

## THE OXIDATION OF SULPHITE BY DIAQUOTETRAKIS(2,2'-BIPYRIDINE)- $\mu$ -OXODIRUTHENIUM(III) ION IN PERCHLORIC ACID

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**ABSTRACT.** The kinetics of the oxidation of sulphite ion by diaquotetrakis(2,2'-bipyridine)- $\mu$ -oxodiruthenium (III) ion, has been investigated. The reaction is first order with respect to sulphite and oxidant. On the basis of the observed anion catalysis, the lack of conclusive evidence for intermediate complex formation and non-conformity of the observed kinetic data with the Michaelis-Menten equation, it is proposed that the reaction most probably occurs by the outer-sphere mechanism.

### INTRODUCTION

Following the reports [1,2] that the  $\mu$ -oxobridged ruthenium (III) complexes constitute potential sources of new materials with distinct chemical and physical properties, we reported on the redox reactions of  $[(bipy)_2ClRuORuCl(bipy)_2]^{2+}$  with  $[Ru(NH_3)_6]^{2+}$  and some aqualons [3] and with  $TiEDTA^-$  [4]. We also investigated the anion-assisted dissociation of this dimer [5], and also the redox reactions of the diaquadimer,  $[(bipy)_2H_2ORuORuH_2O(bipy)_2]^{4+}$  with  $I^-$  [6],  $IO_4^-$  [7],  $BrO_3^-$  [8],  $Fe(H_2O)_6^{2+}$  [9] and hydroquinone [10]. This latter dimer, upon multiple oxidation, has been shown to catalyse the oxidation of chloride to chlorine [11] and water to oxygen [12]. The protolytic splitting of water is said to be one of the most attractive ways of storing solar energy [13]. Moreover, the higher oxidation state of this water-oxidation catalyst [14] and of similar polypyridyl complexes containing aqua ligands [15] have been found to be good stoichiometric and catalytic oxidants [16-20].

In this paper we report the oxidation of the versatile sulphite ion [21-40] by  $[(bipy)_2H_2ORuORuH_2O(bipy)_2]^{4+}$ . We also address the question of one- or two-electron pathway for the sulphite ion and of the subsequent product of the reaction.

### EXPERIMENTAL

**Materials.** Diaquotetrakis(2,2'-bipyridine)- $\mu$ -oxodiruthenium (III) perchlorate was prepared and characterized as reported in literature [1]. The complex has a typical peak at  $\lambda = 658$  nm. The diaquaobridged dimer, unlike its dichloro analog [5], was very stable in water and in the presence of acid and added anions. The absorbance at  $\lambda = 658$  nm remained constant for several days in perchloric acid. The concentration was checked spectrophotometrically before runs. Solutions of  $Na_2SO_3$  (J.T. Baker) were standardized before use [41]. Analar grade  $HClO_4$  and  $NaNO_3$  were obtained from BDH.

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*Kinetics.* The rate of the reaction was monitored by following the decrease in absorbance of the oxobridged dimer at  $\lambda = 658$  nm. Solutions of the sulphite ion and of the product of the reaction were transparent at this wavelength. The kinetic runs were made under pseudo-first-order conditions with the concentration of sulphite at least 3000-fold in excess of that of the dimer concentration. The pseudo-first-order rate constants,  $k_1$ , were obtained from the slopes of the  $\log(A_t - A_\infty)$  vs time plots. ( $A_t$  and  $A_\infty$  are the absorbances of the oxobridged complex at time  $t$  and at the end of the reaction). The second-order rate constants were calculated as  $k_1/[\text{sulphite}]$ . All reported rate constants are at least from duplicate runs which were reproducible within  $\pm 5\%$ . Constant temperature was maintained at  $25.0 \pm 0.1^\circ\text{C}$  for each run by circulating thermostated water through the cell compartments of the spectrophotometer. Ionic strength was maintained at  $2.0 \text{ mol dm}^{-3}$  ( $\text{NaClO}_4$ ) for all runs.

*Spectroscopic test for intermediate complex formation.* The spectrum of the reaction mixture was run one min after the initiation of the reaction and compared to the spectrum of the oxobridged dimer. A red shift of 10 nm observed from the oxobridged dimer suggests the possibility of some interaction, most likely due to ion pair formation between the reactant ions prior to electron transfer. The observed shift of the oxobridged dimer is not enough for a conclusion on an intermediate complex formation to be made.

*Test for radicals.* Acrylonitrile ( $5 \text{ cm}^3$ ) was added to a partially oxidized mixture containing  $[\text{dimer}] = 1.5 \times 10^{-5} \text{ mol dm}^{-3}$  and  $[\text{sulphite}] = 0.10 \text{ mol dm}^{-3}$ . This was followed by the addition of a large excess of methanol. No suspension of polyacrylonitrile was observed suggesting that free radicals may not be important intermediates in this reaction. The reaction therefore, most probably occurs by a direct two-electron transfer. It is however worth mentioning that failure to detect free radicals does not completely rule out the possibility of a free radical mechanism.

*Test for products.* To further confirm that the reaction most probably occurs by a direct two-electron transfer, we tested for the product of the reaction with  $\text{BaCl}_2$  solution using a reaction mixture containing  $[\text{dimer}]$  in five-fold excess of  $[\text{sulphite}]$ . The reaction mixture was allowed to stand for seven days. A positive identification of  $\text{SO}_4^{2-}$  suggests  $\text{SO}_4^{2-}$  and not  $\text{S}_2\text{O}_6^{2-}$  as the product of the reaction.  $\text{S}_2\text{O}_6^{2-}$  would result from one-electron transfer steps [21-24]. Therefore the reaction most probably occurs by a direct two-electron transfer.

## RESULTS AND DISCUSSION

*Stoichiometry.* The stoichiometry of the reaction was determined at  $\lambda = 658$  nm by spectrophotometric titration using the mole ratio method. One mole of the diaquaoxobridged dimer is consumed by one mole of sulphite ion. We observed a similar stoichiometry in the reaction of the oxobridged dimer with  $\text{I}^-$  [6] and  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  [9] and a 5:1 and 2:1 stoichiometry in its reaction with  $\text{BrO}_3^-$  [8] and

hydroquinone [10], respectively. Unlike in the sulphite reaction, the evidence obtained in these latter reactions suggest that they occur by a series of univalent changes. Reports also show that the sulphite ion is capable of reducing ions with varying stoichiometries [23, 25-27].

*Order of reaction.* At  $0.03 \leq [H^+] \leq 0.50 \text{ mol dm}^{-3}$  and with [sulphite] at least 3000-fold in excess of [dimer], the plots of  $\log (A_t - A_\infty)$  vs time were linear to more than 80% completion of reaction confirming that the reaction is first-order in [dimer]. A plot of  $\log k_1$  ( $k_1$  is the pseudo-first-order rate constant) versus [sulphite] was linear passing through the origin with a slope of  $1.1 \pm 0.1$  confirming that the reaction is also first-order in [sulphite]. The rate law for this reaction at any constant acid concentration in the acid range,  $0.03 \leq [H^+] \leq 0.50 \text{ mol dm}^{-3}$  and  $I = 2.0 \text{ mol dm}^{-3}$  ( $\text{NaClO}_4$ ) is,

$$-\frac{d}{dt} [H_2ORuORuH_2O]^{4+} = k_2 [H_2ORuORuH_2O]^{4+} [\text{sulphite}] \quad (1)$$

$$[H_2ORuORuH_2O]^{4+} = [(bipy)_2H_2ORuORuH_2O(bipy)_2]^{4+}$$

We have also observed second-order kinetics for all reactions of the oxobridged dimer so far reported [6-10]. Second-order kinetics has also been a common feature of reactions involving the sulphite ion [28,29] although more complex pathways are also possible [30-32]. The pseudo-first-order rate constants  $k_1$  and the second-order rate constants  $k_2$  obtained from  $k_1$  as  $k_1/[\text{sulphite}]$  are presented in Table 1.

*Acid-dependence.* The  $[H_2ORuORuH_2O]^{4+}$  - sulphite reaction displayed an inverse acid-dependence to the first-order in the acid-range  $0.03 \leq [H^+] \leq 0.50 \text{ mol dm}^{-3}$ . In reactions involving the diaquinoxobridged dimer [6-10] no such dependence has been observed. While its reaction with hydroquinone was independent of acid concentration [10], its reaction with  $\text{BrO}_3^-$  [8] showed both an acid-independence and an  $[H^+]^2$  dependent term. The oxidation of  $\Gamma^-$  [6] and  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  [9] and the reduction of  $\text{IO}_4^-$  [7] by the dimer were all  $[H^+]$  dependent. In the oxidation of the sulphite ion by the dimer, a plot of the acid-dependent rate constant  $k_2$  versus  $[H^+]^{-1}$  was linear with 99.55 correlation coefficient and obeys the equation,

$$k_2 = a + b [H^+]^{-1} \quad (2)$$

Table 1. Pseudo-first-order and second-order rate constants for the reaction of  $[(bipy)_2H_2ORuORuH_2O(bipy)_2]^{4+}$  with sulphite ion.  $[H_2ORuORuH_2O]^{4+} = 1.6 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $I = 2.0 \text{ mol dm}^{-3} (\text{NaClO}_4)$ ,  $T = 25.0 \pm 0.1^\circ\text{C}$ ,  $\lambda_{\text{max}} = 658 \text{ nm}$

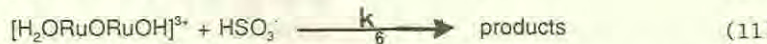
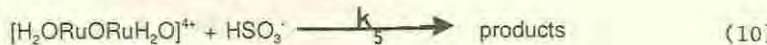
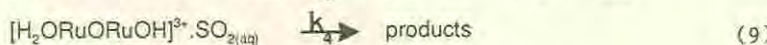
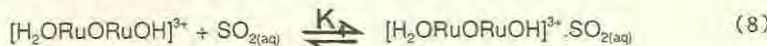
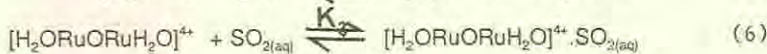
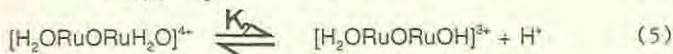
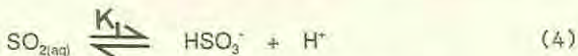
$[\text{SO}_3^{2-}]$ $\text{mol dm}^{-3}$	$[H^+]$ $\text{mol dm}^{-3}$	$10^5 k_1 \text{ s}^{-1}$	$10^4 k_2$ $\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$
0.05	0.05	6.1	12.3
0.07	0.05	8.5	12.1
0.09	0.05	11.1	12.3
0.10	0.05	12.5	12.5
0.20	0.05	25.2	12.6
0.30	0.05	35.3	11.8
0.40	0.05	50.0	12.5
0.10	0.03	17.2	17.2
0.10	0.04	14.0	14.0
0.10	0.07	8.8	8.8
0.10	0.09	8.0	8.0
0.10	0.10	6.1	6.1
0.10	0.20	5.1	5.3
0.10	0.25	4.9	4.9
0.10	0.30	4.7	4.7
0.10	0.40	4.5	4.5
0.10	0.50	4.4	4.4

with  $a = 3.72 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  and  $b = 6.15 \times 10^{-5} \text{ s}^{-1}$ . This suggests that this reaction occurs by two parallel pathways one inverse acid-dependent and the other acid-independent. A similar acid-dependence has also been reported for the oxidation of sulphur(IV) by dodecatungstocobaltate(III) ion [31] while a simpler acid-dependence was observed in the oxidation of sulphite by hexachloroplatinate(IV) [33]. Leipoldt *et al* reported a slightly more complex acid-dependent reduction by the sulphite ion [22]. The rate equation for the title reaction can now be written as,

$$-\frac{d}{dt} [H_2ORuORuH_2O]^{4+} = (a + b [H^+]^{-1}) [H_2ORuORuH_2O]^{4+} [\text{sulphite}] \quad \dots (3)$$

The observed acid dependence could arise from the equilibria established by the sulphite ion in solution [28] and/or by the deprotonation of the potentially acidic aqua ligand of the oxobridged dimer.

In the acid range investigated in this work, the principal sulphite species in solution are  $\text{SO}_{2(\text{aq})}$  and  $\text{HSO}_3^-$  [28] with  $\text{HSO}_3^-$  being the predominant species. The observed acid-dependence suggests that these species react by two parallel pathways with one of these independent of changes in acid concentration. Either of these pathways can occur by the outer- or the inner-sphere mechanism. Previous studies [21,27,33], however, suggest a preference of the sulphite ion for the inner-sphere mechanism although some reactions like those involving  $\text{Mo}(\text{CN})_6^{3-}$  [22] and  $\text{IrCl}_6^{2-}$  [34] with the sulphite ion have been reported as proceeding by the outer-sphere mechanism. The stability of the oxobridged dimer in acid and anionic media, as we have observed in this and previous investigations, suggest that it may be relatively inert. However the bathochromic shift observed when the two reactants are added together suggests some outer-sphere interaction. When this is combined with the observed acid dependence and the non-detection of a free radical intermediate, the following mechanism can be proposed.



With equations (7), (9), (10) and (11) as the rate determining steps, the rate equation can be written as:

$$\begin{aligned}
 -\frac{d}{dt} [H_2ORuORuH_2O]^{4+} &= k_3 [H_2ORuORuH_2O^{4+} \cdot SO_2(aq)] \\
 &+ k_4 [H_2ORuORuOH^{3+} \cdot SO_2(aq)] + k_5 [H_2ORuORuH_2O^{4+}] [HSO_3^-] \\
 &+ k_6 [H_2ORuORuOH^{3+}] [HSO_3^-] \quad (12)
 \end{aligned}$$

When substitution is made into eq (12) from eq (4), (5), (6) and (8) we obtain a rate equation of the form,

$$\begin{aligned}
 -\frac{d}{dt} [H_2ORuORuH_2O]^{4+} &= (k_3K_3 + \frac{k_4K_2K_4 + k_5K_1}{[H^+]}) \\
 &+ \frac{k_6K_1K_2}{[H^+]^2} [H_2ORuORuH_2O]^{4+} [SO_2(aq)] \quad (13)
 \end{aligned}$$

Eq (13) is similar to eq (3) with,

$$k_2 = k_3K_3 + \frac{k_4K_2K_4 + k_5K_1}{[H^+]} + \frac{k_6K_1K_2}{[H^+]^2} \quad (14)$$

However, the linearity of the  $k_2$  vs  $[H^+]^{-1}$  plot with more than 99.5% correlation coefficient shows the relative unimportance of the  $1/[H^+]^2$  term in eq (14) suggesting that the deprotonation of the diaqua-oxo-bridged dimer may not be significant in the acid range investigated. (i.e.  $K_2$  is very small and hence terms involving  $K_2$  in eq (14) can be ignored). If this assumption is made then eq (14) reduces to (15),

$$k_2 = k_3K_3 + \frac{k_5K_1}{[H^+]} \quad (15)$$

This is similar to eq (2) with  $a = k_3K_3$  and  $b = k_5K_1$ , thus supporting the proposed mechanism. From the slope of the  $k_2$  vs  $[H^+]^{-1}$  plot and the value of  $K_1$ , earlier reported [28]  $k_5$  was calculated as  $3.8 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ .

Apart from the linearity of the  $k_2$  vs  $[H^+]^{-1}$  which supports the proposed mechanism, the mechanism is also consistent with the observed absence of free radical intermediates and the failure to detect a binuclear intermediate of appreciable life-time thus suggesting that the reaction most probably occurs by the outer-sphere mechanism.

*Michaelis-Menten plot.* Extrapolating from enzyme kinetics we tried to assess the contribution of the inner-sphere mechanism, if any, to this reaction by using Lineweaver-Burk modification of the Michaelis-Menten equation [42,43]. A plot of  $1/k_2[SO_3^{2-}]$  vs  $1/[SO_3^{2-}]$  was non-linear. The non-linearity of this plot suggests that intermediate complex formation prior to the electron-transfer step is very unlikely thus further suggesting that the reaction most likely occurs by the outer-sphere mechanism.

Table 2. Anion-dependent rate constants  $k_2$  for the reaction of  $[(bipy)_2H_2ORuORuH_2O(bipy)_2]^{4+}$  with the sulphite ion.  $[H_2ORuORuH_2O^{4+}] = 1.6 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[SO_3] = 0.1 \text{ mol dm}^{-3}$ ,  $I = 2.0 \text{ mol dm}^{-3}$  ( $NaClO_4$ ),  $T = 25.0 \pm 0.1^\circ C$ ,  $\lambda_{max} = 658 \text{ nm}$ .

$[H^+]$ mol dm <sup>-3</sup>	$[X]$ mol dm <sup>-3</sup>	$10^5 k_2, s^{-1}$	$10^4 \times k_2$ mol <sup>-1</sup> dm <sup>3</sup> s <sup>-1</sup>
	X = NO <sub>2</sub>		
0.05	0.05	14.8	14.8
0.05	0.10	16.4	16.4
0.05	0.20	19.6	19.6
0.05	0.30	23.0	23.0
0.05	0.40	26.9	26.9
0.05	0.50	30.0	30.0
	X = HCOO		
0.05	0.05	14.0	14.0
0.05	0.10	15.5	15.5
0.05	0.20	17.5	17.4
0.05	0.30	19.4	19.4
0.05	0.40	21.6	21.6
0.05	0.50	25.4	25.4

*Anion catalysis.* Further evidence for the existence of the outer-sphere pathway for this reaction is provided by the observed anion catalysis as reported in Table 2. Plots of  $k_2$ , the anion-dependent second-order rate constants vs  $[X]$ , ( $X = NO_2, HCOO$ ) were linear with a common intercept and obeys an equation of the form,

$$k_2 = c + d[X^-] \quad (16)$$

with  $c = 1.25 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  and  $d = 3.63 \times 10^{-1} \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$  for  $X = NO_2$

and  $2.39 \times 10^{-3} \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$  for  $X = \text{HCOO}$ .

Reactions occurring by the outer-sphere mechanism are expected to be catalysed by the anions but anions should have little or no effect on reactions occurring by the inner-sphere mechanisms [44,45]. The observed anion-catalysis further supports the proposition that the oxidation of the sulphite ion by the oxidised dimer occurs by the outer-sphere mechanism.

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