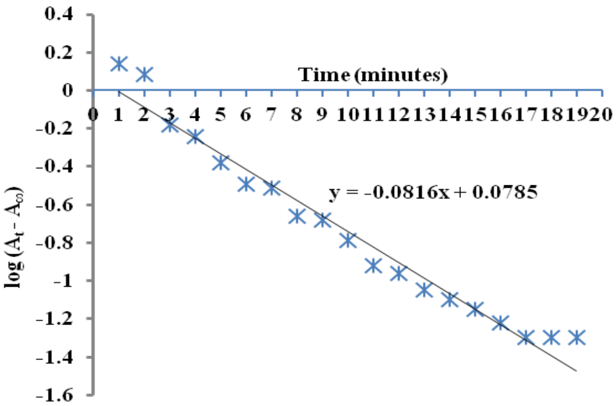


Figure 2: Typical Pseudo-first Order Plot for the Reaction of $[(H_2O)_2Ru_2O]^{4+}$ and *N, N'*-dimethylthiourea (DMTU) at $[(H_2O)_2Ru_2O^{4+}]$ = 7.0 x 10^{-5} mol dm^{-3}, [DMTU] = 3.5 x 10^{-2} mol dm^{-3}, $[H^+] = 5.0 \times 10^{-2}$ mol dm^{-3}, I = 0.5 mol dm^{-3}, T = 31 ± 1°C and λ_{max} = 660 nm

H^+ Dependence on Reaction Rate

The rates of reaction was inversely affected by increase in $[H^+]$ in the acid range used i.e $2 \times 10^{-3} \leq [H^+] \leq 2 \times 10^{-2}$ mol dm^{-3} (Table 1). Similar inverse acid dependence was observed in the reaction of Ru_2O^{4+} and sulphite[20] and L– cysteine[17]. Such inverse acid dependence had been explained in terms of the deprotonation of the sulphyhydryl (- SH) groups in thiols prior to electron transfer[24,25]. A plot of acid dependent second order rate constant, $k_2[H^+]$, against $[H^+]$ was linear with a slope= -0.46 dm^6 mol^{-2} s^{-1} and intercept = 10.43 x 10^{-3} dm^3 mol^{-1} s^{-1} (Fig. 3), 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 Equation 3

$$k_2[H^+] = a + b[H^+]^{-1} \quad \ldots\ldots\ldots \quad (3)$$

where 'a' = 10.43 x 10^{-3} dm^3 mol^{-1} s^{-1} and 'b' = -0.46 dm^6 mol^{-2} s^{-1}

The rate equation for the reaction of diaquotetrakis(2, 2'bipyridine) - μ - oxodiruthenium (III) ion and *N,N',*-dimethylthiourea can now be written as Equation 4.

$$-\frac{d}{dt}[Ru_2O^{4+}] = (a + b[H^+]^{-1})[Ru_2O^{4+}][DMTU] \quad \ldots\ldots\ldots \quad (4)$$

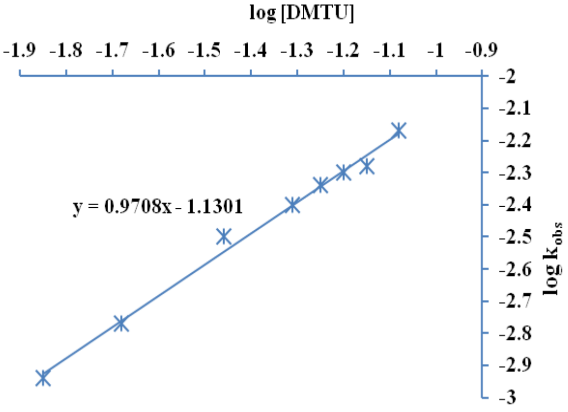


Figure 3: Plot of log k_{obs} against log [DMTU] for the Reaction of $[(H_2O)_2Ru_2O]^{4+}$ and *N,N'*-dimethylthiourea (DMTU) at $[(H_2O)_2Ru_2O^{4+}]$ = 7.0 x 10^{-5} mol dm^{-3}, [DMTU] = (1.4 - 8.4) x 10^{-2} mol dm^{-3}, $[H^+] = 5.0 \times 10^{-2}$ mol dm^{-3}, I = 0.5 mol dm^{-3}, T = 31 ± 1°C and λ_{max} = 660 nm

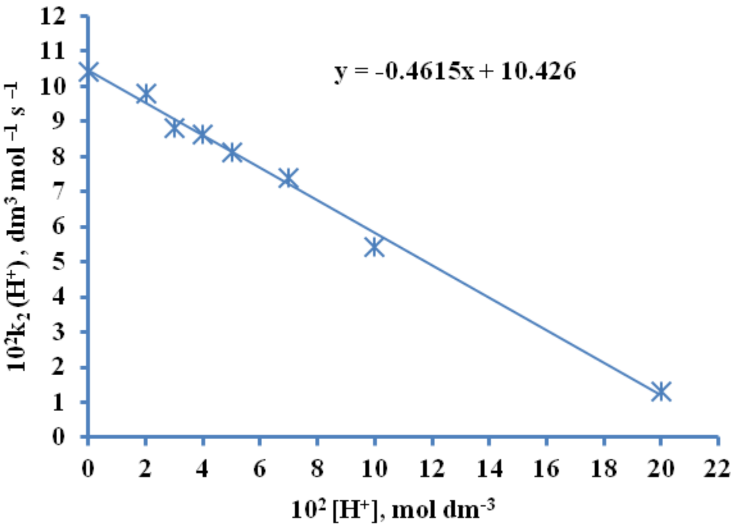


Figure 4: Plot of $k_2(H^+)$against $[H^+]$ for the Reaction of $[(H_2O)_2Ru_2O]^{4+}$ and *N,N′*-dimethythiourea (DMTU) at $[(H_2O)_2Ru_2O^{4+}] = 7.0 \times 10^{-5}$ mol dm^{-3}, [DMTU] = 5.6×10^{-2} mol dm^{-3}, $[H^+] = (2.0 - 20.0) \times 10^{-2}$ mol dm^{-3}, I = 0.5 mol dm^{-3}, T = 31 ± 1°C and λ_{max} = 660 nm

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)

Table 1: Pseudo-first Order and Second Order Rate Constants for the Reaction of $Ru_2O^{4+}$and *N,N'*-dimethylthiourea (DMTU) at $[Ru_2O^{4+}] = 7.0 \times 10^{-5}$ mol dm^{-3}, I = 0.5 mol dm^{-3} ($NaClO_4$), T = 31.5 ± 1°C and λ_{max} = 660 nm

10^2 [DMTU], mol dm^{-3}	$10^3\ [H^+]$, mol dm^{-3}	I, mol dm^{-3}	10^3k_{obs}, s^{-1}	10^2k_2, $dm^3\ mol^{-1}\ s^{-1}$
1.40	5.0	0.5	1.14	8.16
2.10	5.0	0.5	1.71	8.14
3.50	5.0	0.5	2.86	8.16
5.60	5.0	0.5	4.57	8.14
6.30	5.0	0.5	5.03	7.98
7.00	5.0	0.5	5.69	8.13
8.40	5.0	0.5	6.82	8.12
5.60	2.0	0.5	5.49	9.80
5.60	3.0	0.5	4.93	8.80
5.60	5.0	0.5	4.54	8.11
5.60	7.0	0.5	4.14	7.39
5.60	10.0	0.5	3.04	5.43
5.60	20.0	0.5	0.74	1.32
5.60	5.0	0.1	4.55	8.13
5.60	5.0	0.2	4.54	8.11
5.60	5.0	0.5	4.47	7.99
5.60	5.0	0.6	4.56	8.14
5.60	5.0	0.7	4.55	8.13
5.60	5.0	0.9	4.55	8.13

Table 2: Effect of Changes in the Dielectric Constant of Reaction Medium for the Reaction of $[Ru_2O]^{4+}$ and (DMTU) at $[Ru_2O^{4+}] = 7.0 \times 10^{-5}$ mol dm^{-3}, [DMTU] = 5.6×10^{-2} mol dm^{-3}, I = 0.5 mol dm^{-3} ($NaClO_4$), D = (81.0 – 69), T = 31 ± 1°C and λ_{max} = 660 nm

D	$10^3 k_{obs}$, s^{-1}	$10^2 k_2$, dm^3 mol^{-1} s^{-1}
81.0	4.54	8.11
79.2	4.55	8.13
78.0	4.52	8.07
76.8	4.55	8.13
75.6	4.54	8.11
74.4	4.53	8.09
72.0	4.54	8.11
69.0	4.55	8.13

For reactions of ions in aqueous media, the rate of reaction is directly dependent on the square root of the ionic strength of the media. If ionic strength is varied, the various values of k_2 obtained could be plotted as log k_2 against $\sqrt{I}$. The magnitude of the slopes of the plots gives an idea of the product of the charges on the species' reacting in the rate determining step[27]. Non – dependence of rate of reaction on ionic strength will likely be due to no charge on one of the reactants or both of the reactants. Since ion – pair complex does not possess a formal charge, the rate of reaction would also not be affected if ion –pairs are involved in reactions with outer sphere character[24].

Effect of Added Anions on the Rate Constants

Added anions did not affect the rate constants of the reaction (Table 3). Absence of catalysis on added NO_3^- and CH_3COO^- is in line with the formation of ion – pairs in Equations (6) and (9) 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[25].

Table 3: Effect of Added Anions to Reaction Medium for the Reaction of $[Ru_2O]^{4+}$ and *N,N'*-dimethylthiourea (DMTU) at $[Ru_2O]^{4+} = 7.0 \times 10^{-5}$ mol dm^{-3} , [DMTU]= 5.6×10^{-2} mol dm^{-3}, [H^+] = 5×10^{-2} mol dm^{-3}, I = 0.5 mol dm^{-3}, T = 31 ± 1 °C and λ_{max} = 660 nm

Ion	10^3[ion] mol dm^{-3}	$10^3 k_{obs}$, s^{-1}	$10^2 k_2$, dm^3 mol^{-1} s^{-1}
CH_3COO^-	0.00	4.54	8.11
	20.00	4.55	8.13
	50.00	4.54	8.11
	100.00	4.53	8.09
	200.00	4.55	8.13
NO_3^-	0.00	4.51	8.05
	20.00	4.56	8.14
	50.00	4.53	8.09
	100.00	4.55	8.13
	120.00	4.54	8.11

Tests for Intermediate Complex Formation

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}. Also, a plot $1/k_{obs}$ against 1/[DMTU] (Michaelis Menten plot) was linear passing through the origin (Figure 5)., These evidences are suggestive of absence of formation of intermediate complex(es).

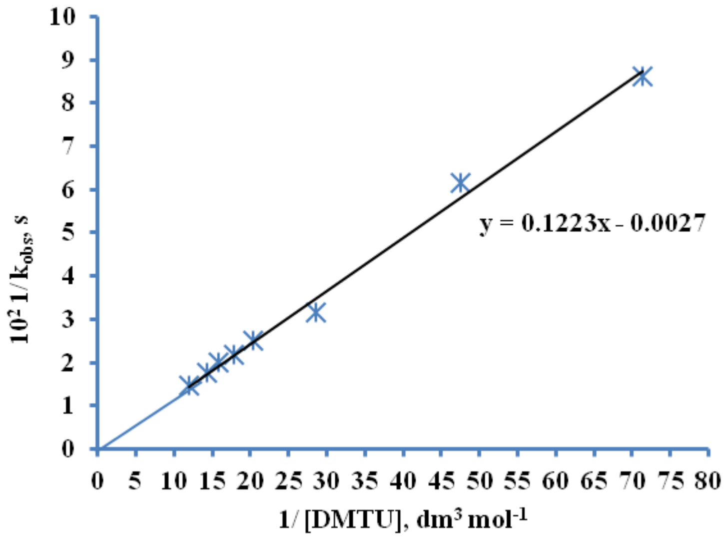


Figure 5: Plot of 1/ k_{obs} versus 1/ [DMTU] for the Reaction of $[(H_2O)_2Ru_2O]^{4+}$ and *N,N'*-dimethylthiourea (DMTU) at $[(H_2O)_2Ru_2O^{4+}]$ = 7.0 x 10^{-5} mol dm^{-3}, [DMTU] = (1.4 - 8.4) x 10^{-2} mol dm^{-3}, $[H^+] = 5.0 \times 10^{-2}$ mol dm^{-3}, I = 0.5 mol dm^{-3}, T = 31 ± 1°C and $\lambda_{max} = 660$ nm

Test for Free Radical 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.

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 *N,N',*-dimethylthiourea (Equation 5). The deprotonated DMTU forms an ion pair with the dimer (Equation 6) prior to a one – electron transfer. Also the neutral DMTU also forms an ion – pair with the dimer (Equation 9) prior to another one – electron transfer. Formation and participation of free radicals which later dimerise to form disulphide as an oxidation product of DMTU has been reported by Khan et al.[28] in the oxidation of thiourea by Cr (VI) and by Amjad et al.[29] in the oxidation of thiourea by vanadium (V), in the oxidation of thiourea[30] and *N*-methylthiourea[31] by diaquotetrakis(2,2'-bipyridine)-µ- oxodiruthenium (III) ion. Based on above considerations, a plausible mechanism for the oxidation of *N,N',*-dimethylthiourea (which is denoted TSH) by diaquotetrakis(2,2'- bipyridine)-µ- oxodiruthenium (III) ion has been proposed to accommodate all the kinetic data generated in our work.

$$\mathrm{TSH} \underset{}{\overset{K_1}{\rightleftharpoons}} \mathrm{TS^-} + \mathrm{H^+} \qquad (5)$$

$$[(H_2O)_2(bipy)_4Ru_2O]^{4+} + TS^- \overset{K_2}{\rightleftharpoons} \{[(H_2O)_2(bipy)_4Ru_2O]^{4+}, TS^-\} \quad .....(6)$$

$$\{[(H_2O)_2(bipy)_4Ru^2O]^{4+}, TS^-\} \xrightarrow[\text{slow}]{k_3} [(H_2O)_2(bipy)_4Ru_2O]^{3+} + TS^* \quad ....(7)$$

$$[(H_2O)_2(bipy)_4Ru_2O]^{3+} + TSH + 2H_2O \xrightarrow{k_4} 2[(H_2O)_2(bipy)_2Ru]^{2+} + TS^* + OH^- \ ...(8)$$

$$[(H_2O)_2(bipy)_4Ru_2O]^{4+} + TSH \overset{K_5}{\rightleftharpoons} \{[(H_2O)_2(bipy)_4Ru_2O]^{4+}, TSH\} \quad .....(9)$$

$$\{[(H_2O)_2(bipy)_4Ru^2O]^{4+}, TSH\} \xrightarrow[slow]{k_6} [(H_2O)_2(bipy)_4Ru_2O]^{3+} + TS^* + H^+ ....(10)$$

$$[(H_2O)_2(bipy)_4Ru_2O]^{3+} + TSH + 2H_2O \xrightarrow{k_7} 2[(H_2O)_2(bipy)_2Ru]^{2+} + TS^* + OH^- .(11)$$

With equations (7) and (10) as the rate determining steps, the rate equation of the reaction can be written as:

$$Rate = k_3[\{[(H_2O)_2(bipy)_4Ru_2O]^{4+}, TS^-\}] + k_6[[(H_2O)_2(bipy)_4Ru_2O]^{4+}, TSH] .. \quad ..(12)$$

But from equation 6:

$$\{[(H_2O)_2(bipy)_4Ru_2O]^{4+}, TS^-\} = K_2[(H_2O)_2(bipy)_4Ru_2O^{4+}] [TS^-] \quad ...(13)$$

Putting Equation 13 into Equation 12 we have:

$$Rate = k_3K_2[[(H_2O)_2(bipy)_4Ru_2O^{4+}] [TS^-] + k_6[[(H_2O)_2(bipy)_4Ru_2O]^{4+}, TSH] .. \quad ..(14)$$

Also from Equation 5:

$$TS^- = K_1 \frac{[TSH]}{[H^+]} \quad (15)$$

Substituting Equation 15 into Equation 14, we have Equation 16:

$$Rate = k_3K_1K_2[[(H_2O)_2(bipy)_4Ru_2O^{4+}] \frac{[TSH]}{[H^+]} + k_6[[(H_2O)_2(bipy)_4Ru_2O]^{4+}, TSH] \quad ...(16)$$

From Equation 9,

$$\{[(H_2O)_2(bipy)_4Ru_2O]^{4+}, TSH\} = K_5[(H_2O)_2(bipy)_4Ru_2O^{4+}] [TSH] \quad ...(17)$$

Substituting Equation 17 into Equation 16 we have Equation 18:

$$Rate = k_3K_1K_2[\{[(H_2O)_2(bipy)_4Ru_2O^{4+}] \frac{[TSH]}{[H^+]} + k_6K_5[(H_2O)_2(bipy)_4Ru_2O^{4+}][TSH] \quad (18)$$

$$= (k_6K_5 + k_3K_1K_2 \frac{1}{[H^+]})[(H_2O)_2(bipy)_4Ru_2O^{4+}][TSH] \quad ..(19)$$

Equation 19 is similar to Equation 4, where k_6K_5 = 'a' and $k_3K_1K_2$ = 'b' and the values of 'a' and 'b' were 10.43 x 10^{-3} dm^3 mol^{-1} s^{-1} and -0.46 dm^6 mol^{-2} s^{-1}, respectively. Free radical formation is rationalized by Equations 7, 8, 10 and 11 in the mechanism of the reaction

Reference

[1]. Kalyanasundaram, K., Photophysics, photochemistry and solar energy conversion with tris (bipyridyl) ruthenium (II) and its analogues. Coord. Chem. Rev. 1982;46:159-247

[2]. Juris, A., Balzani, V., Barigelleti, F., Campagna, S., Belser, P. and vonZelewsky, A.,. Ru (II) polypyridine complexes: Photophysics, photochemistry, electrochemistry and chemiluminescence. Coord. Chem. Rev. 1988;;84:85-277

[3]. Meyer, T.J., Chemical approaches to artificial photosynthesis. Acct. Chem. Res.1989; 22:163

[4]. Balzani, V., Juris, A., Ventura, M., Campagna, S. and Serroni, S., Luminescent and redoxactive polynuclear transition metal complexes. Chem. Rev. 1996;96:759-764

[5]. Newkome, G.R., Cho, T.J., Moorefield, C.N., Mohapatra, P.P. and Grodinez, L.A.,. Towards ordered architectures: Self-assembly and stepwise procedures to the hexameric metallomacrocytes [Arylbis(terpyridinyl)6 FeII6 – n –RuIIn]. (n=0,2,3,5). Chem. Eur. J. 2004;10:1493-1500

[6]. Jiang, C.W., Chao, H., Hong, X.L., Li, H., Mei, W.J. and Ji, L.N., Enantiopreferential DNA- binding of a novel dinuclear complex $[(bpy)_2Ru(bdptb)Ru(bpy)_2]^{4+}$. Inorg. Chem. Commun. 2003;6:773-775

[7]. Gersten, S.W Samuels, G. J and Meyer T.J. Catalytic Oxidation of Water by an oxobridged ruthenium dimer. Journal of American Chemical Society. 1982;104:4029-4030

[8]. Gilbert, J.A, Eggleston, D.S, M, D.S, Murphy, W R, Geselowitz, D.A, eselowitz, D.A, Gersten, S.W, Hodgson, D.J and Meyer, T. J. Structure and redox properties of the water oxidation catalyst $[(bipy)_2(OH_2)RuORu(OH_2)(bpy)_2]^{4+}$. Journal of America Chemical Society. 1985;107:3855-386

[9]. Fox, R.B. Prevention of Granulocyte – Mediated Oxidant Lung Injury in Rats by a Hydroxyl Radical Scavenger Dimethylthiourea. Journal of Clinical Investigation. 1984;74(4):1456 – 1464

[10]. Arifoglu, M.A., Marmer, W.N. and Dudley, R.L.. Reaction of Thiourea with Hydrogen Peroxide: 13C NMR Studies of an Oxidative/ Reductive Bleaching Process. Textile Research Journal. 1992;62: 94-100

[11]. Ayres, J.A. Decontamination of Nuclear Reactors and Equipment 2nd Ed. Ronald Press Co. New York,. 1970: 177

[12]. Hoffmann, M.and Edwards, J.O., Kinetics and mechanism of the oxidation of thiourea and N, N’ – dialklylthioureas by hydrogen peroxide. Inorg. Chem. 1977;16(12):3333–333

[13]. Simoyi, H.S., Epstein, I.R. and Kustin, K., Kinetics and mechanism of the oxidation of thiourea by bromate in acidic medium. J. Phys. Chem. 1994;98(2):551–557

[14]. Bhattacharya, S., Dutta, A. And Banerjee, P., Oxidation of thiourea and its N-substituted derivatives by a nickel (IV) oxime-imine complex in aqueous perchlorate medium. Acta Chemica Scandinavica. 1997;51:676-682

[15]. Rabai, G., Wang, R.T. and Kustin, K., Kinetics and mechanism of the oxidation of thiourea by chlorine dioxide. Int. Journal of Chemical Kinetics. 1993;24(15):53-62

[16]. Chatterjee, D., Rothbart, S.and van Eldik, R., Selective oxidation of thiourea with H_2O_2 catalysed by [RuIII(edta)(H_2O)]: Kinetic and mechanistic studies. Dalton Trans. 2013;42:4725–4729

[17]. Osunlaja, A.A., Idris, S.O. and Uzairu, A., Oxidation of 1, 3-Dimethyl-2-thiourea by 3,7-bis(Dimethylamino)phenazothionium chloride in aqueous hydrochloric acid, International Journal of Pharmaceutical, Chemical and Biological Sciences. 2013;3:861-869

[18]. Weaver, T.R., Meyer, T.J., Adeyemi, S.A., Brown, G.M., Eckberg, R.P., Hatfield, W.E., Johnson, E.C., Murray, R.W. and Untereker, D., Chemically significant interactions between ruthenium ions in oxo-bridged complexes of ruthenium (III). J. Am. Chem. Soc. 1975;97:3039 – 3047

[19]. McAuley, A.and Gomwalk, U.D., Metal ion oxidation in Solution. Part V. Cerium (VI) Oxidation of Thiourea and its N – Substituted Derivatives. Journal of Chemical Society. 1969;2948-2951

[20]. Iyun, J.F., Ayoko, G.A. and Lawal, H.M.,. Kinetics of the reduction of μ - oxobis [aquobis(2, 2I –bipyridine)]ruthenium (III) by L – cysteine in aqueous solution. Indian Journ of Chem.. 1996;35(A):210–213

[21]. Ayoko, G.A., Iyun, J.F. and Ekubo, A.T., Oxidation of glutathione by diaquotetrakis(2, 2I –bipyridine) - μ - oxodiruthenium(III) ion in aqueous acidic solution. Transit Metal Chem. 1993;18(1):6–8

[22]. Iyun, J.F., Ayoko, G.A. and Lawal H.M., Kinetics and mechanism of the oxidation of iodide by diaquotetrakis(2, 2I – bipyridine) - μ - oxodiruthenium(III) ion in acid medium. Transit Metal Chem, 1992;17(1):63–65

[23]. Iyun, J.F., Ayoko, G.A. and Lohdip, Y.N., The oxidation of sulphite by diaquotetrakis(2, 2I – bipyridine) - μ - oxodiruthenium(III) ion in perchloric acid. Bull. Chem. Soc. Ethiop. 1992;6(1):1–9

[24]. Iyun, J.F., Musa, K.Y.and Ayoko, G.A., Oxidation of 2 – mercaptoethanol and 2 –mercaptoethylamine by $[(bpy)_2H_2O]Ru^{III}]_2O^{4+}$ in aqueous media. Indian Journ of Chem. 34(A):635–638, 1995

[25]. Iyun, J.F., Ayoko, G.A. and Lawal, H.M., The kinetics and mechanism of the reduction of diaquotetrakis(2, 2I – bipyridine) - μ - oxodiruthenium(III) by ascorbic acid. Transit Met Chem. 1995;20(1):30–33

[26]. Iyun, J.F., Ayoko, G.A. and Lohdip, Y.N.,. The kinetics and mechanism of the oxidation ofdiaquotetrakis(2, 2I – bipyridine) - μ - oxodiruthenium(III) by bromate in aqueous perchloric acid. Polyhedron. 1992;11(18):2277-2433

[27]. .BrØnsted, J.M., Activities of ions in solution. Z. Phys. Chem. 1922;102:106

[28]. Khan, K., Yousuf-Dar, M., Babu, P.S.S., A kinetic study of the reduction of chromium (VI) by thiourea in the absence and presence of manganese (II), cerium (IV) and ethlenediamminetetra acetic acid [EDTA]. Indian Journ. Chem. 2004.;42A:1060-1068.

[29]. Amjad, Z.and McAuley, A., Kinetics of the oxidation of thiourea by vanadium (V) in 1065 perchlorate media. Inorg. Chim. Acta., 1977;25:127-130

[30]. Mohammed, Y., Idris, S.O. and Iyun J.F., Redox Kinetics and Mechanism of the Oxidation of Thiourea by Diaquotetrakis (2, 2’-bipyridine) - μ - oxodiruthenium (III) ion in Aqueous Perchloric Acid. International Research Journal of Pure and Applied Chemistry. 2014;4(6):819 – 833

[31]. Mohammed, Y., Idris, S.O. and Iyun J.F., Investigations into the Kinetics and Mechanism of the Electron Transfer Reactions of N – Methylthiourea and Diaquotetrakis (2, 2’- bipyridine) - μ - oxodiruthenium(III) ion, in Aqueous Acidic Medium. International Research Journal of Natural and Applied Sciences. 2014;1(7):13 – 34

Mohammed, Y, et. Al. "Oxidation Of N, N-Dimethylthiourea By Diaquotetrakis(2,2’-BIPYRIDINE) - μ - Oxodiruthenium (III) Ion In Aqueous Acid Medium: A Kinetic Approach To Mechanism Of Reaction." *IOSR Journal of Applied Chemistry (IOSR-JAC)*, 13(7), (2020): pp 08-16.