KINETIC APPROACH TO THE MECHANISM OF THE REDOX REACTION OF N–ALLYLTHIOUREA AND µ–OXOBIS[AQUOBIS(2,2'-BIPYRIDINE)]DIRUTHENIUM(III) ION IN ACIDIC MEDIUM

*[1]Y. Mohammed, [2]S. O. Idris, [3]A. D. Onu

[1]Department of Chemistry, Nasarawa State University, Keffi, Nigeria

[2]Department of Chemistry, Ahmadu Bello University, Zaria, Nigeria;

[3]Department of Chemistry, Federal College of Education, Zaria, Nigeria

*Corresponding Author: yahaya@nsuk.edu.ng

ABSTRACT

The kinetics and mechanism of the oxidation of *N*-allylthiourea (hereafter denoted as ASH) by µ–oxobis[aquobis(2,2'-bipyridine)]diruthenium(III) ion, $[(bipy)_2(H_2O)RuORu(H_2O)(bipy)_2]^{4+}$ (hereafter denoted as Ru_2O^{4+} or $[(H_2O)_2(bipy)_4Ru_2O]^{4+}$) was studied in perchloric acid medium, $[H^+] = 5.0 \times 10^{-3}$ mol dm^{-3}, ionic strength (I), = 0.5 mol dm^{-3} (NaClO$_4$), temperature (T) = 31 ± 1°C and wavelength, $\lambda_{max} = 660$ nm. The stoichiometry of the reaction was 2:1 (ASH/Ru$_2$O^{4+}) and the order of the reaction was first order with respect to [ASH] and [Ru$_2$O^{4+}], respectively. Addition of acid had inverse effect on the rate of reaction. Changing the ionic strength and dielectric constant of, and addition of increasing amounts of various ions to the reaction medium had no significant effect on the reaction rate. Free radicals were identified in the reaction steps. There was no evidence of intermediate complex formation prior to electron transfer. $[(H_2O)_2(bipy)_2Ru]^{2+}$, the reduction product of $[(H_2O)_2(bipy)_4Ru_2O]^{4+}$ and formamidine disulphide, the oxidation product of *N*-allylthiourea, were identified in the product solution. Based on the results, it is suggested that the reaction proceeded through the outersphere pathway. A plausible mechanism for the reaction is proposed.

Keywords: dielectric constant; free radicals; ionic strength; rate constant; stoichiometry

INTRODUCTION

Thiourea and its derivatives have been used as effective scavenger of reactive oxygen intermediates [1]. Due to their reducing properties, they have been used in the textile industry [2], as corrosion inhibitors [3] 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. Gaining an insight into the redox pattern of this important class of reductants would be of immense value to knowledge, thus making *N*–Allylthiourea, a thiourea derivative, as a reductant in this study. *N*–Allylthiourea, as well as thiourea and its other derivatives can be oxidised by a wide variety of oxidising agents [4-8]. The reaction pathways and final products of the oxidation reaction depend on the reagents used and condition of the reaction mixtures [9]. The oxidation products may be urea, disulphide, and in some cases, it may undergo either oxidative cyclisation or degradation.

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 [10-17]   molecular electronic devices [18-21]. These polypyridyl complexes have been used as photoactive DNA cleavage agents for therapeutic purposes [22-25].   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 their use in organic and inorganic transformations. Polypyridyl complexes of ruthenium with aqua ligands are used extensively for the oxidation of organic substrates and multiple oxidative pathways have been detected including atom transfer, C-H insertion and proton coupled electron transfer [26-29). The suitability of ruthenium polypyridyl aqua complexes in the design of redox catalysts has been documented for a variety of reasons. Firstly, these compounds are useful catalysts in redox reactions since one or more oxidation states are frequently available, thus enabling multiple electron transfers to occur. Also, their inertness to substitution allows for chemically reversible electron transfer uncomplicated by ligand exchange. This, therefore, makes these ruthenium complexes retain their integrity in solution and are relatively easy to study. Finally, the oxo-aqua ligands provide for rapid proton transfer concomitant with electron transfer, permitting the accessibility of reversal oxidation states via gain or loss of protons.

The oxidant selected for this study is the the ruthenium oxo–bridged dimer, μ–oxobis[aquobis(2,2'-bipyridine)]diruthenium(III) ion, which has been shown in various studies to be an effective oxidant [30-43].

The aim of the research is to generate kinetic data which would give an insight into the mechanism of the redox reactions of μ–oxobis[aquobis(2,2'-bipyridine)]diruthenium(III) ion and *N*–Allylthiourea,. The findings would contribute to knowledge of the redox behaviour of this versatile μ-oxo–bridged ruthenium complex and μ-oxo–bridged systems, in general. The objectives to achieve the aim of the study are to synthesize and characterize the μ–oxobis[aquobis(2,2'-bipyridine)]diruthenium(III) complex ions, determine the stoichiometries of the reactions, determine the pseudo–first order and second order rate constants of the reactions, determine the order of reaction with respect to the reductant concentration, determine the effects of changing the hydrogen ion concentration on the rates of the reaction, determine the effects of changes of ionic strength and dielectric constant of reaction medium on the rates of the reaction, determine the effect of added ions to the reaction medium on the rates of reactions, determine the participation of free radicals in the reaction and to determine the formation of intermediate complexes in the course of the reaction.

MATERIALS AND METHODS

Materials

The oxo-bridged ruthenium binuclear complex, μ–oxobis[aquobis(2,2'-bipyridine)]diruthenium (III) perchlorate, $[(bipy)_2(H_2O)RuORu(H_2O)(bipy)_2](ClO_4)_4$ was synthesized according to literature [44]. A 3.0×10^{-4} mol dm^{-3} standard solution of the ruthenium dimer was prepared by dissolving 3.83×10^{-2} g of the synthesized complex in a 100 cm^3 volumetric flask and made up to the mark. A stock solution of *N* – allylthiourea ($CH_2=CHCH_2HNCSNH_2$) of concentration 0.5 mol dm^{-3} was prepared by dissolving 5.81 g of *N*–allylthiourea (Sigma-Aldrich) in a 100 cm^3 volumetric flask and made up to the mark. A 2.0 mol dm^{-3} stock solution of NaClO$_4$ was prepared by dissolving 24.5 g of NaClO$_4$ (May and Baker, Analytical grade, $\geq 98.0\%$) in distilled water in a 100 cm^3 volumetric flask and volume made up to the mark. The solution was standardized gravimetrically.

A 2.0 mol dm^{-3} stock solution of MgCl$_2$ was prepared by dissolving 19.0 g of MgCl$_2$ (Sigma-Aldrich, Analar grade 98%) in distilled water in a 100 cm^3 volumetric flask and volume made to the mark in a 100 cm^3 volumetric flask. The solution obtained was standardized gravimetrically. Stock solution of CH$_3$COONa of concentration 2.0 mol dm^{-3} was prepared by dissolving 16.4 g of CH$_3$COONa (May and Baker, 99.8%) in distilled water in 100 ml volumetric flask and the volume made up to the mark. Accurate concentrations of the salt solution were determined gravimetrically. Stock solution of 2.0 mol dm^{-3} perchloric acid was prepared by diluting concentrated solution of HClO$_4$ (Sigma–Aldrich, Analar grade, 60%) in standard flask. The solution was standardized volumetrically using sodium tetraborate decahydrate (borax) as primary standard and methyl red as indicator [45]..

Methods

Determination of Stoichiometry

The stoichiometry of the reaction was determined by spectrophotometric titration using the mole ratio method [7, 31-37, 46–50]. The concentration of the oxo-bridged ruthenium complex was kept constant while that of the reductant was varied between the mole ratio 1:0.25 to 1:4 ([Ru$_2$O^{4+}]/ [ASH]) as follows: [Ru$_2$O^{4+}] = 5.75 x 10^{-5} mol dm $^{-3}$, [ASH] = (1.44 − 23.0) x 10^{-5} mol dm^{-3}, [H$^+$] = 5.0 x 10^{-2} mol dm^{-3}, I = 0.5 mol dm^{-3}(NaClO$_4$). The reactions were allowed to go to completion and the absorbances of the completely reacted mixtures (A$_\infty$) were monitored at 660 nm (the λ$_{max}$ of Ru$_2$O^{4+}) using Seward Biomedical Digital Colorimeter. The absorbances obtained were plotted against the mole ratios of the reactants. Point of sharp break in the plot gave the stoichiometry of the reaction.

Kinetic Measurements

The rate of reaction of the Ru$_2$O^{4+} and ASH was studied by monitoring the decrease in absorbance of the dimer at its wavelength of maximum absorption, λ$_{max}$ (660 nm) using Seward biomedical digital colorimeter. All kinetic measurements were carried out under pseudo–first order conditions with respect to Ru$_2$O^{4+} concentrations in excess of the ASH concentration at stated temperature. Ionic strength, as well as [H$^+$], was maintained constant unless otherwise stated [7, 31-37, 46-50]

The 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_{obs}. The second order rate constants, k_2 , were determined from k_{obs} as $k_{obs}/$ [ASH] [7,31-37, 46-50].

The effect of changes in the hydrogen ion concentration on the reaction rate was investigated by keeping the concentrations of the dimer and the reductant constant, while that of [H$^+$] was varied. Ionic strength, I, was maintained constant at 0.50 mol dm$^{−3}$ [NaClO$_4$] and reaction was carried out at the stated temperature. Order of reaction with respect to acid concentration was obtained as the slope of the plot of log k_{obs} against log [H$^+$]. Variation of acid dependent second order rate constant, k_2(H$^+$) with [H$^+$] was obtained by plotting k_2(H$^+$) against [H$^+$] [7,31-37, 46-50].

The ionic strength of the reaction mixture was varied while maintaining [Ru$_2$O^{4+}], [ASH] and [H$^+$]   constant at stated reaction temperature and k_{obs} for the reaction was determined, from which k_2 was obtained for each of the values of the ionic strength.

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. [Ru$_2$O^{4+}], [ASH] and [H$^+$], as well as I were maintained constant. The relationship between the second order rate constant and the dielectric constant, D was obtained from the plot of log k_2 against 1/D [51].
The effect of added ions on the reaction rate was observed by the addition of various amounts of ions (Mg$^+$, CH$_3$COO$^−$) while maintaining [Ru$_2$O^{4+}], [ASH] and [H$^+$] constant. The ionic strength and temperature were maintained constant, also [7,31-37, 46-50].

Test for free radicals was carried out by adding 2 g of acrylamide to a partially oxidised reaction mixture containing various concentrations of Ru$_2$O^{4+}, ASH and H$^+$. A large excess of methanol was added to the reaction mixture. Control experiment was carried out by adding acrylamide to solutions of Ru$_2$O^{4+} and ASH separately at the same conditions of [H$^+$], I and temperature. Any polymerisation as indicated by gel formation suggested the presence of free radicals in the reaction mixture [7, 31-37, 46-50].

Test for the presence of stable, detectable intermediate complexes formed in the course of the reaction was carried out by recording the electronic spectrum of partially reacted reaction mixture at various time intervals depending on the speed of the reaction. Similar runs

were made for reactants separately in each case. A shift in, or consistent, λ_{max} and/ or enhancement of peak as the reaction progressed is determined. Furthermore, identification or non–identification of intercepts in the Michaelis–Menten plots of $1/k_{obs}$ versus $1/[\text{reductant}]$ would give an idea of the presence or absence of intermediate complex formation [7,31-37, 46-50].

Product Analyses

Completely reacted solution was analysed for the type of products that will be formed. Test for the presence of disulphide formed was carried out according to literature [52, 53]. The *N*-allylthiourea was reacted with a little excess of the Ru_2O^{4+} in acid medium and ionic strength of reaction. At the completion of the reaction, the mixture was extracted six times with diethyl ether. The combined ether extracts were washed and dried with anhydrous Na_2SO_4 and left overnight to dry. Appearance of crystals suggested that the products of reaction included disulphide.

RESULTS AND DISCUSSION

Stoichiometric Studies

Results of stoichiometric studies for the oxidation of *N*-allylthiourea by Ru_2O^{4+} showed that two moles of ASH were consumed by one mole of Ru_2O^{4+}. The titration curve for the reaction was determined, and is presented in Fig. 1.

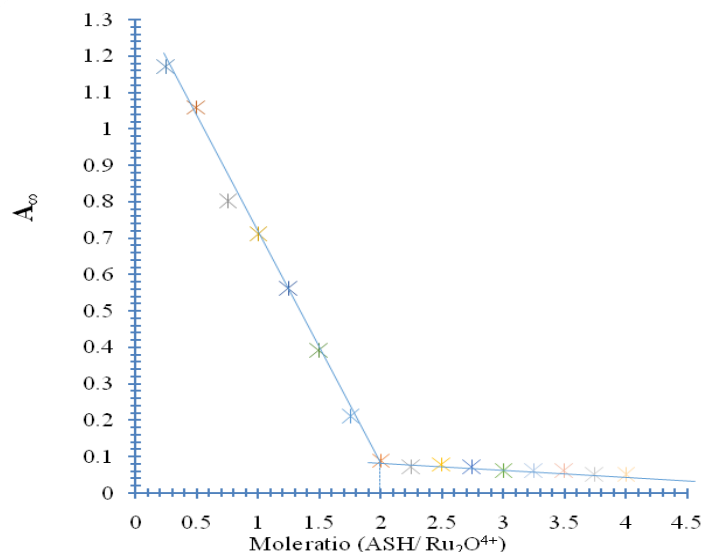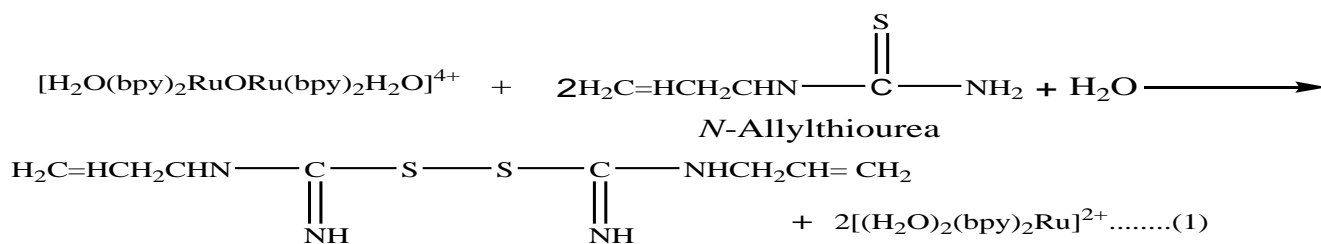Fig. 1: Plot of Absorbance versus Mole Ratio for the Reaction of $Ru_2O]^{4+}$ and *N*-allylthiourea (ASH) at $[Ru_2O^{4+}] = 5.75 \times 10^{-5}$ mol dm^{-3}, [ASH] = (1.44 - 23.0) x10^{-5} mol dm^{-3}, [H$^+$] = 5.0 x 10^{-2} mol dm^{-3}, I = 0.5 mol dm^{-3} and λ_{max} = 660 nm

Based on the above findings, the stoichiometric equation for the reaction can be represented by Eq. (1)

$[H_2O(bpy)_2RuORu(bpy)_2H_2O]^{4+}$ + $2H_2C=HCH_2CHN$——$\overset{\overset{S}{\|}}{C}$——$NH_2$ + H_2O ——→

N-Allylthiourea

$H_2C=HCH_2CHN$——$\overset{C}{\underset{\|}{NH}}$——S——S——$\overset{C}{\underset{\|}{NH}}$——$NHCH_2CH=CH_2$

$+ \ 2[(H_2O)_2(bpy)_2Ru]^{2+}$........(1)

A similar stoichiometry has been reported for the reaction of the oxo-bridged ruthenium dimer with glutathione [30] and L-cysteine [37]. However, a stoichiometry of 1:1 was found for the reaction of Ru_2O^{4+} with iodide (33), sulphite [34], mercaptoethanol and mercaptoethylamine [36]. Also, a stoichiometry of 2:1 (Ru_2O^{4+}/ reductant) was found for the reaction of Ru_2O^{4+} and ascorbic acid [35] and 1:5 (Ru_2O^{4+} / reductant) for the reaction of Ru_2O^{4+} and bromate [32].

The 1:2 stoichiometry observed in the reaction of Ru_2O^{4+} and ASH confirms that the *N*-allylthiourea is a two electron reductant. The formation of disulphides as the only organic

products in the reaction was confirmed by using the method of McAuley and Gomwalk [52,53] as earlier reported. In the oxidation of glutathione by Ru_2O^{4+}, disulphide formation had been documented [30], where the oxo-bridged dimer was reduced to Ru^{2+}. Disulphide has, similarly, been identified as the predominant product in the oxidation of thiols possessing the –SH group [52 – 55] U-V spectrum of the completely reacted mixture reaction indicated that the mixture absorbed maximally at 485nm, which is the characteristic λ_{max} of $[Ru(bipy)_2(H_2O)_2]^{2+}$ [56]. As reported earlier for the oxo-bridged chloro dimer, $[(bipy)_2ClRuORuCl(bipy)_2]^{4+}$, reduction of the aqua dimer by one electron initially occurs to give a compound which may formally be a Ru^{III}-O-Ru^{II} dimer (however, the odd electron may be delocalised between the two ruthenium ions [46]. This initial product, being unstable, undergoes a slow bridge cleavage upon further reduction (56) to give two equivalents of $[Ru (bipy)_2(H_2O)_2]^{2+}$.

Determination of Pseudo–first Order and Second Order Rate Constants and Order of Reaction

Pseudo-first order plots of log $(A_t - A_\infty)$ versus time (where A_t and A_∞ are absorbances at time 't' and at infinity, respectively) were linear to more than 90% extent of reaction. This suggests a first order dependence of rate on $[Ru_2O^{4+}]$ for the reaction. The pseudo-first order plot for the reaction of the oxo- bridged ruthenium dimer and ASH is presented as Fig. 2.

The slopes of the plots gave the pseudo-first order rate constants, k_{obs}. The values of k_{obs} for the reaction are presented in Table 1. The second order rate constants, k_2, were determined as the ratio of k_{obs} to [ASH], and were fairly constant [Table 1].

The second order rate constants for the reaction was 20.22 ± 0.01 x 10^{-2} dm^3 mol^{-1} s^{-1} . Similar second order kinetics have been reported for other reactions of Ru_2O^{4+} with benzenediol [31-34, 37]. Order of reaction with respect to [ASH] as obtained from the slope of the plot of log k_{obs} versus log [ASH] at constant $[H^+]$ and constant ionic strength were 1.06, indicating first order dependence of the rate of reaction on [ASH] (Fig. 3).

The rate law at constant $[H^+]$ for the reaction of Ru_2O^{4+} and ASH can be represented as Eq. (2)
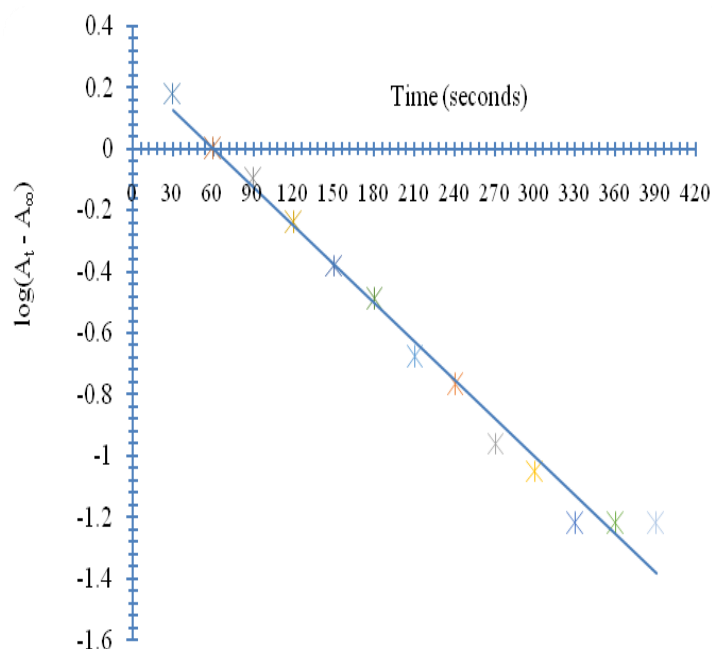
$$\frac{-d}{dt}[Ru_2O^{4+}] \ = \ k_2[Ru_2O^{4+}][ASH] \qquad .... \qquad (2)$$

Fig. 2: Typical Pseudo-First Order Plot for the Reaction of $[Ru_2O^{4+}]$ and *N*-alllthiourea (ASH) at $[Ru_2O^{4+}] = 5.75 \times 10^{-5}$ mol dm^{-3}, [ASH] = 2.3×10^{-2} mol dm^{-3}, [H$^+$] = 5.0×10^{-2} mol dm^{-2}, I = 0.5 mol dm^{-3}, T = 31 ± 1°C and λ_{max} = 660 nm

Table 1: Pseudo-first Order and Second Order Rate Constants for the Reaction of $[Ru_2O]^{4+}$ and *N*-allylthiourea (ASH) at $[Ru_2O^{4+}] = 5.75 \times 10^{-5}$ mol dm^{-3}, I = 0.5 mol dm^{-3} (NaClO$_4$), T = 31 ± 1°C and λ_{max} = 660 nm

10^2 [ASH], mol dm^{-3}	10^3 [H$^+$], mol dm^{-3}	I, mol dm^{-3}	$10^3 k_{obs}$, s^{-1}	k_2, dm^3 mol^{-1} s^{-1}
1.15	5.0	0.5	2.19	0.19
1.73	5.0	0.5	3.58	0.21
2.30	5.0	0.5	4.60	0.20
3.45	5.0	0.5	6.18	0.18
4.60	5.0	0.5	10.46	0.23
5.75	5.0	0.5	12.04	0.21

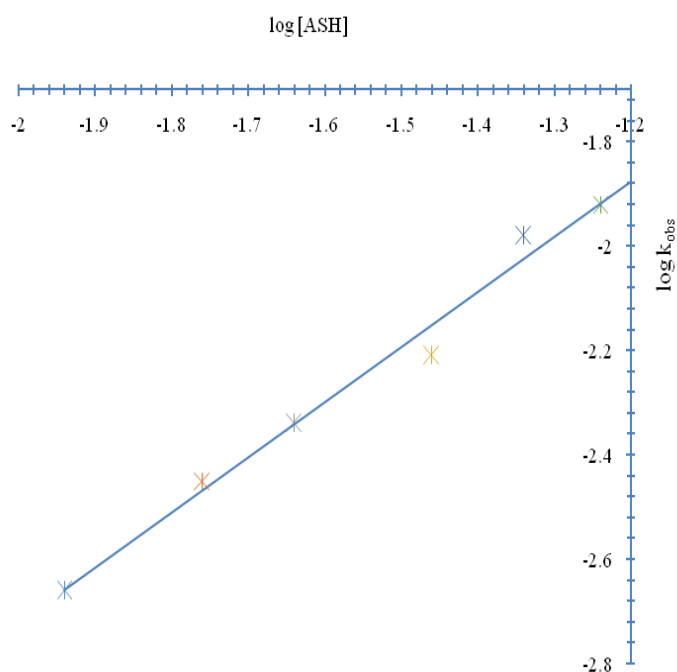|				
3.45	1.0	0.5	8.97	0.26
3.45	3.0	0.5	7.56	0.22
3.45	5.0	0.5	6.55	0.19
3.45	7.0	0.5	5.19	0.15
3.45	10.0	0.5	3.81	0.11
3.45	14.0	0.5	1.05	0.03
3.45	5.0	0.1	6.21	0.18
3.45	5.0	0.2	7.56	0.22
3.45	5.0	0.5	7.01	0.20
3.45	5.0	0.6	6.54	0.19
3.45	5.0	0.7	6.21	0.18
3.45	5.0	0.9	7.31	0.21

Fig. 3: Plot of log k_{obs} against log [ASH] for the Reaction of $[Ru_2O]^{4+}$ and *N*-allylthiourea (ASH) at $[Ru_2O^{4+}]$ = 5.75 x 10^{-5} mol dm^{-3}, [ASH] = (1.15 - 5.75) x 10^{-2} mol dm^{-3}, [H$^+$] = 5.0 x 10^{-2} mol dm^{-3}, I = 0.5 mol dm^{-3}, T = 31 ± 1°C and λ_{max} = 660nm

Chemical Characterization of the Reaction

Within the hydrogen ion concentration [H$^+$] range, $1.0 \times 10^{-2} \leq$ [H$^+$] $\leq 10.0 \times 10^{-2}$ mol dm^{-3}, kinetic runs were carried out at constant ionic strength, while keeping oxidant and reductant concentrations constant. Inverse acid dependence was observed for this reaction at I = 0.5 mol dm^{-3} (NaClO$_4$), and T = 31 ± 1°C. The pseudo-first order and second order rate constants at increasing [H$^+$], but constant [Ru$_2$O^{4+}], [ASH], I and T are presented in Table 1. The plot of the hydrogen ion-dependent second order rate constants, k$_2$(H$^+$), versus [H$^+$] was linear with intercept for the reaction under study (Fig. 4).
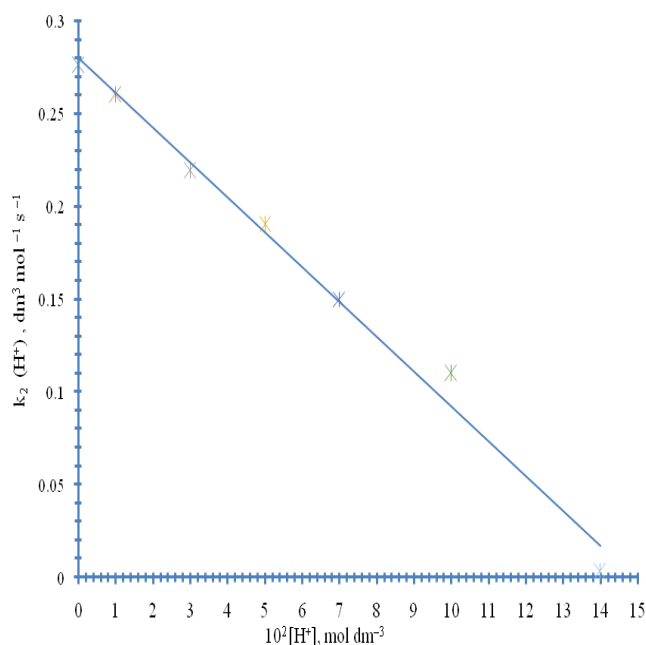

Fig. 4: Plot of k$_2$[H$^+$]against [H$^+$] for the Reaction of [Ru$_2$O]$^{4+}$ and *N*-Allylthiourea (ASH) at [Ru$_2$O^{4+}] = 5.75 x 10^{-5} mol dm^{-3} , [ASH]   =   3.45 x 10^{-2} mol dm^{-3}, [H$^+$] = (1.0 - 14.0) x 10^{-2} mol dm^{-3}, I = 0.5 mol dm^{-3}, T = 31 ± 1°C and λ$_{max}$ = 660 nm

 The dependence of rate constants on [H$^+$] can be represented by Eq. (3)

$$K_2[H^+] = a + b[H^+]^{-1} \tag{3}$$

Where, intercept = 'a' = 27.61 x 10^{-2} dm^3 mol^{-1} s^{-1} and slope = 'b'= - 1.78 dm^6 mol^{-2} s^{-1}

This suggests that this reaction occurs by two parallel pathways, one of the pathways is inverse acid dependent and the other, acid independent.

Similar inverse acid dependence was reported in the reduction of Ru_2O^{4+} by glutathione [30] bromate [32], sulphite [34], mercaptoethylamine [36]   and L-cysteine [37]. However, the oxidation of I^- by Ru_2O^{4+} displayed direct H^+ dependence [33]. Decrease in rate of reaction with increase in $[H^+]$ is attributable to the deprotonation of the thiourea and its derivatives under study. Although the deprotonation of $(bipy)_2(H_2O)RuORu(H_2O)(bipy)_2]^{4+}$ to give $[(bipy)_2(OH)Ru^{III}ORu^{II}(H_2O)(bipy)_2]^{3+}$ and $[[(bipy)_2(OH)Ru^{III}ORu^{II}(OH)(bipy)_2]^{2+}$ can not be ruled out under the acid conditions of this reaction (56) . On the basis of our observed products it seems more plausible to attribute the present inverse acid dependence to the deprotonation of ASH. In this respect, therefore, ASH is behaving as a thiol, in which there is the deprotonation of its sulphyhydryl (–SH) groups prior to electron transfer [53,56].

The overall rate equation for the Ru_2O^{4+} / ASH reaction can be represented by Eq. (4)

$$\frac{-d}{dt}[Ru_2O^{4+}] \; = \; (a \; + \; b[H^+]^{-1})[Ru_2O^{4+}][ASH] \qquad .... \qquad (4)$$

Effect of Changes of Ionic Strength of Reaction Medium

Within the range of ionic strength of the media $0.1 \leq$ I ≤ 0.9 mol dm^{-3} ($NaClO_4$), effect of changes in I on the reaction rates was investigated for the reaction of $Ru_2O^{4+.}$. At T = 31 ± 1º C, $[H^+] = 5 \times 10^{-2}$ mol dm^{-3} and maintaining $[Ru_2O^{4+}]$ and [ASH] constant, the rate of reaction was not markedly affected by changes in ionic strength. Pseudo-first order, k_{obs}, and second order rate constants, k_2, remained fairly constant and results are presented in Table 1.

Non-dependence of rate of reaction on ionic strength will likely be due to no charge on one or both of the reactants. Since ion-pair complex does not possess a formal charge, the rate of reaction would also not be affected by changes in ionic strength if ion-pairs are involved in reactions with outersphere character [32,37].

Effect of Changes in Dielectric Constant of Reaction Medium on Rate

The effect of changes in the dielectric constant (D) of the reaction medium on the rates of the reactions of Ru_2O^{4+} and ASH was investigated at constant $[Ru_2O^{4+}]$, [ASH], $[H^+]$ and I of the medium and T of reaction, but varying the dielectric constant of the medium using acetone-water mixture. Progressively decreasing the dielectric constant from $81 - 71$ (CH_3COCH_3/H_2O) had no effect on k_{obs}, and consequently k_2 of the reaction (Table 2)

Table 2: Effect of Changes in the Dielectric Constant of Reaction Medium for the Reaction of $[(H_2O)_2Ru_2O]^{4+}$ and N-allylthiourea [(ASH) at $(H_2O)_2Ru_2O^{4+}$] = 5.75 x 10^{-5} mol dm^{-3}, [ASH] = 3.45 x 10^{-2} mol dm^{-3}, $[H^+]$ = 5 x 10^{-2} mol dm^{-3}, I = 0.5 mol dm^{-3} ($NaClO_4$), D = (81.0 – 70.2), T = 31 ± 1°C and λ_{max} = 660 nm

D	$10^3 k_{obs}$, s^{-1}	k_2, dm^3 mol^{-1} s^{-1}
81.0	6.14	0.18
79.8	7.25	0.21
78.6	6.54	0.19
77.4	7.60	0.22
75.0	6.97	0.20
72.6	6.62	0.19
71.4	6.78	0.20
70.2	6.94	0.20

The non-dependence of the reaction rate on changes in the dielectric constant of the reaction medium suggests that the charges on any of the reacting species, Z_a or Z_b, is zero (Eq. 5). This means that the reaction occurred between cation and neutral molecule or free radical. This is also consistent with a reaction involving ion-pairs with outersphere character [31,36].

$$\ln k_2 = \ln k_0 - \frac{Z_a Z_b e^2 R_{ab}}{2.303\kappa TD} \qquad [51] \qquad\qquad (5)$$

Effect of Added Ions

At constant concentrations of all other reactants, the effect of added ions on the rates of the reaction was investigated by adding various concentrations of magnesium ion (Mg^{2+}) and acetate ion (CH_3COO^-). For the reaction under study, the rate constants were found to be unaffected by the addition of the ions as shown in Table 3.

Table 3: Effect of added ions (Mg^{2+} and CH_3COO^-) to Reaction Medium for the Reaction of $[(H_2O)_2Ru_2O]^{4+}$ and N-allylthiourea (ASH) at $[(H_2O)_2Ru_2O]^{4+}$ = 5.75 x 10^{-5} mol dm^{-3}, [ASH]= 3.45 x 10^{-2} mol dm^{-3}, $[H^+]$ = 5 x 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}
Mg^{2+}	0.00	6.28	18.20
	1.00	7.25	21.01
	20.00	6.56	19.01
	40.00	6.67	19.33
	60.00	6.89	19.97
	100.00	6.44	18.67
CH_3COO^-	0.00	7.12	20.64
	1.00	6.54	18.96
	20.00	7.28	21.10
	40.00	6.88	19.94
	60.00	6.93	20.09
	100.00	7.12	20.64
	200.00	6.56	19.01

Absence of ion catalysis is in line with the formation of ion – pairs in the reaction prior to electron transfer. Since the ion - pair complex does not have a formal charge, interaction with added ions will not be possible suggesting that the reaction might have proceeded via the

outersphere pathway. Iyun *et al* [36] have reported formation of ion-pair intermediates in the reaction of Ru_2O^{4+} with 2-mercaptoethanol and 2-mercaptoethylamine.

Test for the Formation of Intermediate Complex

Spectroscopic test

Spectroscopic tests were carried out to ascertain whether any spectroscopically determinable intermediate complex was formed from the reaction of the oxidant and the reductant. The electronic spectrum of the reacting mixture was run between 400 – 800 nm at intervals of one, three and six minutes of reaction. These studies showed that, for the reaction under study, there was no enhancement of absorption, neither was there any shift in λ_{max}.

Michaelis-Menten Plot

Least square plot of $1/k_{obs}$ versus $1/[ASH]$ for the reaction gave a straight line with negligible intercept. This plot is presented in Fig. 5
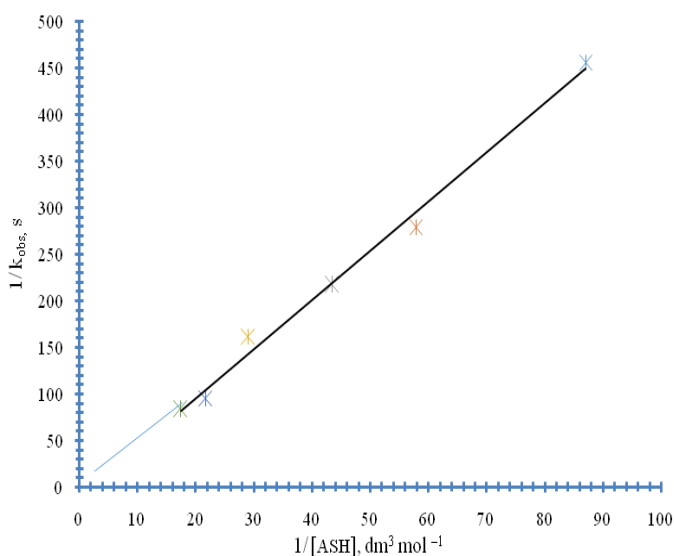

Fig. 5: Plot of $1/k_{obs}$ versus $1/[ASH]$ for the Reaction of $[Ru_2O]^{4+}$ and *N*-allylthiourea (ASH) at $[Ru_2O^{4+}] = 5.75 \times 10^{-5}$ mol dm^{-3}, $[ASH] = (1.15-5.75) \times 10^{-2}$ mol dm^{-3}, $[H^+] = 5.0 \times 10^{-2}$ mol dm^{-3}, $I = 0.5$ mol dm^{-3}, $T = 31 \pm 1°C$ and $\lambda_{max} = 660$ nm

Free Radical Test
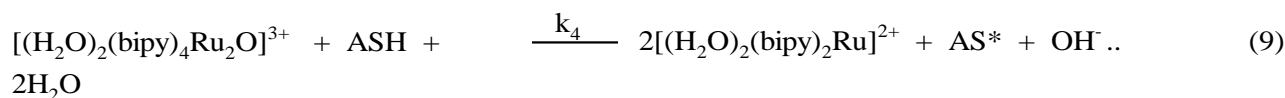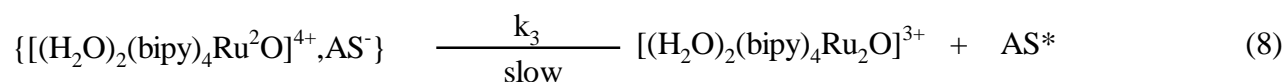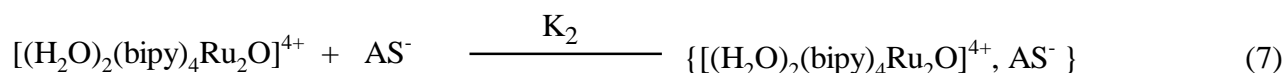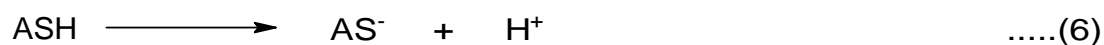
For the reaction of Ru_2O^{4+} and ASH, the addition of acrylamide to partially reacted mixture of Ru_2O^{4+} and the reductant followed by excess methanol showed gel formation, suggesting that polymerisation has occurred. This confirms the participation of free radicals during the reactions.
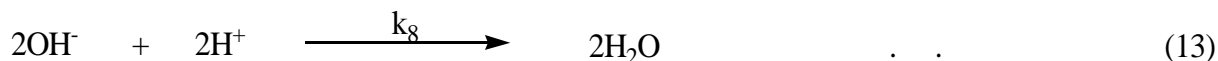
Product Analysis

Isolation and characterization of the products of a reaction could give hints or suggestions about the possible pathway for the redox reaction under study.

The formation of disulphides as the only organic products in the reaction was confirmed using the method of McAuley and Gomwalk [52,53]. In this aspect, ASH is behaving as a thiol, where disulphide has been identified as the predominant product in their oxidation due the possession of the –SH group [52 – 55]. Also, U-V spectrum of the completely reacted mixture of the reaction indicated that the mixture absorbed maximally at 485nm, the characteristic λ_{max} of $[Ru(bipy)_2(H_2O)_2]^{2+}$ [56], which is the reduction product of $[(H_2O)_2(bipy)_4Ru_2O]^{4+}$.

Based on the above findings and discussions, it is proposed that the oxidation of *N*-allylythiourea by Ru_2O^{4+} most probably occur by the outersphere mechanism and the following mechanistic scheme is proposed for the reaction.

$$ASH \longrightarrow AS^- + H^+ \qquad \qquad .....(6)$$

$$[(H_2O)_2(bipy)_4Ru_2O]^{4+} + AS^- \xrightarrow{\quad K_2 \quad} \{[(H_2O)_2(bipy)_4Ru_2O]^{4+}, AS^- \} \qquad (7)$$

$$\{[(H_2O)_2(bipy)_4Ru^2O]^{4+}, AS^- \} \xrightarrow[slow]{\quad k_3 \quad} [(H_2O)_2(bipy)_4Ru_2O]^{3+} + AS^* \qquad (8)$$

$$[(H_2O)_2(bipy)_4Ru_2O]^{3+} + ASH + 2H_2O \xrightarrow{\quad k_4 \quad} 2[(H_2O)_2(bipy)_2Ru]^{2+} + AS^* + OH^- .. \qquad (9)$$

$$[(H_2O)_2(bipy)_4Ru_2O]^{4+} \;+\; ASH \;\xrightarrow{\;K_5\;}\; \{[(H_2O)_2(bipy)_4Ru_2O]^{4+}, ASH\} \;..... \tag{10}$$

$$\{[(H_2O)_2(bipy)_4Ru^2O]^{4+}, ASH\} \;\xrightarrow[\text{slow}]{\;k_6\;}\; [(H_2O)_2(bipy)_4Ru_2O]^{3+} \;+\; AS^* \;+\; H^+... \tag{11}$$

$$[(H_2O)_2(bipy)_4Ru_2O]^{3+} \;+\; ASH \;+\; 2H_2O \;\xrightarrow{\;k_7\;}\; 2[(H_2O)_2(bipy)_2Ru]^{2+} \;+\; AS^* \;+\; OH^- \tag{12}$$

$$2OH^- \;+\; 2H^+ \;\xrightarrow{\;k_8\;}\; 2H_2O \qquad . \;\; . \tag{13}$$

$$2AS^* \;+\; 2AS^* \;\xrightarrow{\hspace{3cm}}\; 2ASSA \qquad . \;.. \qquad\quad . \tag{14}$$
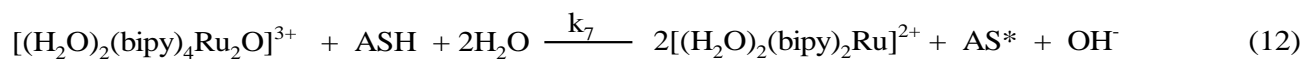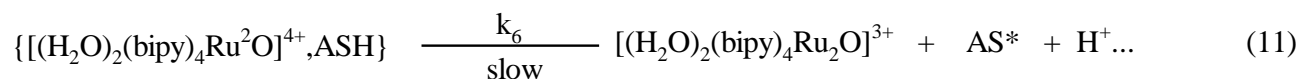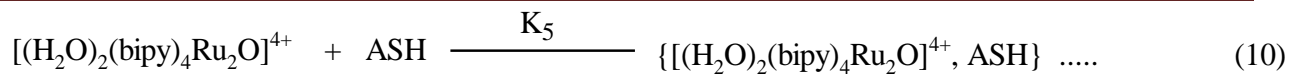
With Eqs. (8) and (11) as the rate determining steps,

$$\text{Rate} \;=\; k_3[\{[(H_2O)_2(bipy)_4Ru_2O]^{4+}, AS\text{-}\}] \;+\; k_6[[(H_2O)_2(bipy)_4Ru_2O]^{4+}, ASH] \;.. \quad . \tag{15}$$

But from Eq. (11)

$$\{[(H_2O)_2(bipy)_4Ru_2O]^{4+}, AS^-\} \;=\; K_2[(H_2O)_2(bipy)_4Ru_2O^{4+}]\,[AS^-] \qquad\quad ... \tag{16}$$

Putting Eq. (16) into (15) we have Eq. (17)

$$\text{Rate} \;=\; k_3K_2[[(H_2O)_2(bipy)_4Ru_2O^{4+}]\,[AS\text{-}] \;+\; k_6[[(H_2O)_2(bipy)_4Ru_2O]^{4+}, ASH] \;.. \quad .. \tag{17}$$

Also from Eq. (6):

$$AS^- \;=\; K_1\frac{[ASH]}{[H+]} \qquad\qquad ... \tag{18}$$

Substituting Eq. (18) into Eq. (17) we have Eq. (19)

$$\text{Rate} \;=\; k_3K_1K_2[[(H_2O)_2(bipy)_4Ru_2O^{4+}]\frac{[ASH]}{[H+]} \;+\; k_6[[(H_2O)_2(bipy)_4Ru_2O]^{4+}, ASH] \tag{19}$$

From Eq. (14)

$$\{[(H_2O)_2(bipy)_4Ru_2O]^{4+}, ASH\} = K_5[(H_2O)_2(bipy)_4Ru_2O^{4+}] [ASH] \qquad ...(20)$$

Substituting Eq. (20) into Eq. (19) we have Eq. (21)

$$Rate = k_3K_1K_2[\{[(H_2O)_2(bipy)_4Ru_2O^{4+}]\frac{[ASH]}{[H+]} + k_6K_5[(H_2O)_2(bipy)_4Ru_2O^{4+}][ASH] \qquad (21)$$

$$= (k_6K_5 + k_3K_1K_2 \frac{I}{[H+]})[(H_2O)_2(bipy)_4Ru_2O^{4+}][ASH] \qquad ..(22)$$

Eq. (22) is similar to Eq. (4), where k_6K_5 = 'a' and $k_3K_1K_2$ = 'b' and the values of 'a'and 'b' has been reported earlier as 27.61 x 10^{-2} dm^3 mol^{-1} s^{-1} and 1.78 dm^6 mol^{-2} s^{-1}, respectively.

The inverse acid dependence is consistent with the deprotonation of the *N-* allylthiourea (ASH) in Eq. (6), while the positive polymerisation test is rationalized by the participation of free radicals in Eqs (8), (9), (11) and (12).

Formamidine disulphide was confirmed to be the product of the oxidation of the *N-*allylthiourea in this reaction. Similar products have been obtained in the oxidation of thiourea by copper(II) perchlorate in acetonitrile [57], thiourea by diaquotetrakis(2,2'-bipyridine) - μ - oxodiruthenium (III) ion in perchloric acid [38]. *N-* methylthiourea by diaquotetrakis(2,2'-bipyridine) - μ - oxodiruthenium (III) ion in perchloric acid [39] and *N,N-* diemethylthiourea by diaquotetrakis(2,2'-bipyridine) - μ - oxodiruthenium (III) ion in perchloric acid [43]. An outersphere oxidant, $IrCl_6{}^{2-}$, was used to oxidise thiourea to formamidine disulphide [57]. Other thiourea derivatives such as *N,N'*-dimethylthiourea also afforded corresponding disulphide derivatives as oxidation products. Henry *et al* [57]. used hexacyanoferrate(III) to oxidise thiourea and *N*-substituted thiourea under acidic condition. The reaction proceeds by an outersphere mechanism to yield formamidine disulphide.

CONCLUSIONS

The redox kinetics and mechanisms of the oxidation of *N*–Allylthiourea (ASH) by μ –oxobis[aquobis(2,2' - bipyridine)]diruthenium (III) ion (Ru_2O^{4+}) was studied. The stoichiometry of the reaction was determined to be 1:2 (Ru_2O^{4+} / ASH) and the reaction showed a second order dependence with respect to both [Ru_2O^{4+}] and [ASH], and an inverse acid dependence. The rates of the reaction were unaffected by changes in I and D, and addition of ions to the reaction

medium. This phenomenon is attributable to the formation of ion-pairs. Polymerization was induced on addition of acrylamide, suggesting the participation of free radicals in the reaction. Based on the stoichiometry, order of reactions, rate constants, effect of changes of H^+ concentrations, effect of changes in ionic strength and dielectric constant of the reaction medium, effect of addition of ions to the reaction medium, polymerization test as well as the absence of kinetic and spectroscopic evidence for intermediate complex formation prior to electron transfer, the outersphere mechanism has been postulated for the reaction.

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