Redox Kinetics and Mechanism of the Reactions of μ –Oxobis[aquobis(2,2' – Bipyridine)]diruthenium (III) Ion and some Aliphatic Alcohols in Acidic Medium

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Abstract

The redox kinetics and mechanisms of the reactions of μ – oxobis[aquobis(2,2' – bipyridine)]diruthenium (III) ion, [(bipy)2(H2O)RuORu(H2O)(bipy)2]4+ (hereafter denoted as Ru2O4+ or [(H2O)2(bipy)4Ru2O]4+) and some primary aliphatic alcohols was studied in perchloric acid medium, [H+] = 5.0 x 10-3 mol dm-3, ionic strength (I), = 0.5 mol dm−3 (NaClO4), temperature (T) = 31 ± 1°C and wavelength, λmax = 660 nm. The reactions, which led to the formation of corresponding aldehydes had a stoichiometry of 1:1, were all first order with respect to each reactant, and second order overall. The reactions proceeded in the absence of acid but when acid was added, the reactions ceased. Varying the ionic strength and dielectric constants of the reaction medium had no effect on the reaction. Added ions catalysed the reaction and free radicals were identified in the reaction mixtures in the course of the reactions. There was no evidence for the formation if intermediate complex in the course of the reaction. The order of reactivity is of the order CH3OH > C2H5OH > C3H7OH Based on the results, it is suggested that all the reactions proceeded through the outer – sphere electron transfer mechanism and a plausible mechanism that represented all the reactions is proposed.

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

Introduction

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 [1-4]. 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. Oxidation of alcohols by Cr(VI) is regarded as a two–step reaction with the initial equilibrium formation of chromate ester followed by the decomposition of the latter to products in the rate-determining step [5]. The three possible modes of hydrogen transfer proposed for the ester decomposition mechanism include cyclic H–transfer with concerted bond making and breaking, cyclic H–transfer without the formation of free radical intermediates and cyclic

H–transfer with the formation of free radical intermediate [5-7]. Mechanisms involving hydride ion transfer have also been implicated in the oxidation of nine aliphatic alcohols by quinolinium bromochromate in dimethylsulphoxide [8]; nine alcohols by pyridinium hydrobromide perbromide in aqueous acetic acid [9], some alcohols by periodate [10].

The kinetics of the oxidation of methanol, ethanol, *n*–propanol, *n*–butanol, isopropanol and benzyl alcohols by periodate in the presence of rhodium(III) chloride in basic medium revealed the formation of a complex between Rh(III) and alcohol followed by its disproportionation in the rate-determining step [10]. The reactivity of the alcohols was found to follow the order: benzyl alcohols > methanol > ethanol > n – propanol > *n*–butanol > isopropanol. Increase in chain length and branching at the α–carbon decreased the rate, probably due to increase in electron density at this carbon, which renders it difficult to part with the hydrogen. This is suggesting cleavage of an α–CH proton from an acid [11]. The oxidation of nine aliphatic primary alcohols by quinolinium bromochromate in dimethylsulphoxide, identification of a substantial primary kinetic isotopic effect confirms the cleavage of an α–CH in the rate-determining step [8].

In the oxidation of fifteen alcohols (methanol, 2–chloroethanol, 2–methoxyethanol, ethanol, 1–chloropropan–2–ol, 1–propanol, 1– butanol, 1–pentanol, 2– methylpropan –1– ol, 1– methoxypropan–1– ol, 2–propanol, 2–butanol, 2–pentanol, 3–methylbutan–1–ol and 2–hexanol) by butyltriphenylphosphonium dichromate, it is observed that the rate of oxidation shows excellent correlation with the polar and steric substituent constants [12]. Also, in the oxidation of nine primary alcohols by pyridinium bromochromate [13] and in the oxidation of nine primary alcohols by pyridinium hydrobromide perbromide in aqueous acetic acid [9], reactivity of the alcohols was susceptible to both polar and steric effects. The objective of this work was to study the redox kinetics of the reactions of the versatile ruthenium dimer, μ – oxobis[aquobis(2,2' - bipyridine)]diruthenium (III) ion, and some primary aliphatic alcohols in acid medium

Materials and Methods

μ – oxobis[aquobis(2,2' – bipyridine)]diruthenium (III) perchlorate

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 prepared according to literature [14].

Standard solution of methanol was prepared by diluting accurately measured volumes of methanol (BDH, Analar grade, 97%) with doubly distilled water by taking into consideration the specific gravity of the alcohol. Lower concentrations were obtained by serial dilution.

Standard solution of ethanol was prepared by diluting accurately measured volumes of ethanol (BDH, Analar grade, 99.5%) with doubly distilled water by taking into consideration the specific gravity of the alcohol. Lower concentrations were obtained by serial dilution.

Standard solution of propan–1–ol was prepared by diluting accurately measured volumes of propanol (BDH, Analar grade, 99.5%) with doubly distilled water by taking into consideration the specific gravity of the alcohol. Lower concentrations were obtained by serial dilution.

Stock solution of 5.0 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 [15].

A 2.0 mol dm^{-3} stock solution of sodium perchlorate ($NaClO_4$) was prepared by dissolving 24.5g of $NaClO_4$ (May and Baker, Analytical grade, ≥ 98.0%) in distilled water in a 100 cm^3 volumetric flask and volume made up to the mark. The solutions were 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 solutions obtained were standardized gravimetrically.

Ammonium chloride (NH_4Cl) stock solutions of 2.0 mol dm^{-3} concentration were prepared by dissolving 10.7 g of NH_4Cl (BDH, Analar grade 99.5%) in a 100 cm^3 volumetric flask and the volume made up to the mark. The solutions were standardized gravimetrically. Stock solutions of CH_3COONa (May and Baker, 99.8%) of concentration 2.0 mol dm^{-3} were prepared by dissolving 16.4 g of the salt in distilled water in 100 cm^3 volumetric flasks and the volumes made up to the mark. Accurate concentrations of the salt solutions were determined gravimetrically.

A 2.0 mol dm^{-3} stock solution of HCOONa was prepared by dissolving 13.6 g of HCOONa (May and Baker, 99.5%) in 100 cm^3 volumetric flasks with distilled and the volumes made to the mark. The solutions were standardized gravimetrically.

The stoichiometry of each system was determined by spectrophotometric titration using the mole ratio method [16, 17]. The concentration of the oxo-bridged ruthenium complex was kept constant while that of the reductants was varied between the mole ratio 1:0.25 to 1:4 ([reductant]/[oxidant]) as follows:

For CH_3OH as reductant:$[Ru_2O^{4+}] = 5.5$ x 10^{-5} mol dm^{-3}, $[CH_3OH] = (1.4 – 22.0)$ x10^{-5} mol dm^{-3}, I = 0.5 mol dm^{-3} ($NaClO_4$).

For C_2H_5OH) as reductant: $[Ru_2O^{4+}] = 6.0$ x 10^{-5} mol dm^{-3}, $[C_2H_5OH] = (1.5 – 24.0)$ x 10^{-5} mol dm^{-3}, I = 0.5 mol dm^{-3} ($NaClO_4$).

For C_3H_7OH as reductant: $[Ru_2O^{4+}] = 6.0$ x 10^{-5} moldm^{-3}, $[C_3H_7OH] = (1.5 – 24.0)$ x 10^{-5} 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_∞) were monitored at 660 nm (the λ_{max} of Ru_2O^{4+}) using Seward Biomedical Digital Colorimeter. The absorbances obtained were plotted against the mole ratios of the reactants. Points of sharp breaks in these plots gave the stoichiometries of the reactions.

Kinetic measurements

The rates of reactions of the Ru_2O^{4+} with the reductants 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 for each system unless otherwise stated [17].

The pseudo – first order plots of log ($A_t – A_\infty$) 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}/ [reductant] [18, 19].

Effect of change in ionic strength of reaction medium on rate of reaction

The ionic strength of the reaction mixture was varied while maintaining the concentrations of the dimer, reductant and hydrogen ion constant at stated reaction temperature.

Relationship of reaction rate with changes in the ionic strength was determined by plotting log k_2 against $\sqrt{I}$ [20].

Effect of change in dielectric constant of reaction medium on rate of reaction

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. The concentrations of the dimer, reductant and hydrogen ion as well as the ionic strength 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 $1/D$ [21].

Effect of addition of ions to reaction medium on rate of reaction

The effect of added ions on the reaction rate was observed by the addition of various amounts of ions (Mg^+, NH_4^+, NO_3^-, CH_3COO^-, $HCOO^-$) while maintaining the dimer, reductant and hydrogen ion concentrations constant. The ionic strength and temperature were maintained constant [22].

Test for participation of free radicals in the course of reaction

Test for free radicals was carried out by adding 2 g of acrylamide to a partially oxidised reaction mixture containing various concentrations of oxidant, reductant and hydrogen ion for each system. A large excess of methanol was added to the reaction mixture. Control experiment was carried out by adding acrylamide to solutions of oxidant and reductant 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 [23].

Test for formation of intermediate complex prior to electron transfer

Test for the presence of stable, detectable intermediate complexes formed in the course of the reaction was carried out by recording the electronic spectra of partially reacted reaction mixtures 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/[reductant] would give an idea of the presence or absence of intermediate complex formation [24].

Product analysis

Where possible, completely reacted solutions were analysed for the type of products that will be formed. The presence or absence of aldehydes is tested as follows: to 1 cm^3 of Fehling's solution A, Fehling's solution B was added until precipitation occurs. More of the Fehling's Solution B was added until the precipitation just disappears. A small quantity of the product was added and boiled. A brick-red colouration indicated the presence of aldehydes in the products.

Results and Discussion

Results of the stoichiometric studies for the reaction of the oxo – bridged ruthenium dimer with CH_3OH, C_2H_5OH and C_3H_7OH showed a stoichiometry of 1:1 Ru_2O^{4+}/ ROH, indicating that for every mole of ROH oxidised, one mole of Ru_2O^{4+} was consumed. This stoichiometry is represented by Equation 1.

$[(H_2O)_2(bipy)_4Ru_2O]^{4+}$ + ROH + H_2O → $2[(H_2O)_2(bipy)_2Ru]^{2+}$ + RCHO . (1)
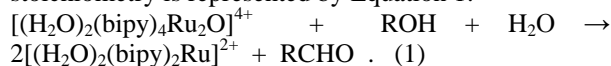
Similar stoichiometry has been reported for most reactions of aliphatic alcohols with other oxidising agents such as quinolinium bromochromate [8], ruthenate and perruthenate [25], pyridinium dichromate [26] and sodium *N*-chloroethylcarbamate [27]. The oxidation of benzyl alcohol by dichromate [28-30], quinolinium fluorochromate [31] and benzimidazolium fluorochromate [32] also gave the same stoichiometry of 1:1. Even oxidation of substituted benzyl alcohols by sodium *N*–chlorobenzenesulphonamide [33] and sodium *N*–bromobenzenesulphonamide [34] had the same stoichiometry. The oxidation of chloramphenicol by 1–chlorobenzotriazole in acidic medium also had same stoichiometry [35].

From kinetic studies, the reactions between Ru_2O^{4+} and ROH have been shown to have a first order dependence with respect to the oxidant concentrations, [Ru_2O^{4+}]. Evidence of this assertion is based on the linearity of the pseudo-first order plots of log ($A_t − A_\infty$) versus time for greater than 85% extent of reaction. The values for the second order rate constans, k_2, at I = 0.5 mol dm^{-3} and T = 31± 1C^O for the three systems have been reported In Table 1 and reproduced below: (12.01 ± .03) x 10^{-3} dm^3 mol^{-1} s^{-1} for Ru_2O^{4+}/ CH_3OH system; (8.79 ± .02) x 10^{-3} dm^3 mol^{-1} s^{-1} for Ru_2O^{4+}/ C_2H_5OH system and (3.51 ± .02) x 10^{-3} dm^3 mol^{-1} s^{-1} for Ru_2O^{4+}/ C_3H_7OH system.

Also, plots of log k_{obs} versus log [ROH] for the three alcohols under study, were linear with slopes = 0.98 for the CH_3OH system, 1.03 for the C_2H_5OH system and 0.91 for the C_3H_7OH system, suggesting first order dependence with respect to [ROH] for the three alcohols. Similar first order dependence with respect to [ROH] has been reported for the oxidation of aliphatic alcohols by quinolinium bromochromate [8], ruthenate and perruthenate [25], Cerium(IV) catalysed by chromium (III) [36], chromium(VI) [30], and pyridinium dichromate [26]. Also, similar first order dependence with respect to alcohol concentration was reported for the oxidation of benzyl alcohol by sodium dichromate [25, 29-30], quinolinium fluorochromate [31] and benzimidazolium fluorochromate [32]. The oxidation of substituted benzyl alcohols by sodium *N*, chlorobenzenesulphonate [33] and sodium *N*, bromobenzenesulphonate [34] also had first order dependence with respect to [ROH].

The overall rate law for the reaction, therefore, can be written as Equation 2

$$. $$

(**where** R = CH$_3$, C$_2$H$_5$, C$_3$H$_7$)

Table 1: Pseudo-first order and second order rate constants for the reaction of [(H$_2$O)$_2$Ru$_2$O]$^{4+}$ and ROH at [(H$_2$O)$_2$Ru$_2$O^{4+}] = 5.50 x 10^{-5} mol dm^{-3}, I = 0.5 mol dm^{-3} (NaClO$_4$), T = 31 ± 1°C and λ$_{max}$ = 660 nm

10^2[ROH], mol dm^{-3}			10^{4}k$_{obs}$, s^{-1}			10^{3}k$_2$, dm^3 mol^{-1} s^{-1}		
R = (CH$_3$)	(C$_2$H$_5$)	(C$_3$H$_7$)	(CH$_3$)	(C$_2$H$_0$)	(C$_3$H$_7$)	(CH$_3$)	(C$_2$H$_5$)	(C$_3$H$_7$)
5.50	1.44	3.00	6.60	1.59	1.06	12.01	11.03	3.50
8.25	2.01	6.00	9.87	2.21	2.12	11.96	10.99	3.53
11.00	2.88	9.00	13.19	2.94	2.94	11.99	11.02	3.50
13.75	4.31	12.00	16.55	4.73	4.15	12.04	10.97	3.48
16.50	5.75	15.00	19.85	6.34	5.23	12.03	11.02	3.49
19.25	8.36	18.00	23.08	9.10	6.34	11.99	10.89	3.52
22.00	11.50	21.00	26.41	12.59	7.39	12.00	10.95	3.52
24.75	14.38	24.00	29.82	15.88	8.47	12.05	11.04	3.53

Table 2: Effect of varying ionic strength of reaction medium on the reaction of [(H$_2$O)$_2$Ru$_2$O]$^{4+}$ and ROH at [(H$_2$O)$_2$Ru$_2$O^{4+}] = 5.50 x 10^{-5} mol dm^{-3}, T = 31 ± 1°C and λ$_{max}$ = 660 nm

10^2[ROH], mol dm^{-3}			I, mol dm^{-3}	10^{4}k$_{obs}$, s^{-1}			10^{3}k$_2$, dm^3 mol^{-1} s^{-1}		
R = (CH$_3$)	(C$_2$H$_5$)	(C$_3$H$_7$)		(CH$_3$)	(C$_2$H$_5$)	(C$_3$H$_7$)	(CH$_3$)	(C$_2$H$_5$)	(C$_3$H$_7$)
16.50	4.31	12.00	0.2	19.86	4.72	4.24	12.01	10.95	3.53
16.50	4.31	12.00	0.3	19.85	4.76	4.18	11.96	11.04	3.48
16.50	4.31	12.00	0.4	19.82	4.74	4.25	11.99	11.00	3.54
16.50	4.31	12.00	0.5	19.87	4.75	4.21	12.04	11.02	3.51
16.50	4.31	12.00	0.6	19.82	4.73	4.24	12.03	10.97	3.53
16.50	4.31	12.00	0.7	19.77	4.71	4.20	11.99	10.93	3.50
16.50	4.31	12.00	0.8	19.87	4.74	4.22	12.00	11.00	3.52
16.50	4.31	12.00	0.9	19.83	4.71	4.19	12.05	10.93	3.41

Table 3: Effect of varying dielectric constant of reaction medium on the reaction of [(H$_2$O)$_2$Ru$_2$O]$^{4+}$ and ROH at [(H$_2$O)$_2$Ru$_2$O^{4+}] = 5.50 x 10^{-5} mol dm^{-3}, T = 31 ± 1°C and λ$_{max}$ = 660 nm

10^2[ROH], mol dm^{-3}			D	10^{4}k$_{obs}$, s^{-1}			10^{3}k$_2$, dm^3 mol^{-1} s^{-1}		
R = (CH$_3$)	(C$_2$H$_5$)	(C$_3$H$_7$)		(CH$_3$)	(C$_2$H$_5$)	(C$_3$H$_7$)	(CH$_3$)	(C$_2$H$_5$)	(C$_3$H$_7$)
16.50	13.00	12.00	81.0	19.73	11.43	4.25	11.96	8.79	3.54
16.50	13.00	12.00	79.2	19.93	11.45	4.20	12.08	8.81	3.50
16.50	13.00	12.00	78.0	19.87	11.41	4.16	12.04	8.78	3.47
16.50	13.00	12.00	76.8	19.87	11.48	4.24	12.04	8.83	3.53
16.50	13.00	12.00	75.6	19.83	11.43	4.19	12.02	8.79	3.49
16.50	13.00	12.00	73.2	19.88	11.47	4.22	12.05	8.82	3.52
16.50	13.00	12.00	72.0	19.77	11.38	4.22	11.98	8.75	3.52
16.50	13.00	12.00	70.8	19.82	11.44	4.19	12.01	8.80	3.48

Addition of acid to the reaction mixture leads to the cessation of the reaction. Possibly, due to the protonation of the alcohol to form ROH$^+$ which undergoes electrostatic repulsion in the vicinity of the highly positively charged Ru$_2$O^{4+}. However, the reaction proceeded in the absence of acid and was subsequently monitored. This is in contrast to the H$^+$ catalysis reported for the oxidation of aliphatic alcohols by chromium(VI) [30], ruthenate and perruthenate [25], chromium(III) [36], quinolinium bromochromate [8] , sodium N–chloroethylcarbamate [29] and pyridium dichromate [26]. Similar H$^+$ was reported for the oxidation of benzyl alcohols by acidified dichromate [28-30], benzimidazolium fluorochromate [32] and quinolinium fluorochromate [31], while oxidation of substituted benzyl alcohols with sodium-N-chlorobenzenesulphonamide [33] and sodium-N-bromobenzenesulphonamide [34] was also catalysed by

H$^+$. The H$^+$ catalysis in all the above reactions was rationalised on the basis of the protonation of the oxidant prior to electron transfer.

Rates of reaction of Ru$_2$O^{4+} and ROH were unaffected by variation of the ionic strength (Table 2) and reduction in the dielectric constant of the reaction medium (Table 3). This could mean that in the rate determining step one of the reactants is a neutral species or the reaction involved an ion – pair or adduct [37]. The lack of dependence of rate of reaction on variation in I is seen in the oxidation of chloramphenicol by 1 – chlorobenzotriazole [35]. However, in the oxidation of primary alcohols by pyridium dichromate [26] and benzyl alcohol by benzimidazolinium fluorochromate [32], the reaction rate increased with increase in I and with decrease in D. Added ions inhibited the rates of the reactions (Tables 4 and 5).

This points to an outersphere electron transfer process in operation. This assertion is supported by the lack of spectrophotometric evidence for the formation of precursor complexes prior to electron transfer. When the reaction mixture was scanned as reaction progressed, λ_{max} remained at 660 nm, an indication that the reaction proceeded without the formation of intermediate complexes. This view was further reinforced by lack of intercept obtained from the Michaelis-Menten plot of $1/k_{obs}$ versus $1/[ROH]$. These observations denote that the formation constants for such intermediates are negligible. On addition of acrylamide to reaction mixture followed by excess

methanol, polymerisation was induced. This is inferred from the formation of a gel, suggesting that free radicals are participating in the reaction.

On the basis of the above results and conclusions inferred from the results, the possibility of the oxidation of ROH by Ru_2O^{4+} occurring via the outer sphere pathway is very high. A concerted mechanism involving the transfer of hydride ion from the C–H bond of the alcohol to the oxidant and removal of a proton from the O–H group is proposed for the reaction and is depicted in Equations 3 – 5.

Assuming Equation 4 to be the rate determining step, then the rate law is represented by Equation 6

Rate $= k_3 [[(H_2O)_2(bipy)_4Ru_2O]^{4+} // ROH]$ (6)

From Equation 3,

$[[(H_2O)_2(bipy)_4Ru_2O]^{4+} // ROH] = K_1[(H_2O)_2(bipy)_4Ru_2O^{4+}][ROH]$ (7)

Substitution of Equation 7 into Equation 6 gives Equation 8.

Rate $= k_3 K_1[[(H_2O)_2(bipy)_4Ru_2O^{4+}][ROH\}]$ (8)

Equation 8 resembles Equation 2.

Table 4: Effect of added cations to reaction medium on the reaction of $[(H_2O)_2Ru_2O]^{4+}$ and ROH at $[(H_2O)_2Ru_2O^{4+}] = 5.50 \times 10^{-5}$ mol dm^{-3}, T = 31 ± 1°C and λ_{max} = 660 nm

$10^2[ROH]$, mol dm^{-3}			$10^2[Mg^{2+}]$, mol dm^{-3}	$10^4 k_{obs}$, s^{-1}			$10^3 k_2$, dm^3 mol^{-1} s^{-1}		
R = (CH$_3$)	(C$_2$H$_5$)	(C$_3$H$_7$)		(CH$_3$)	(C$_2$H$_5$)	(C$_3$H$_7$)	(CH$_3$)	(C$_2$H$_5$)	(C$_3$H$_7$)
16.50	13.00	12.00	0.00	19.72	11.45	4.26	11.95	8.81	3.55
16.50	13.00	12.00	10.00	19.14	10.78	4.20	11.60	8.29	3.50
16.50	13.00	12.00	20.00	18.18	10.15	4.16	11.02	7.81	3.47
16.50	13.00	12.00	40.00	17.16	9.39	4.12	10.40	7.22	3.43
16.50	13.00	12.00	60.00	15.38	8.13	4.06	9.32	6.25	3.38
16.50	13.00	12.00	100.00	12.99	6.12	3.91	7.87	4.71	3.26
16.50	13.00	12.00	120.00	11.22	4.84	3.85	6.80	3.72	3.20
			$10^2[NH_4^+]$, mol dm^{-3}						
16.50	13.00	12.00	0.00	19.81	11.43	4.23	12.01	8.79	3.52
16.50	13.00	12.00	20.00	19.16	11.05	4.18	11.61	8.50	3.48
16.50	13.00	12.00	60.00	18.81	10.80	4.09	11.40	8.31	3.41
16.50	13.00	12.00	120.00	17.84	10.04	4.01	10.81	7.72	3.34
16.50	13.00	12.00	140.00	16.70	9.13	3.80	10.12	7.02	3.17
16.50	13.00	12.00	160.00	15.08	7.74	3.71	9.14	5.95	3.09
16.50	13.00	12.00	240.00	13.53	6.81	2.91	8.20	5.24	2.43

Table 5: Effect of added anions to reaction medium on the reaction of $[(H_2O)_2Ru_2O]^{4+}$ and ROH at $[(H_2O)_2Ru_2O^{4+}] = 5.50 \times 10^{-5}$ mol dm^{-3}, T = 31 ± 1°C and λ_{max} = 660 nm

$10^2[ROH]$, mol dm^{-3}			$10^2[CH_3COO^-]$, mol dm^{-3}	$10^4 k_{obs}$, s^{-1}			$10^3 k_2$, dm^3 mol^{-1} s^{-1}		
R = (CH$_3$)	(C$_2$H$_5$)	(C$_3$H$_7$)		(CH$_3$)	(C$_2$H$_5$)	(C$_3$H$_7$)	(CH$_3$)	(C$_2$H$_5$)	(C$_3$H$_7$)
16.50	13.00	12.00	0.00	19.78	11.41	4.18	11.99	8.78	3.48
16.50	13.00	12.00	10.00	19.62	10.79	3.97	11.89	8.30	3.31
16.50	13.00	12.00	20.00	19.17	10.17	3.54	11.62	7.82	2.95
16.50	13.00	12.00	40.00	18.16	9.39	3.18	11.01	7.22	2.65
16.50	13.00	12.00	60.00	16.38	8.16	2.71	9.93	6.28	2.26
16.50	13.00	12.00	120.00	12.99	6.15	1.15	7.87	4.73	0.96
16.50	13.00	12.00	160.00	10.22	4.77	0.61	6.80	3.67	0.62
			$10^2[HCOO^-]$, mol dm^{-3}						
16.50	13.00	12.00	0.00	19.78	11.48	4.21	11.99	8.83	3.51
16.50	13.00	12.00	10.00	19.31	11.06	4.02	11.70	8.51	3.35
16.50	13.00	12.00	20.00	19.01	10.76	3.84	11.52	8.28	3.20
16.50	13.00	12.00	40.00	18.24	10.04	3.37	11.05	7.72	2.81
16.50	13.00	12.00	60.00	17.78	9.16	2.94	10.78	7.05	2.41
16.50	13.00	12.00	100.00	14.28	7.62	2.15	8.65	5.86	1.79
16.50	13.00	12.00	120.00	12.45	6.77	0.98	7.42	5.21	0.82

The mechanism is rationalised on the formation of an alcohol/Ru_2O^{4+} adduct in a rapid equilibrium step (Equation 3) followed by rate limiting decomposition of the adduct to give the products (Equation 4).

Comparison of the redox reactions of Ru_2O^{4+} and the various aliphatic alcohols under study revealed that the stoichiometries of the three reactions were consistently 1:1. The second order rate constants increased in the order: $CH_3OH > C_2H_5OH > C_3H_7OH$. This is consistent with the findings of Rao *et al.* [10], who reported the order of reactivity of the alcohols to be: benzyl alcohol > methanol > ethanol > *n*–propanol > *n*–butanol > isopropanol. This order is expected, taking into consideration the increase in chain length and branching at the α–carbon, which decreased the rate probably due to increase in electron density at this carbon. This, invariably, renders it difficult to part with the hydrogen, suggesting the cleavage of α–CH proton in the transition state analogous to cleavage of α–CH proton in acids [11].

Conclusion

The redox kinetics and mechanisms of the reactions of μ – oxobis[aquobis(2,2' - bipyridine)]diruthenium (III) ion and some primary aliphatic alcohols was studied in perchloric acid medium. The reactions, which led to the formation of corresponding aldehydes had a stoichiometry of 1:1, were all first order with respect to each reactant, and second order overall. The reactions proceeded in the absence of acid but when acid was added, the reactions ceased. Varying the ionic strength and dielectric constants of the reaction medium had no effect on the reaction. Added ions catalysed the reaction and free radicals were identified in the reaction mixtures in the course of the reactions. There was no evidence for the formation if intermediate complex in the course of the reaction. The order of reactivity is of the order $CH_3OH > C_2H_5OH > C_3H_7OH$.

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