Abstract: The kinetics and mechanism of the electron transfer reaction of diaquotetrakis(2,2'-bipyridine)-µ-

oxodiruthenium(III) ion (hereafter denoted as RuO4+ or [(H2O)2RuO4+] and dithionate ions (SO42-) 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 [RuO4+] and [SO42-] respectively, second order overall. Rate equation for the reaction has been proposed as:

\[
d = k_0 + k_1 \left[ \left( \frac{1}{[H_2O]_R} \right) \right] \left[ \left( \frac{1}{[H_2O]_R} \right) \right] = k_2 \left[ \left( \frac{1}{[H_2O]_R} \right) \right] \left[ \left( \frac{1}{[H_2O]_R} \right) \right]
\]

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 [(H2O)3(bpy)2RuO2(bpy)] as the reduction product of [(bpy)2RuO4(bpy)]. Spectroscopic evidence of formation of stable intermediate complex was lacking which, in addition to absence of intercept in the Michaelis – Menten plot 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

Aqua bipyridyl complexes of ruthenium with aquagligands 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 (Lebeau and Meyer, 1999; Catalano et al., 2000; Rodríguez 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 (Genston et al., 1982; Gilbert et al., 1985). Electron transfer reactions of diaquotetrakis(2,2'-bipyridine)-µ-

oxodiruthenium(II) 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. Dithionate, 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). Dithionate 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

Diquaquotetrakis(2,2'-bipyridine)-µ-

oxodiruthenium(III) perchlorate was synthesized according to literature (Weaver et al., 1979). The other reagents include sodium dithionate, sodium thiosulphate, sodium perborate, magnesium chloride, ammonium chloride, sodium acetate, sodium formate, acrylamide, acetone and methanol.
Kinetics and mechanism of electron transfer reaction of ruthenium dimer and dithionite

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 molar ratio method (Iyun and Adegoke, 1990; Vaidya et al., 1991; Iyun et al., 1992a, 1992b, 1992c, 1992d, 1995a, 1996b, 1996c; Ukhda and Iyun, 2001, 2002; Ukhda and Ibrahim, 2004). The concentration of the oxo-bridged ruthenium complex was kept constant while that of the dithionite was varied between the molar 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 ($A_w$) were monitored at 660 nm (the $\lambda_{max}$ of Ru$_3$O$_5^{2+}$) using Seward Biomedical Digital Colorimeter. The absorbances obtained were plotted against the molar 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$_3$O$_5^{2+}$ with the reductant were studied by monitoring the decrease in absorbance of the dimers at its $\lambda_{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 $\log (A_t - A_s)$ against time were made and the slope 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 $k_2 = k_{obs}$[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 $\lambda$ (Brønsted, 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$_3$COO$^-$, HCOO$^-$) while maintaining the dimer and reductant constant concentrations. 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 oxidized 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 time 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, $\lambda_{max}$ 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/$k_2$ 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$_3$O$_5^{2+}$ and S$_2$O$_4^{2-}$ reaction was found to be in the ratio 1:1 (Fig. 1), suggesting that the stoichiometric equation for the reaction to be:

$$\text{Ru}_3\text{O}_5^{2+} + 2\text{S}_2\text{O}_4^{2-} \rightarrow \text{Ru}_3\text{O}_5^{\text{all}} + 4\text{S}_2\text{O}_4^{2-}$$

Similar stoichiometry of 1:1 was found for the reaction of Ru$_3$O$_5^{2+}$ with iodide (Iyun et al., 1992c), sulphite (Iyun et al., 1992d), mercapto ethanol and mercaptoethylamine (Iyun et al., 1995a) and 1:5 (Ru$_3$O$_5^{2+}$/reductant) for the reaction of Ru$_3$O$_5^{2+}$ and bromate (Iyun et al., 1992b). Comparably, a stoichiometry of 1:2 (Fe$_2$O$_4^{3+}$/reductant) has been reported in the reaction of Fe$_2$O$_4^{3+}$ with mercaptoacetic acid, mercapto ethanol, and mercaptoethylamine (Ukhda and Iyun, 2001). In addition, a 1:1 stoichiometry was reported for the reaction of dithionite with malachite green (Idins et al., 2015), dicyanomorpholinatoerrith III complex (Wathong and Hambright, 1980), p-phenylazo benzenesulphonic 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 $\log (A_t - A_s)$ 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$_3$O$_5^{2+}$]. Also a plot of $\log k_{obs}$ versus log [S$_2$O$_4^{2-}$] was linear with a slope of 0.98 (Fig. 3), suggesting a first with respect to [S$_2$O$_4^{2-}$].

Similar second order kinetics have been reported for other reactions of Ru$_3$O$_5^{2+}$ with benzeneol (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, 2014a), N-methylthiourea (Mohammed, 2014b) and thiosulphate (Mohammed et al., 2015). In the reactions of dithionite with malachite green (Idins et al., 2015) and toluidine blue (Hamza et al., 2012) a first order dependence on [S$_2$O$_4^{2-}$] was reported. However, in the reduction of p-phenylazo benzenesulphonic acid by S$_2$O$_4^{2-}$ (Wasmuth et al., 2008) and in the reduction of some azo dyes by S$_2$O$_4^{2-}$ (Gamey, 2002) half order dependence on [S$_2$O$_4^{2-}$] was reported.
Kinetics and mechanism of electron transfer reaction of ruthenium dimer and dithionite

Fig. 1: Plot of Absorbance versus Mole ratio for the Reaction of \([\text{H}_2\text{O}]_2\text{Ru}^2\text{O}_4^+\) and \(\text{S}_2\text{O}_4^{2-}\) at \([\text{H}_2\text{O}]_2\text{Ru}^2\text{O}_4^+\] = 5.75 x 10^{-5} mol dm^{-3}, \([\text{S}_2\text{O}_4^{2-}\] = (1.44 - 23.0) x 10^{-5} mol dm^{-3}, I = 0.5 mol dm^{-3} and \(\lambda_{\text{max}} = 660 \text{ nm}\)

\[r = -0.92213\]
Figure 2: Typical Pseudo-first Order Plot for the Reaction of $\left[\text{H}_2\text{O}\right]_2\text{Ru}_2\text{O}^{4+}$ and $\text{S}_2\text{O}_4^{2-}$ at $\left[\text{H}_2\text{O}\right]_2\text{Ru}_2\text{O}^{4+} = 5.75 \times 10^{-5}$ mol dm$^{-3}$, $\left[\text{S}_2\text{O}_4^{2-}\right] = 4.31 \times 10^{-2}$ mol dm$^{-3}$, $I = 0.5$ mol dm$^{-3}$, $T = 31 \pm 1$ °C and $\lambda_{\text{max}} = 660$ nm.

\[
y = -0.003x + 0.080
\]
Kinetics and mechanism of electron transfer reaction of ruthenium dimer and dithionite

Figure 3: Plot of $\log k_{\text{obs}}$ against $\log [S_2O_4^{2-}]$ for the reaction of $[(H_2O)_2RuO_4]^4+$ and $S_2O_4^{2-}$ at $[(H_2O)_2RuO_4^{4+}] = 5.75 \times 10^{-5}$ mol dm$^{-3}$, $[S_2O_4^{2-}] = (1.44 - 14.38) \times 10^{-2}$ mol dm$^{-3}$, $I = 0.5$ mol dm$^{-3}$, $T = 31 \pm 1^\circ$C and $\lambda_{\text{max}} = 660$ nm

$y = 1.037x - 0.915$
Kinetics and mechanism of electron transfer reaction of ruthenium dimer and dithionite

The overall rate equation for the oxidation of dithionite by RuO$_4^{2-}$ can, therefore, be written as Equation 2:

\[ \frac{d}{dt}(\text{RuO}_4^{2-}) = k_{\text{obs}}(\text{RuO}_4^{2-}) \]

At [RuO$_4^{2-}$] = 5.75 x 10$^{-3}$ mol dm$^{-3}$, I = 0.5 mol dm$^{-3}$ (NaClO$_4$) and T = 31 ± 1 °C, $k_{\text{obs}}$ was found to be (10.99 ± 0.04) x 10$^2$ dm$^{-3}$ mol$^{-1}$ s$^{-1}$. Dithionite was only studied at pH 7 due to its high solubility in acid. This means that the hydrogen ion concentration of 5 x 10$^{-6}$ mol dm$^{-3}$ (pH = 1.3) caused dithionite to 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 mol dm$^{-3}$ (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 RuO$_4^{2-}$ 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$_2$O)$_2$RuO$_4$]$^{2+}$ and (S$_2$O$_4^{2-}$) at [(H$_2$O)$_2$RuO$_4$]$^{2+}$ = 5.75 x 10$^{-3}$ mol dm$^{-3}$, I = 0.5mol dm$^{-3}$ (NaClO$_4$), T = 31 ± 1°C and $\lambda_{max} = 660$ nm

<table>
<thead>
<tr>
<th>[S$_2$O$_4^{2-}$]</th>
<th>I</th>
<th>$k_{\text{obs}}, s^{-1}$</th>
<th>$10^3 k_{\text{obs}}, \text{dm}^{-3} \text{mol}^{-1} \text{s}^{-1}$</th>
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<tr>
<td>1.44</td>
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<td>1.59</td>
<td>1103</td>
</tr>
<tr>
<td>2.01</td>
<td>0.5</td>
<td>2.21</td>
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<td>2.94</td>
<td>1102</td>
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<td>0.5</td>
<td>4.73</td>
<td>1097</td>
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<td>5.75</td>
<td>0.5</td>
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<td>12.59</td>
<td>1095</td>
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<td>0.5</td>
<td>15.88</td>
<td>1104</td>
</tr>
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<td>4.31</td>
<td>0.2</td>
<td>4.72</td>
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<td>4.76</td>
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<td>0.4</td>
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<td>1100</td>
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<tr>
<td>4.31</td>
<td>1.4</td>
<td>4.71</td>
<td>1093</td>
</tr>
</tbody>
</table>

Table 2: Effect of Change in the Dielectric Constant of Reaction Medium for the Reaction of [(H$_2$O)$_2$RuO$_4$]$^{2+}$ and S$_2$O$_4^{2-}$ at [(H$_2$O)$_2$RuO$_4$]$^{2+}$ = 5.75 x 10$^{-3}$ mol dm$^{-3}$, [S$_2$O$_4^{2-}$] = 4.31 x 10$^{-3}$ mol dm$^{-3}$, I = 0.5 mol dm$^{-3}$ (NaClO$_4$), D = (81.0 - 70.8), T = 31 ± 1°C and $\lambda_{max} = 660$ nm

<table>
<thead>
<tr>
<th>D</th>
<th>$10^3 k_{\text{obs}}, \text{dm}^{-3} \text{mol}^{-1} \text{s}^{-1}$</th>
<th>$10^3 k_{\text{obs}}, s^{-1}$</th>
</tr>
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<td>81.0</td>
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<td>76.8</td>
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</tr>
<tr>
<td>70.8</td>
<td>4.71</td>
<td>10.99</td>
</tr>
</tbody>
</table>

The reaction is a first order and a second-order rate constants, $k_1(X)$ and $k_2(X)$, were captured in the last square plots of $k_1(X)$ versus [X] (Figs 4-7), which were linear with intercepts and slopes and the results are represented by Equations 3 and 4.

Table 3: Effect of Added Anions to Reaction Medium for the Reaction of [(H$_2$O)$_2$RuO$_4$]$^{2+}$ and S$_2$O$_4^{2-}$ at [(H$_2$O)$_2$RuO$_4$]$^{2+}$ = 5.75 x 10$^{-3}$ mol dm$^{-3}$, [S$_2$O$_4^{2-}$] = 4.31 x 10$^{-3}$ mol dm$^{-3}$, I = 0.5 mol dm$^{-3}$, T = 31 ± 1°C and $\lambda_{max} = 660$ nm

<table>
<thead>
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<th>Ion</th>
<th>10$^3$ k$_{\text{obs}}$, s$^{-1}$</th>
<th>10$^3$ k$_{\text{obs}}$, dm$^{-3}$ mol$^{-1}$ s$^{-1}$</th>
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<td>HCOO$^-$</td>
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<td>7.16</td>
</tr>
<tr>
<td>HCOO$^-$</td>
<td>240.00</td>
<td>8.37</td>
</tr>
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</table>

Table 4: Effect of Added Cations to Reaction Medium for the Reaction of [(H$_2$O)$_2$RuO$_4$]$^{2+}$ and S$_2$O$_4^{2-}$ at [(H$_2$O)$_2$RuO$_4$]$^{2+}$ = 5.75 x 10$^{-3}$ mol dm$^{-3}$, [S$_2$O$_4^{2-}$] = 4.31 x 10$^{-3}$ mol dm$^{-3}$, I = 0.5 mol dm$^{-3}$, T = 31 ± 1°C and $\lambda_{max} = 660$ nm

<table>
<thead>
<tr>
<th>Ion</th>
<th>10$^3$ k$_{\text{obs}}$, s$^{-1}$</th>
<th>10$^3$ k$_{\text{obs}}$, dm$^{-3}$ mol$^{-1}$ s$^{-1}$</th>
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Results obtained showed that the anion catalysis (CH$_3$COO$^-$ and HCOO$^-$) with $q' = 10.95 x 10^{-2}$ dm$^{-3}$ mol$^{-1}$ s$^{-1}$ and $p' = 3.90 x 10^{-2}$ dm$^{-3}$ mol$^{-1}$ s$^{-1}$, and the cation catalysis (NH$_4^+$) with $q' = 10.95 x 10^{-2}$ dm$^{-3}$ mol$^{-1}$ s$^{-1}$ and $p' = 3.90 x 10^{-2}$ dm$^{-3}$ mol$^{-1}$ s$^{-1}$.

The anion catalysis and cation inhibition observed has been associated with outer sphere electron transfer process (Pryztais and Satin, 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$^{-3}$, $T = 32 \pm 1$ °C and $\lambda_{max} = 660$ nm

$y = 0.034x + 10.94$
Figure 5: Plot of $k_2(\text{HCOO}^-)$ versus $[\text{HCOO}^-]$ for the Reaction of $[\text{H}_2\text{O}_2\text{Ru}_2\text{O}]^{4+}$ and $\text{S}_2\text{O}_4^{2-}$ at $[\text{H}_2\text{O}_2\text{Ru}_2\text{O}]^{4+} = 5.75 \times 10^{-5}$ mol dm$^{-3}$, $[\text{S}_2\text{O}_4^{2-}] = 4.31 \times 10^{-2}$ mol dm$^{-3}$, $[\text{HCOO}^-] = (0.0 - 24.0) \times 10^{-2}$ mol dm$^{-3}$, $I = 0.5$ mol dm$^{-3}$, $T = 31 \pm 1^\circ$C and $\lambda_{\text{max}} = 660$ nm.

$y = 0.029x + 11.11$
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$_2$O$_4^{4+}$ and S$_2$O$_4^{2-}$. 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 Deren’ikov et al. (2013) reported that in the reaction...
of dithionite and super-reduced cobalamin and cobinamide the reactive species was \( \text{SO}_2^- \). The electrochemical behaviour of sodium dithionite at a gold electrode in alkaline solution shows that dithionite is oxidised with \( \text{SO}_2^- \) as intermediate (Westbroek et al., 2001).

Scanning the reaction mixture spectrophotometrically as the reaction progressed did not show any shift in \( \lambda_{\text{max}} \), thereby ruling out the formation of an intermediate complex prior to electron transfer. Also, Michaelis-Menten plot of \( 1/k_{\text{obs}} \) versus \( 1/[\text{S}_2\text{O}_4^{2-}] \) 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 outer sphere mechanism operating in the oxidation of \( \text{S}_2\text{O}_4^{2-} \) by \( \text{Ru}_2\text{O}^{4+} \).

\[
y = -0.032x + 10.90
\]

**Figure 7: Plot of \( k_2(\text{Mg}^{2+}) \) versus \([\text{Mg}^{2+}]\) for the Reaction of \([\text{H}_2\text{O})_2\text{Ru}_2\text{O}^{4+}\) and \( \text{S}_2\text{O}_4^{2-} \) at \([\text{H}_2\text{O})_2\text{Ru}_2\text{O}^{4+}]=5.75 \times 10^{-5} \text{ mol dm}^{-3}\), \([\text{S}_2\text{O}_4^{2-}] = 4.31 \times 10^{-2} \text{ mol dm}^{-3}\), \([\text{Mg}^{2+}] = (0.0 - 12.0) \times 10^{2} \text{ mol dm}^{-3}\), \( I = 0.5 \text{ mol dm}^{-3}\), \( T = 31 \pm 1^\circ \text{C} \) and \( \lambda_{\text{max}} = 660 \text{ nm} \)**
Figure 8: Plot of $1/k_{obs}$ versus $1/[S_2O_4^{2-}]$ for the Reaction of $[(H_2O)_{2}Ru_2O]^{4+}$ and Dithionite ($S_2O_4^{2-}$) at $[(H_2O)_{2}Ru_2O]^{4+} = 5.75 \times 10^{-5}$ mol dm$^{-3}$, $[S_2O_4^{2-}] = (1.44-14.38) \times 10^{-2}$ mol dm$^{-3}$, $[H^+] = 5.0 \times 10^{-2}$ mol dm$^{-3}$; $I = 0.5$ mol dm$^{-3}$; $T = 31 \pm 1^\circ C$ and $\lambda_{max} = 660$ nm
Kinetics and mechanism of electron transfer reaction of ruthenium dimer and dithionite

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

\[ \text{S}_2\text{O}_8^{2-} + 2\text{H}_2\text{O} \xrightarrow{K_1} \text{H}_2\text{S}_2\text{O}_4 + 2\text{OH}^- \] ... (5)

\[ [(\text{H}_2\text{O})_2(\text{bpy})_4\text{Ru}_2\text{O}^{4+} + \text{H}_2\text{S}_2\text{O}_4 \xrightarrow{k_3} [(\text{H}_2\text{O})_2(\text{bpy})_4\text{Ru}_2\text{O}^{4+}/\text{S}_2\text{O}_4^{2-}] \] (slow)

\[ \xrightarrow{k_4} [(\text{H}_2\text{O})_2(\text{bpy})_4\text{Ru}_2\text{O}^{3+} + \text{S}_2\text{O}_4^{2-}] \] ... (7)

If Equation 7 is the rate determining step, then:

\[ \text{Rate} = k_4[[(\text{H}_2\text{O})_2(\text{bpy})_4\text{Ru}_2\text{O}^{4+}]/\text{S}_2\text{O}_4^{2-}] \]. . . (9)

From Equations 7 and 6 we get Equation 10.

\[ [[(\text{H}_2\text{O})_2(\text{bpy})_4\text{Ru}_2\text{O}^{4+}]/\text{S}_2\text{O}_4^{2-})] = k_3K_1[(\text{H}_2\text{O})_2(\text{bpy})_4\text{Ru}_2\text{O}^{4+}][\text{S}_2\text{O}_4^{2-}] \] . . . (10)

Substituting Equation 10 into Equation 9 we have Equation 11:

\[ \text{Rate} = k_4k_3K_1[(\text{H}_2\text{O})_2(\text{bpy})_4\text{Ru}_2\text{O}^{4+}][\text{S}_2\text{O}_4^{2-}] \] . . . (11)

Equation 11 agrees with Equation 2, where \( k_4k_3K_1 = k_3 = (10.99 \pm 0.4) \times 10^{-6}\text{dm}^3\text{mol}^{-1}\text{s}^{-1} \).

In the reaction under study, the oxidation product of S\(_2\)O\(_8^{2-}\) is SO\(_2\), while in the reaction of dithionite with potassium ferrate, the product has been reported to be sulphite (Reader et al., 2001). However, in the oxidation of sodium dithionite at a platinum electrode in alkaline solution, the final product of S\(_2\)O\(_4^{2-}\) oxidation is sulphate. The reduction product of \( [(\text{bpy})(\text{H}_2\text{O})\text{RuO}_2\text{Ru}(\text{H}_2\text{O})(\text{bpy})]^3+ \) was found to be \( [(\text{H}_2\text{O})(\text{bpy})_2\text{Ru}]^5+. \) This agreed with the findings of Davies and Mullins (1967).

Conclusion

The kinetics and mechanism of the reaction of diazaquatetrakis(2,2'-bipyridine)-μ-oxoruthenium(II) ion, \( [(\text{bpy})(\text{H}_2\text{O})(\text{H}_2\text{O})\text{Ru}(\text{H}_2\text{O})(\text{bpy})]^3+ \) and dithionite ions (S\(_2\)O\(_4^{2-}\)) 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 Michales - Menten plot, lack of shift in λ\(_{max}\) of the reaction mixture in course of reaction and ion catalysts / inhibition, it is proposed that the reaction most probably proceeded through the outer sphere pathway.

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Kinetics and mechanism of electron transfer reaction of ruthenium dimer and dithionite


