STUDIES OF THE KINETICS AND MECHANISM OF THE ELECTRON TRANSFER REACTIONS OF DIAQUOTETRAKIS(2,2'-BIPYRIDINE)-μ-OXODIRUTHENIUM(III) ION AND DITHIONITE IN AQUEOUS MEDIUM

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Abstract: The kinetics and mechanism of the electron transfer reaction of diaquotetrakis(2,2'-bipyridine)-μ-oxodiruthenium(III) ion (hereafter denoted as Ru_2O^{4+} or $[(H_2O)_2Ru_2O]^{4+}$) and dithionite ions ($S_2O_4^{2-}$) has been studied in aqueous medium at ionic strength, I, = 0.5 mol dm^{-3} and temperature, T = 31±1 °C. The stoichiometry of the reaction was found to be 1:1. The rate of reaction showed first order kinetics with respect to $[Ru_2O^{4+}]$ and $[S_2O_4^{2-}]$ respectively, second order overall. Rate equation for the reaction has been proposed as; $d[((H_2O)_2Ru_2O^{4+}]/dt = k_{obs}[((H_2O)_2Ru_2^{4+}] = k_2[((H_2O)_2Ru_2O^{4+}][S_2O_4^{2-}]$. Varying I and dielectric constant, D, of the reaction medium had no effect on the reaction rates, while free radicals were not detected in the course of the reaction. Product analysis revealed $[(H_2O)_2(bpy)_2Ru]^{2+}$ as the reduction product of $[(bpy)_2(H_2O)RuORu(H_2O)(bpy)_2]^{4+}$. Spectroscopic evidence of formation of stable intermediate complex was lacking which, in addition to absence of intercept in the Michaelis – Mentenplot and catalysis/ inhibition of the reaction due to added ions, suggest the implication of outer sphere mechanism operating in the reaction. A plausible mechanism was proposed.

Keywords: Catalysis/inhibition, electron, intermediate complex, kinetics, mechanism, transfer.

Introduction

Polypyridyl complexes of ruthenium with aqua ligands are used extensively for the oxidation of organic substrates and multiple oxidative pathways have been detected induding atom transfer, C – H insertion and proton coupled electron transfer (Lebeau and Meyer, 1999; Catalano *et al*., 2000; Rodriguez *et al*., 2001; Geneste and Moinet, 2004). The catalytic oxidation of water and chloride with diaquotetrakis(2,2'-bipyridine)-μ-oxodiruthenium(III) ion, otherwise known as the *blue dimer*, was reported by Meyer and his co-workers (Gersten *et al*., 1982; Gilbert *et al*., 1985). Electron transfer reactions of diaquotetrakis (2,2'-bipyridine)-μ-oxodiruthenium(III) ion and various reductants have been studied and various mechanisms have been proposed for the reactions (Iyun *et al*, 1992a, 1992b, 1992c, 1992d; Ayoko *et al*, 1993, Iyun *et al*., 1995a, 1995b, 1996). A further investigation into the redox behavior of the dimer with other reducing agents is necessary, considering the versatility of the dimer. Dithionite, as a strong two-electron reducing agent, is very suitable as a bleaching agent as well as for chemicals manufacture (Hamza *et al*., 2012) and as a biochemical reductant (Mayhew, 1978; Davis and Lawther, 1989). Dithionite oxidation has been used to measure oxygen transfer parameters (Camacho *et al*., 1997) and is studied only at high pH values because of its rapid hydrolysis at pH below 10 (Read *et al*., 2001).

Materials and Methods

Materials

Diaquotetrakis(2,2'-bipyridine)-μ-oxodiruthenium(III) perchlorate was synthesised according to literature (Weaver *et al*., 1979). The other reagents include sodium dithionite, sodium thiosulphate, sodium perchlorate, magnesium chloride, ammonium chloride, sodium acetate, sodium formate, acrylamide, acetone and methanol.

Methods

A 3.0 x 10^{-4} mol dm^{-3} stock solution of the oxobridged ruthenium dimer was prepared by dissolving 3.83 x 10^{-2} g of the synthesized complex in a 100 cm^3 volumetric flask and making up to the mark.

2.0 mol dm^{-3} stock solution of $Na_2S_2O_4$ was prepared by dissolving 31.6 g of $Na_2S_2O_4$ (Sigma-Aldrich, Analar grade, 85%) in distilled water in a 100 cm^3 volumetric flask and making up to the mark. Its accurate concentration was determined by iodometric titration using starch as indicator. A 2.0 mol dm^{-3} of $NaClO_4$ was prepared by dissolving 24.5 g 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.

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 the reaction was determined by spectrophotometric titration using the mole ratio method (Iyun and Adegite, 1990; Vaidya *et al*., 1991; Iyun *et al*., 1992a, 1992b, 1992c, 1992d, 1995a, 1995b, 1996; Ukoha, 1999; Ukoha and Iyun, 2001, 2002; Ukoha and Ibrahim, 2004). The concentration of the oxo-bridged ruthenium complex was kept constant while that of the dithionite was varied between the mole ratio 1:0.25 to 1:4 ([oxidant]/[reductant]). 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. The point of sharp break in this plot gave the stoichiometry of the reaction.

The rates of reaction of the Ru_2O^{4+} with the reductant were studied by monitoring the decrease in absorbance of the dimer at its λ_{max} (660 nm) colorimetrically using the same colorimeter used to determine the stoichiometry. All kinetic measurements were carried out under pseudo–first order conditions with respective reductant concentrations in excess of the oxidant concentration at stated temperature while maintaining the ionic strength constant, unless otherwise stated. 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]. The effect of changes in ionic strength of the reaction medium on rates of reaction by varying the ionic strength of the reaction mixture while maintaining the concentrations of the dimer and reductant constant, at stated reaction temperature. Relationship of reaction rate with changes in the ionic strength was determined by plotting log k_2 against $\sqrt{I}$ (Bronsted, 1922). Effect of changes 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 and reductant and 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 (Zaidi, 1991).

The effect of added ions on the reaction rate was observed by the addition of various amounts of ions (Mg^+, NH_4^+, CH_3COO^-, $HCOO^-$) while maintaining the dimer and reductant concentrations constant. The ionic strength and temperature were maintained constant, also. Test for free radicals was carried out by adding 2 g of acrylamide to a partially oxidised reaction mixture containing various concentrations of oxidant and reductant. 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 I and temperature. Any polymerisation as indicated by gel formation suggested the presence of free radicals in the reaction mixture. 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 intercept in the Michaelis–Menten plot of 1/ k_{obs} versus 1/[reductant] would give an idea of the presence or absence of intermediate complex formation.

Results and Discussion

Stoichiometry

The stoichiometry of the Ru_2O^{4+} and $S_2O_4^{2-}$ reaction was found to be in the ratio 1:1 (Fig. 1), suggesting that the stoichiometric equation for the reaction to be:

$$[(H_2O)_2(bpy)_2ORu]^{4+} + S_2O_4^{2-} + 3H_2O \longrightarrow 2[Ru(H_2O)_2(bpy)_2]^{2+} + 2SO_2 + 2OH^- \quad \ldots\ldots\ldots(1)$$

Similar stoichiometry of 1:1 was found for the reaction of Ru_2O^{4+} with iodide (Iyun *et al*., 1992c), sulphite (Iyun *et al*., 1992d), mercaptoethanol and mercaptoethylamine (Iyun *et al*., 1995b). However, a stoichiometry of 1:2 (Ru_2O^{4+}/ reductant) was reported for the reaction of Ru_2O^{4+} and thiourea (Mohammed *et al*., 2014a), *N*-methylthiourea (Mohammed *et al*., 2014b) and thiosulphate (Mohammed *et al*., 2015) while, a stoichiometry of 2:1 (Ru_2O^{4+}/ reductant) was found for the reaction of Ru_2O^{4+} and ascorbic acid (Iyun *et al*., 1995a) and 1:5 (Ru_2O^{4+}/ reductant) for the reaction of Ru_2O^{4+} and bromate (Iyun *et al*., 1992b). Comparably, a stoichiometry of 1:2 (Fe_2O^{4+}/reductant) has been reported in the reaction of Fe_2O^{4+} with mercaptoacetic acid, mercaptoethanol, and mercaptoethylamine (Ukoha and Iyun, 2001). In addition, a 1:1 stoichiometry was reported for the reaction of dithionite and malachite green (Idris *et al*., 2015), dicyanoporphyrinatoferrate(III) complex (Worthington and Hambright, 1980), p-phenylazobenzenesulphonic acid (Wasmuth *et al*., 2008), toluidine blue (Hamza *et al*., 2012; Babatunde and Ajayi, 2013) and potassium ferrate (Read *et al*., 2001).

Pseudo-first order plots of log (A_t - A_∞) versus time was linear to over 85% extent of reaction. A typical plot is depicted in Fig. 2. Linearity of the plots suggest a first order dependence on [Ru_2O^{4+}]. Also a plot of log k_{obs} versus log [$S_2O_4^{2-}$] was linear with a slope of 0.98 (Fig. 3), suggesting a first with respect to [$S_2O_4^{2-}$].

Similar second order kinetics have been reported for other reactions of Ru_2O^{4+} with benzenediol (Iyun *et al*., 1992a), bromate (Iyun *et al*., 1992b), iodide (Iyun *et al*., 1992c), sulphite (Iyun *et al*., 1992d), glutathione (Ayoko *et al*., 1993b) and L – cysteine (Iyun *et al*., 1996), thiourea (Mohammed *et al*., 2014a), *N*-methylthiourea (Mohammed *et al*., 2014b) and thiosulphate (Mohammed *et al*., 2015). In the reactions of dithionite with malachite green (Idris *et al*., 2015) and toluidine blue (Hamza *et al*., 2012) a first order dependence on [$S_2O_4^{2-}$] was reported. However, in the reduction of p-phenylazobenzenesulphonic acid by $S_2O_4^{2-}$ (Wasmuth *et al*., 2008) and in the reduction of some azo-dyes by $S_2O_4^{2-}$ (Gameay, 2002) half- order dependence on [$S_2O_4^{2-}$] was reported.

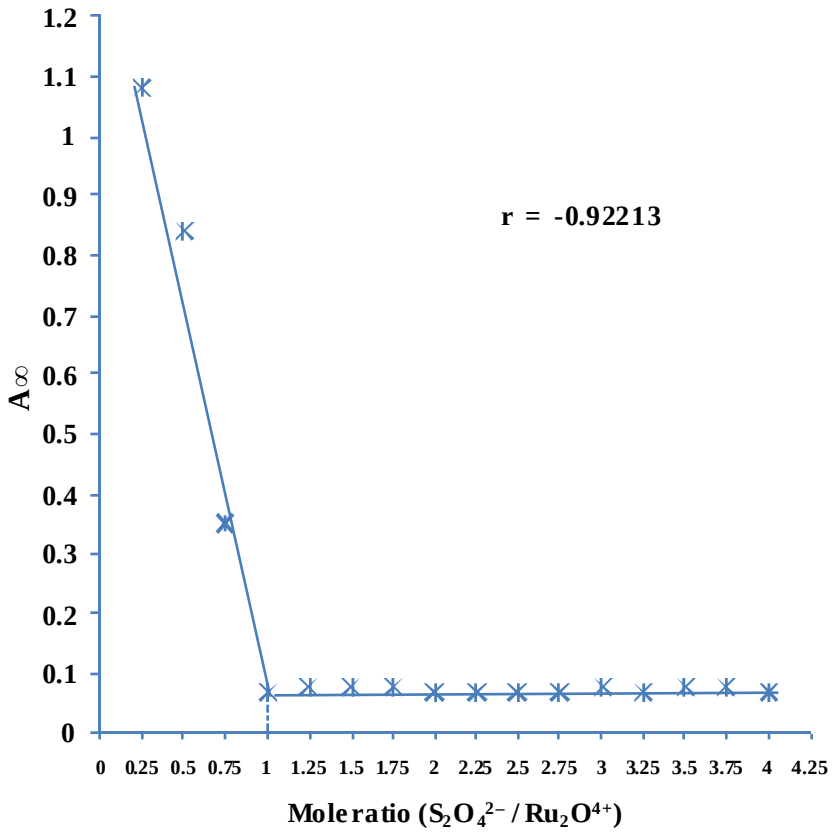


Fig. 1: Plot of Absorbance versus Mole ratio for the Reaction of $[(H_2O)_2Ru_2O]^{4+}$ and $S_2O_4^{2-}$ at $[(H_2O)_2Ru_2O^{4+}] = 5.75 \times 10^{-5}$ mol dm^{-3}, $[S_2O_4^{2-}] = (1.44 - 23.0) \times 10^{-5}$ mol dm^{-3}, I = 0.5 mol dm^{-3} and λ_{max} = 660 nm

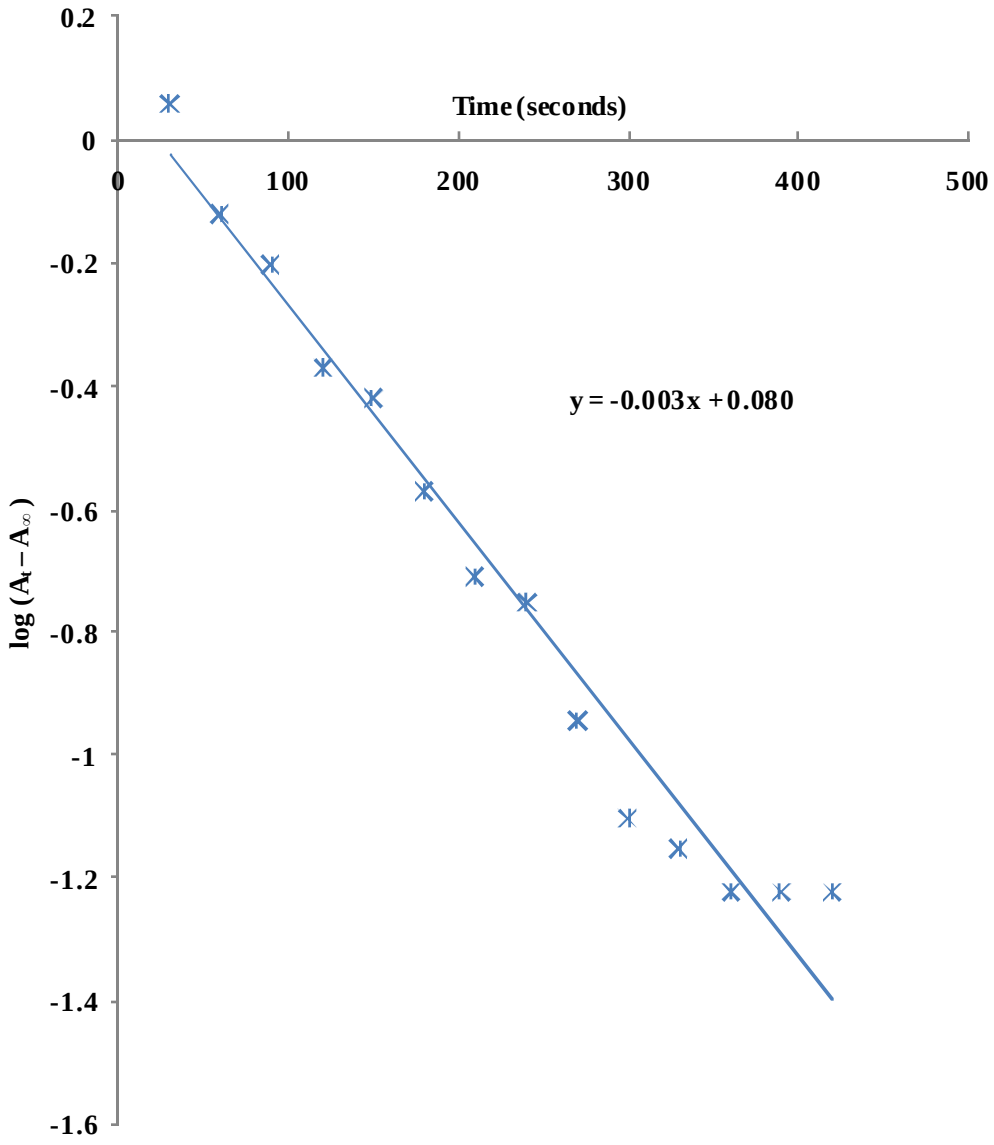


Figure 2: Typical Pseudo-first Order Plot for the Reaction of $[(H_2O)_2Ru_2O^{4+}]$ and $S_2O_4^{2-}$ at $[(H_2O)_2Ru_2O^{4+}] = 5.75 \times 10^{-5}$ mol dm^{-3}, $[S_2O_4^{2-}] = 4.31 \times 10^{-2}$ mol dm^{-3}, I = 0.5 mol dm^{-3}, T = 31 ± 1°C and λ_{max} = 660 nm

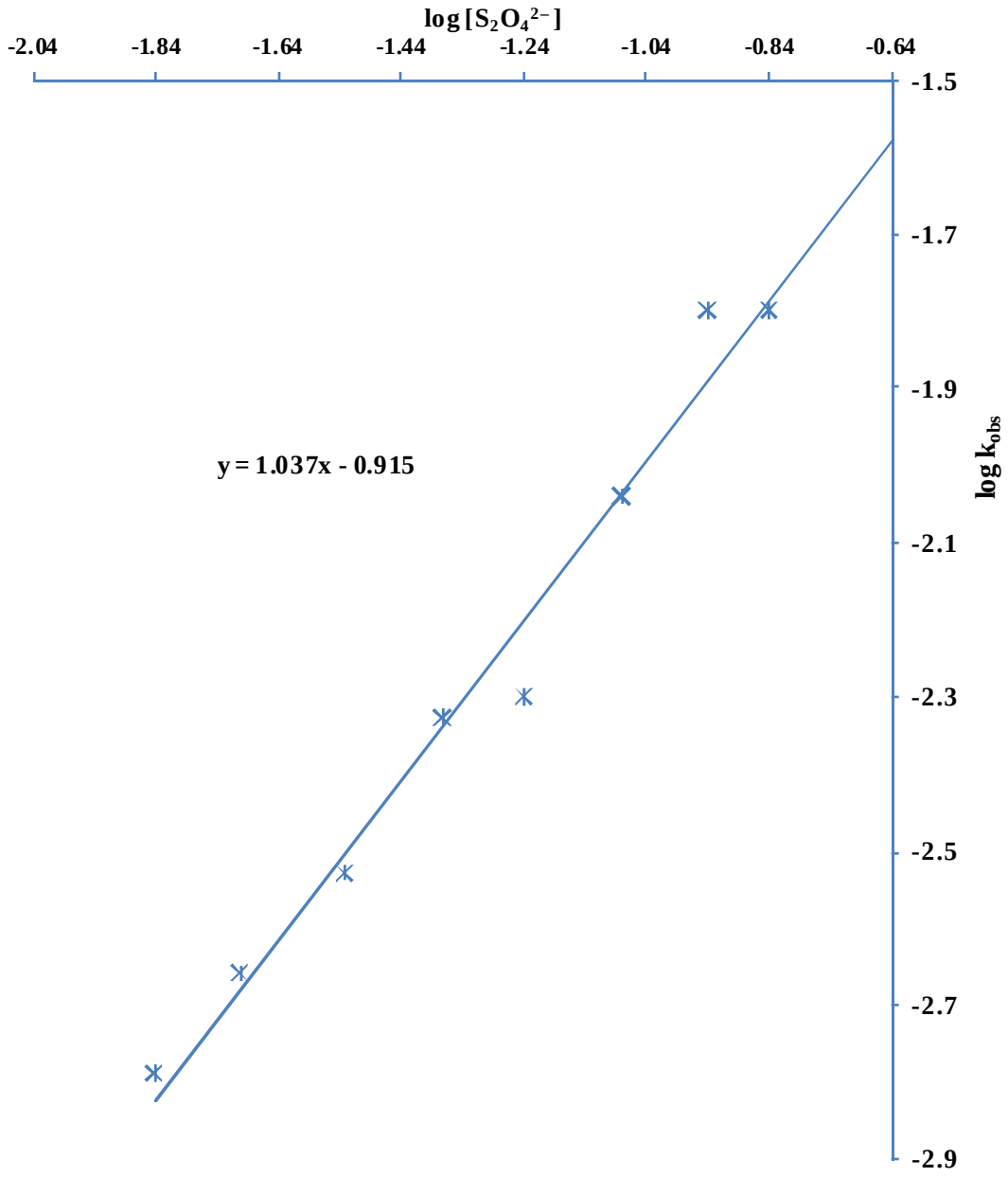


Figure 3: Plot of log k_{obs} against log $[S_2O_4^{2-}]$ for the Reaction of $[(H_2O)_2Ru_2O]^{4+}$ and $S_2O_4^{2-}$ at $[(H_2O)_2Ru_2O^{4+}]$ = 5.75 x 10^{-5} moldm^{-3}, $[S_2O_4^{2-}]$ = (1.44 - 14.38) x 10^{-2} mol dm^{-3}, I = 0.5 mol dm^{-3}, T = 31 ± 1°C and λ_{max} = 660 nm

The overall rate equation for the oxidation of dithionite by Ru_2O^{4+} can, therefore, be written as Equation 2:

$$-\frac{d}{dt}[Ru_2O^{4+}] = k_{obs}[Ru_2O^{4+}] = k_2[Ru_2O^{4+}][S_2O_4^{2-}] \quad ..(2)$$

At $[Ru_2O^{4+}] = 5.75 \times 10^{-5}$ moldm^{-3}; I = 0.5 moldm^{-3} ($NaClO_4$) and T = 31±1°C, k_2 was found to be $(10.99 \pm .04) \times 10^{-2}$ dm^{3}mol^{-1}s^{-1}. Dithionite was only studied at high pH because it undergoes hydrolysis at pH < 10 (Read *et al.*, 2001). This means that at the hydrogen ion concentration of 5×10^{-2} moldm^{-3} (pH = 1.3) the dithionite would be decomposed. Therefore, the study was carried out in the absence of acid.

Varying the ionic strength of the medium from 0.2 – 1.1 moldm^{-3} ($NaClO_4$) had no effect on the rate constants of the reaction (Table 1). This suggests that charged ions are reacting with a neutral species in the rate determining step. This is supported by the effect of changes in the dielectric constant, D, from 81 - 70.8 on the rates of the reaction. It was observed that the rate constants remained constant for all the values of D (Table 2). Similar zero salt effect was reported for the reaction of Ru_2O^{4+} and thiourea (Mohammed *et al.*, 2014a) and *N*-methylthiourea (Mohammed *et al.*, 2014b).

Table 1: Pseudo-first Order and Second Order Rate Constants for the Reaction of $[(H_2O)_2Ru_2O]^{4+}$ and ($S_2O_4^{2-}$) at $[(H_2O)_2Ru_2O^{4+}] = 5.75 \times 10^{-5}$ moldm^{-3}, I = 0.5 moldm^{-3} ($NaClO_4$), T = 31 ± 1°C and λ_{max} = 660 nm

$10^2[S_2O_4^{2-}]$, moldm^{-3}	I, moldm^{-3}	$10^3 k_{obs}$, s^{-1}	$10^2 k_2$, dm^{3}mol^{-1} s^{-1}
1.44	0.5	1.59	11.03
2.01	0.5	2.21	10.99
2.88	0.5	2.94	11.02
4.31	0.5	4.73	10.97
5.75	0.5	6.34	11.02
8.36	0.5	9.10	10.89
11.50	0.5	12.59	10.95
14.38	0.5	15.88	11.04
4.31	0.2	4.72	10.95
4.31	0.3	4.76	11.04
4.31	0.4	4.74	11.00
4.31	0.5	4.75	11.02
4.31	0.6	4.73	10.97
4.31	0.8	4.71	10.93
4.31	0.9	4.74	11.00
4.31	1.1	4.71	10.93

Table 2: Effect of Change in the Dielectric Constant of Reaction Medium for the Reaction of $[(H_2O)_2Ru_2O]^{4+}$ and $S_2O_4^{2-}$ at $[(H_2O)_2Ru_2O^{4+}] = 5.75 \times 10^{-5}$ moldm^{-3}, $[S_2O_4^{2-}] = 4.31 \times 10^{-2}$ moldm^{-3}, I = 0.5 moldm^{-3} ($NaClO_4$), D = (81.0 – 70.8), 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	4.74	11.00
79.2	4.76	11.04
78.0	4.75	11.02
76.8	4.71	10.93
75.6	4.72	10.95
73.2	4.75	11.02
72.0	4.75	11.02
70.8	4.71	10.93

Added anions (CH_3COO^- and $HCOO^-$) led to increase in rates of reaction (Table 3) while added cations led to decrease in rates (Table 4). The relationship between the anion-dependent second order rate constants, $k_2(X)$ and [X] was captured in the least square plots of k_2[X] versus [X] (Figs 4–7), which were linear with intercepts and slopes and the results are represented by Equations 3 and 4.

$$k_2(X) = p + q(X) \quad .....(3)$$

Where: X = CH_3COO^- and $HCOO^-$; p = intercept and q = slope and

$$k_2(X) = p - q(X) \quad .....(4)$$

Table 3: Effect of Added Anions to Reaction Medium for the Reaction of $[(H_2O)_2Ru_2O]^{4+}$ and $S_2O_4^{2-}$ at $[(H_2O)_2Ru_2O]^{4+} = 5.75 \times 10^{-5}$moldm^{-3}, $[S_2O_4^{2-}] = 4.31 \times 10^{-2}$moldm^{-3}, I = 0.5 moldm^{-3}, T = 31 ± 1 °C and λ_{max} = 660 nm

Ion	10^3[ion] moldm^{-3}	$10^4 k_{obs}$, s^{-1}	$10^2 k_2$, dm^{3}mol^{-1}s^{-1}
CH_3COO^-	0.00	4.72	10.95
	20.00	5.09	11.81
	60.00	5.52	12.81
	120.00	6.56	15.22
	140.00	6.72	15.59
	160.00	7.16	16.61
	240.00	8.37	19.42
$HCOO^-$	0.00	4.76	11.04
	20.00	5.01	11.62
	60.00	5.68	13.18
	120.00	6.21	14.41
	140.00	6.59	15.29
	160.00	6.81	15.80
	240.00	7.89	18.31

Table 4: Effect of Added Cations to Reaction Medium for the Reaction of $[(H_2O)_2Ru_2O]^{4+}$ and $S_2O_4^{2-}$ at $[(H_2O)_2Ru_2O]^{4+} = 5.75 \times 10^{-5}$moldm^{-3}, $[S_2O_4^{2-}] = 4.31 \times 10^{-2}$moldm^{-3}, I = 0.5 moldm^{-3}, T = 31 ± 1 °C and λ_{max} = 660 nm

Ion	10^3[ion] moldm^{-3}	$10^3 k_{obs}$, s^{-1}	$10^2 k_2$, dm^{3}mol^{-1} s^{-1}
Mg^{2+}	0.00	4.92	10.95
	10.00	4.56	10.59
	20.00	4.48	10.40
	40.00	4.06	9.42
	60.00	3.84	8.91
	100.00	3.19	7.40
	120.00	3.10	7.19
NH_4^+	0.00	4.74	11.00
	20.00	4.66	10.81
	60.00	3.96	9.19
	120.00	3.37	7.82
	140.00	2.94	6.82
	160.00	2.84	6.59
	240.00	2.03	4.71

Results obtained showed that for:

CH_3COO^- 'p' = 10.95×10^{-2} dm^{3}mol^{-1} s^{-1} and 'q' = 3.50×10^{-2} dm^{6}mol^{-2} s^{-1}

$HCOO^-$ 'p' = 11.12×10^{-2}dm^{3}mol^{-1} s^{-1} and 'q' = 2.90×10^{-2} dm^{6}mol^{-2} s^{-1}

NH_4^+ 'p' = 11.04×10^{-2}dm^{3}mol^{-1} s^{-1} and 'q' = 2.80×10^{-2} dm^{6}mol^{-2} s^{-1}

Mg^{2+} 'p' = 10.97×10^{-2}dm^{3}mol^{-1} s^{-1} and 'q' = 33.85×10^{-2} dm^{6}mol^{-2} s^{-1}.

The anion catalysis and cation inhibition observed has been associated with outersphere electron transfer process (Pryztas and Sutin, 1973).

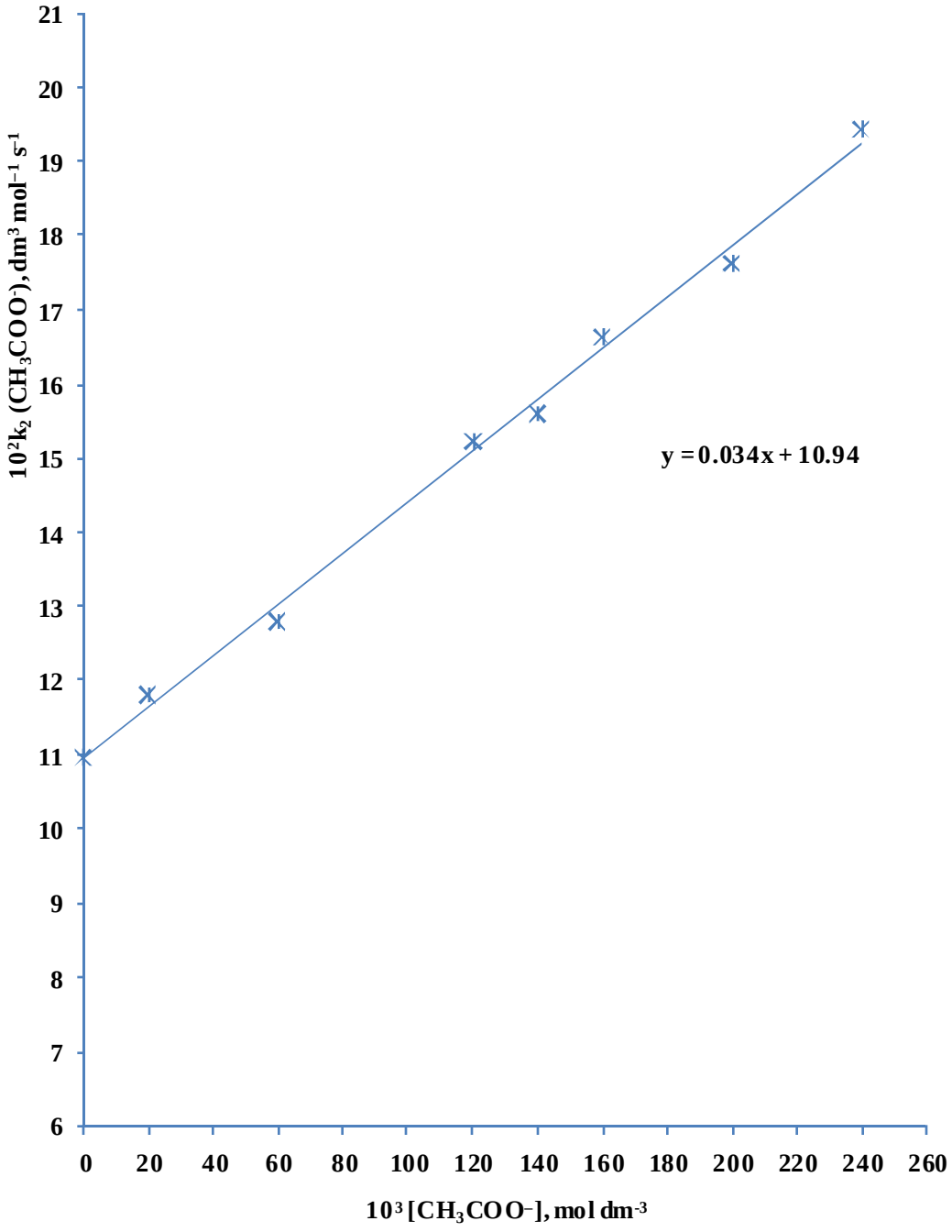


Figure 4: Plot of $k_2(CH_3COO^-)$ versus $[CH_3COO^-]$ for the Reaction of $(H_2O)_2Ru_2O]^{4+}$ and $S_2O_4^{2-}$ at $[(H_2O)_2Ru_2O^{4+}] = 5.75 \times 10^{-5}$ mol dm^{-3}, $[S_2O_4^{2-}] = 4.31 \times 10^{-2}$ mol dm^{-3}, $[CH_3COO^-] = (0.0 - 24.0) \times 10^{-2}$ mol dm^{-3}, I = 0.5 mol dm^{-3}, T = 32± 1°C and λ_{max} = 660 nm

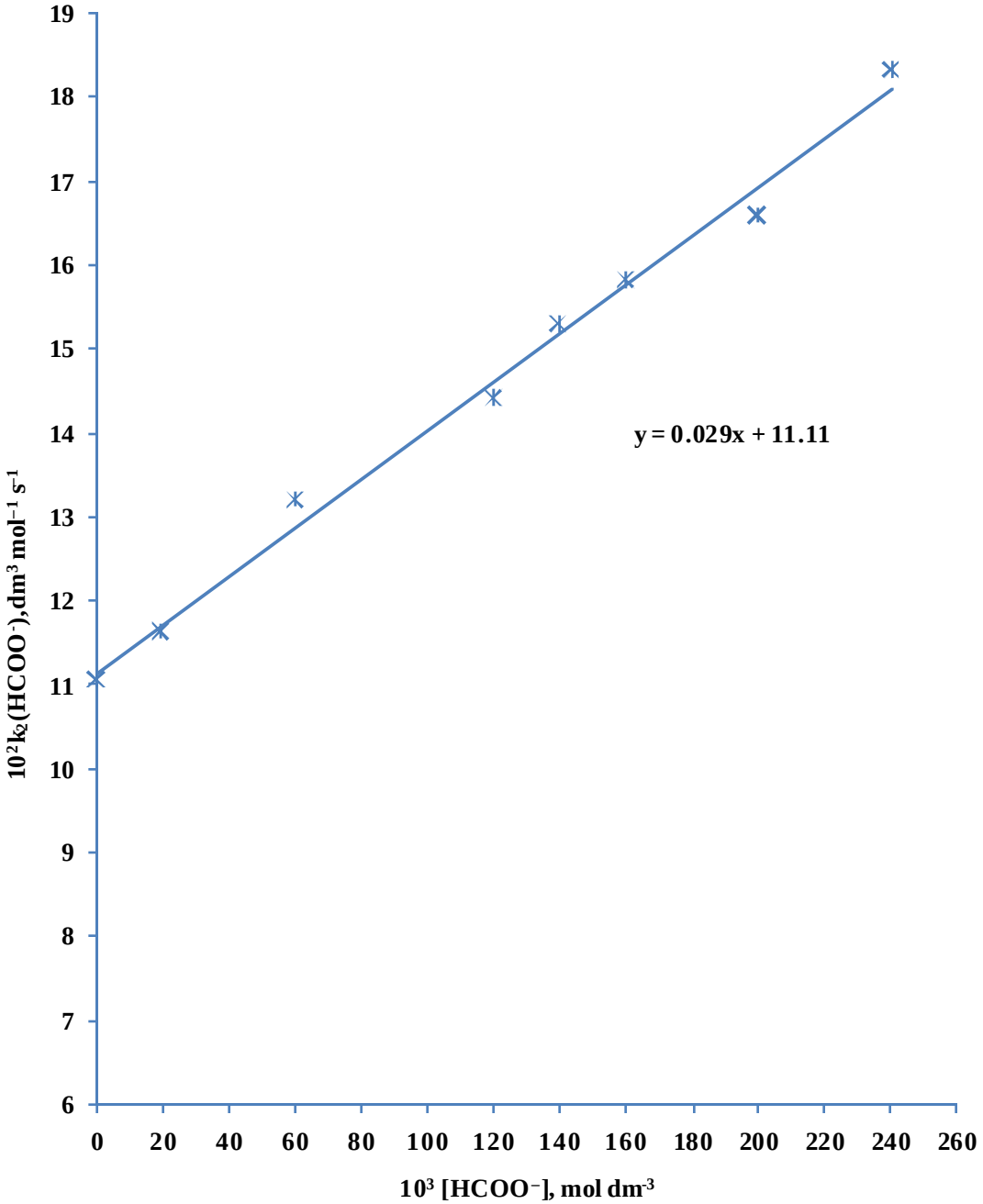


Figure 5 : Plot of $k_2(HCOO^-)$ versus [HCOO⁻] for the Reaction of $[(H_2O)_2Ru_2O]^{4+}$ and $S_2O_4^{2-}$ at $[(H_2O)_2Ru_2O^{4+}] = 5.75 \times 10^{-5}$ mol dm^{-3}, $[S_2O_4^{2-}] = 4.31 \times 10^{-2}$ mol dm^{-3}, $[HCOO^-] = (0.0 - 24.0) \times 10^{-2}$ mol dm^{-3}, I = 0.5 mol dm^{-3}, T = 31 ± 1°C and λ_{max} = 660 nm

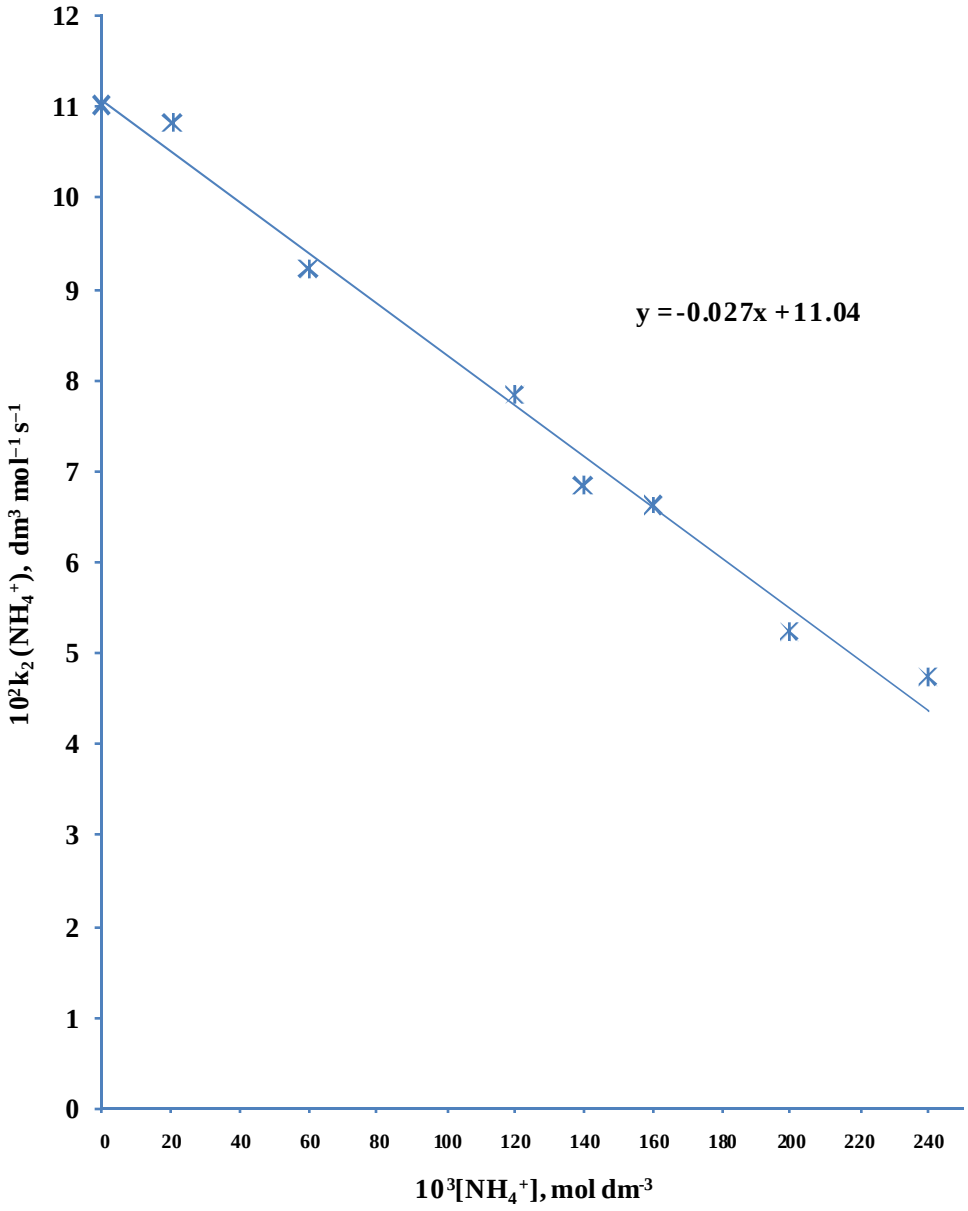


Figure 6: Plot of k_2 (NH_4^+) versus $[NH_4^+]$ for the Reaction of $[(H_2O)_2Ru_2O]^{4+}$ and $S_2O_4^{2-}$ at $[(H_2O)_2Ru_2O^{4+}]$ = 5.75 x 10^{-5} mol dm^{-3}, $[S_2O_4^{2-}]$ = 4.31 x 10^{-2} mol dm^{-3}, $[NH_4^+]$ = (0.0 - 24.0) x 10^{-2} mol dm^{-3}, I = 0.5 mol dm^{-3}, T = 31 ± 1°C and λ_{max} = 660 nm

Polymerisation was not induced on addition of acrylamide to the reaction mixture followed by excess methanol at 1 min, 2 min and 3 min after onset of reaction. This suggests that free radicals were not produced in the reaction of Ru_2O^{4+} and $S_2O_4^{2-}$. This agrees with the lack of free radical participation in the reaction of malachite green and dithionite (Idris *et al*., 2015). However, in the reaction of dithionite and toluidine blue, free radicals were detected (Hamza *et al.*, 2012), while Derven'iko *et al.* (2013) reported that in the reaction

of dithionite and super-reduced cobalamin and cobinamide the reactive species was SO_2^-. The electrochemical behaviour of sodium dithionite at a gold electrode in alkaline solution shows that dithionite is oxidised with SO_2^- as intermediate (Westbroek *et al.*, 2001).

Scanning the reaction mixture spectrophotometrically as the reaction progressed did not show any shift in λ_{max}, thereby ruling out the formation of an intermediate complex prior to electron transfer. Also, Michaelis-Menten plot of $1/k_{obs}$ versus $1/[S_2O_4^{2-}]$ was linear without any appreciable intercept (Fig. 8). This confirms the absence of stable intermediates with large enough formation constants. The above facts support the suggestion of an outersphere mechanism operating in the oxidation of $S_2O_4^{2-}$ by Ru_2O^{4+}.

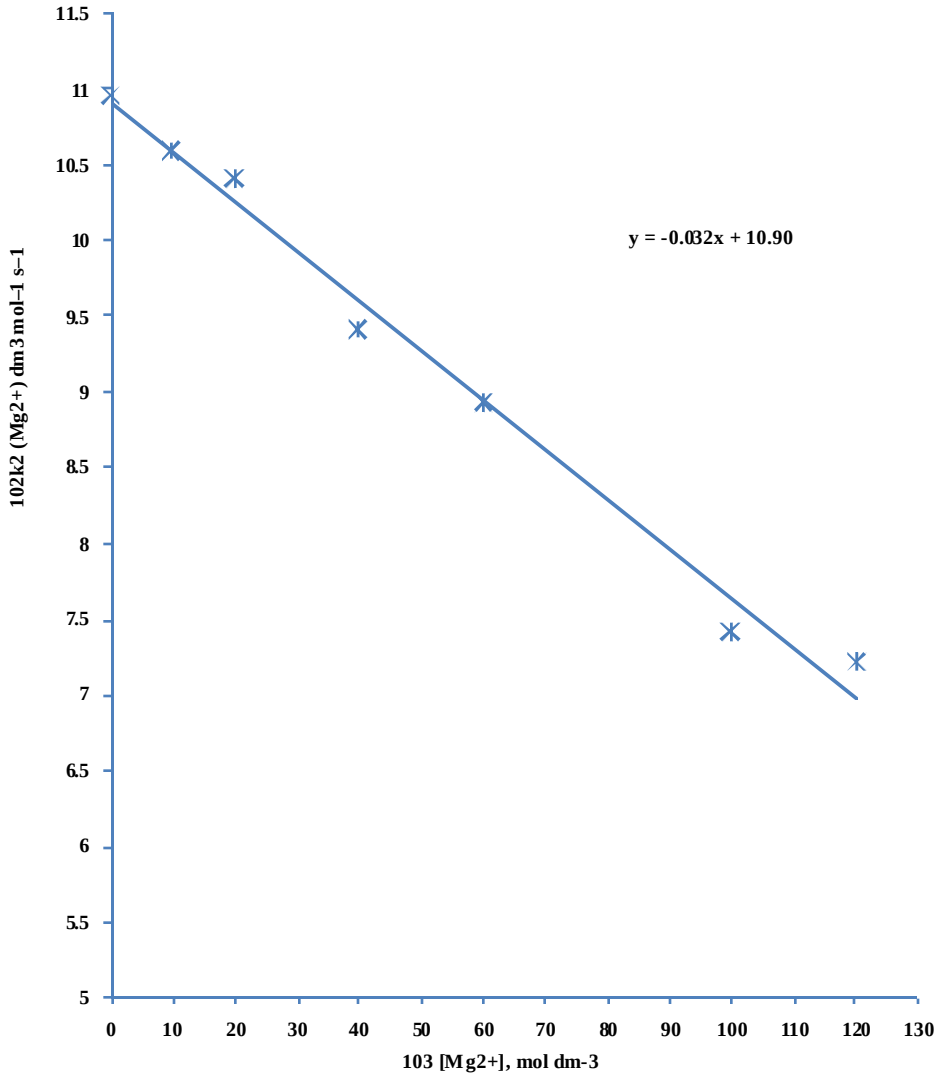


Figure 7: Plot of $k_2(Mg^{2+})$ versus $[Mg^{2+}]$ for the Reaction of $[(H_2O)_2Ru_2O]^{4+}$ and $S_2O_4^{2-}$ at $[(H_2O)_2Ru_2O^{4+}] = 5.75 \times 10^{-5}$ mol dm^{-3}, $[S_2O_4^{2-}] = 4.31 \times 10^{-2}$ mol dm^{-3}, $[Mg^{2+}] = (0.0 - 12.0) \times 10^{-2}$ mol dm^{-3}, I = 0.5 mol dm^{-3}, T = 31 ± 1°C and λ_{max} = 660 nm

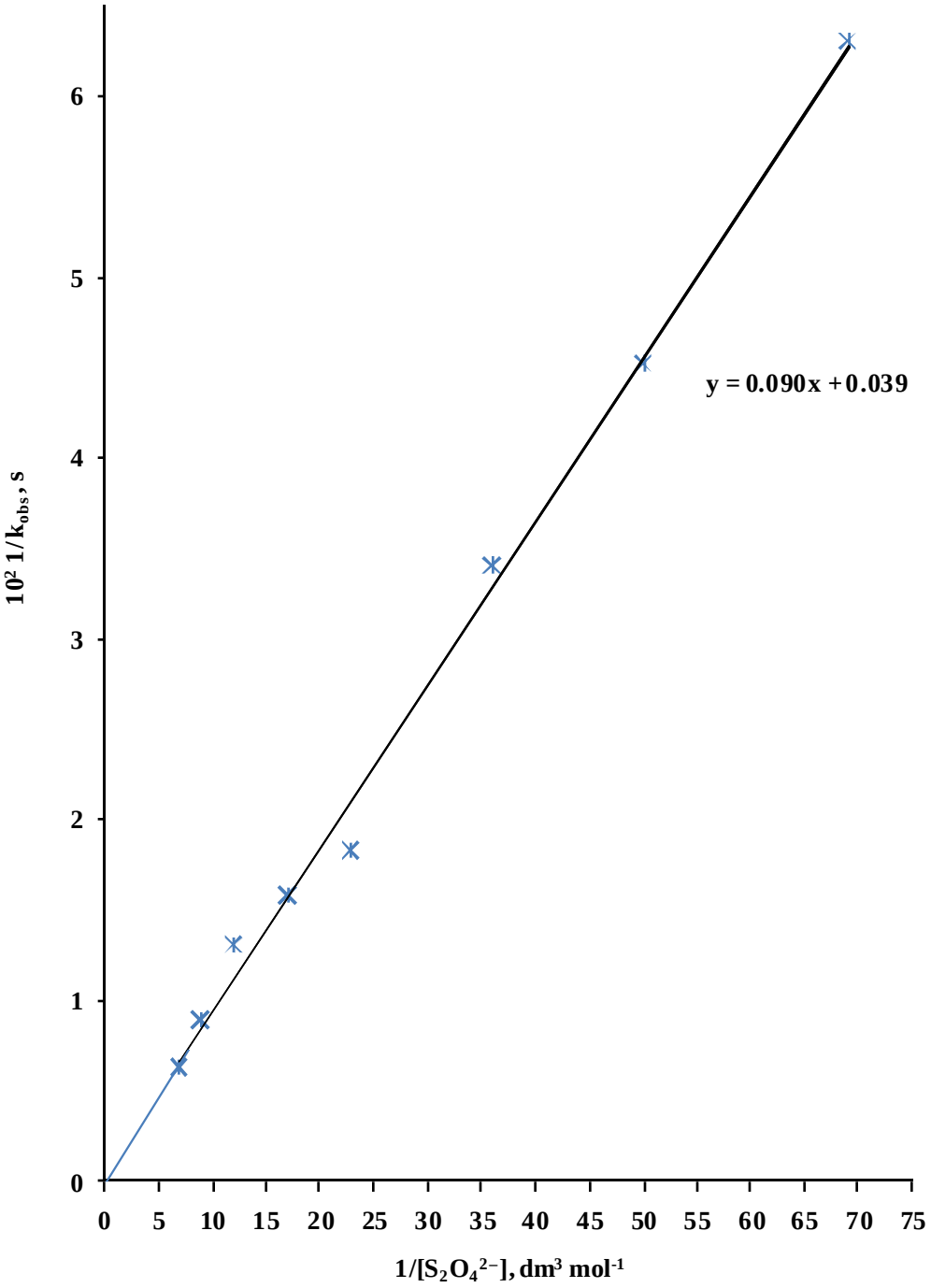


Figure 8: Plot of $1/k_{obs}$ versus $1/[S_2O_4^{2-}]$ for the Reaction of $[(H_2O)_2Ru_2O]^{4+}$ and Dithionite ($S_2O_4^{2-}$) at $[(H_2O)_2Ru_2]O^{4+}$ = 5.75 x 10^{-5} mol dm^{-3}, $[S_2O_4^{2-}]$ = (1.44-14.38) x 10^{-2} mol dm^{-3}, $[H^+]$ = 5.0 x 10^{-2} mol dm^{-3} ; I = 0.5 mol dm^{-3} ; T = 31 ± 1°C and λ_{max} = 660 nm

Based on the results and observations therefrom, a mechanism for reaction is hereby proposed.

$$S_2O_4^{2-} + 2H_2O \underset{}{\overset{K_1}{\rightleftharpoons}} H_2S_2O_4 + 2OH^- \quad ...(5)$$

$$[(H_2O)_2(bipy)_4Ru_2O]^{4+} + H_2S_2O_4 \xrightarrow{k_3} \{[(H_2O)_2(bipy)_4Ru_2O]^{4+} // S_2O_4^{2-}\} + 2H^+ \quad .(6)$$

$$\{(H_2O)_2(bipy)_4Ru_2O^{4+} // S_2O_4^{2-}\} \xrightarrow[(slow)]{k_4} [(H_2O)_2(bipy)_4Ru_2O]^{3+} + S_2O_4^- \quad ...(7)$$

$$[(H_2O)_2(bipy)_4Ru_2O]^{3+} + S_2O_4^- + 2H^+ + H_2O \xrightarrow{k_5} 2[(H_2O)_2(bipy)_2Ru]^{2+} + 2SO_2 . \quad (8)$$

If Equation 7 is the rate determining step, then:

$$\text{Rate} = k_4[[(H_2O)_2(bipy)_4Ru_2O]^{4+} // S_2O_4^{2-}] \quad . \quad . \quad (9)$$

From Equations 7 and 6 we get Equation 10.

$$[\{[(H_2O)_2(bipy)_4Ru_2O]^{4+} // S_2O_4^{2-}\}] = k_3K_1[(H_2O)_2(bipy)_4Ru_2O^{4+}][S_2O_4^{2-}] \quad .(10)$$

Substituting Equation 10 into Equation 9 we have Equation 11:

$$\text{Rate} = k_4k_3K_1[(H_2O)_2(bipy)_4Ru_2O^{4+}][S_2O_4^{2-}] \quad .(11)$$

Equation 11 agrees with Equation 2, where $k_4k_3K_1 = k_2 = (10.99 \pm .04) \times 10^{-2} dm^3mol^{-1}s^{-1}$.

In the reaction under study, the oxidation product of $S_2O_4^{2-}$ is SO_2, while in the reaction of dithionite with potassium ferrate; the product has been reported to be sulphite (Read *et al*., 2001). However, in the oxidation of sodium dithionite at a platinum electrode in alkaline solution, the final product of $S_2O_4^{2-}$ oxidation is sulphate. The reduction product of $[(bpy)_2(H_2O)RuORu(H_2O)(bpy)_2]^{4+}$ was found to be $[(H_2O)_2(bpy)_2Ru]^{2+}$. This agreed with the findings of Davies and Mullins (1967).

Conclusion

The kinetics and mechanism of the reaction of diaquotetrakis(2,2'-bipyridine)-μ-oxodiruthenium(III) ion, $[(bpy)_2(H_2O)RuORu(H_2O)(bpy)_2]^{4+}$ and dithionite ions ($S_2O_4^{2-}$) has been studied in aqueous medium. The stoichiometry of the reaction was found to be 1:1 and the reaction showed a first order dependence with respect to each of the reactant concentrations. In view of lack of identifiable intermediate complex formation evidenced by absence of intercept in the Michaelis – Menten plot, lack of shift in λ_{max} of the reaction mixture in course of reaction and ion catalysis/inhibition, it is proposed that the reaction most probably proceeded through the outer sphere pathway.

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