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**Research Article** 

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Kinetics and Mechanisms of the Oxidation of Thiosulphate by Potassium Trisoxalatoferrate (iii) in Aqueous Hydrochloric Acid Medium

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Abstract The kinetics of oxidation of  $S_2O_3^{2-}$  by  $K_3[Fe(C_2O_4)_3]$ .3H<sub>2</sub>O has been investigated in aqueous acid medium at  $\lambda_{max} = 420$ nm, T = 27.0 ± 1.0 °C, I = 0.4 moldm<sup>-3</sup> (NaCl) and [H<sup>+</sup>] = 0.02 moldm<sup>-3</sup> (HCl). The reaction is first order with respect to oxidant and reductant concentrations and obeyed the general rate law:

 $\frac{-d[Fe(C_2O_4)_3^{3-}]}{dt} = (a + b[H^+])[Fe(C_2O_4)_3^{3-}] [S_2O_3^{2-}]$ 

where  $a = 0.0402 \text{ s}^{-1}$  and  $b = 1.26 \text{ dm}^6 \text{ mol}^2 \text{ s}^{-1}$ . Added ions affected the rate of the reaction. The reaction was acid dependent and was unaffected by changes in ionic strength of the reaction medium. A plausible mechanism is proposed for the reaction.

### Keywords Kinetics, Oxidation, Thiosulphate, Potassium Trisoxalatoferrate, Hydrochloric Acid

### Introduction

Thiosulphate ion,  $(S_2O_3^{2-})$  is one of the most important sulphur oxyanions. It is a moderately strong reducing agent that has been widely used in photographic industries to fix images in film development, and in paper and textile industries to remove excess chlorine in bleaching processes [1]. Aqueous solutions of thiosulphate are used in spray solutions in nuclear reactors to lower temperature and react with radio-iodine in the event of a loss-of-coolant accident [2]. Thiosulphate is important to various bacteria as a source of energy. It is also a common constituent of urine in animals, attributed to the chemical breakdown of cystein and methionine [3]. The redox reactions of thiosulphate with a variety of metal complexes have continued to receive attention, owing to their Industrial and Biological importance [4-6].

Trisoxalato complexes of the general formula:  $K_3[M(C_2O_4)_3]$ .XH<sub>2</sub>O have played a leading role in many aspects of co-ordination chemistry especially in their spectroscopic behavior, kinetic behavior in solution and in some cases their resolution into enantiomers [7]. These complexes have found useful applications in photography, medicine and in actinometry [8-9]. The redox reactions of these complexes with a variety of substrates are also receiving attention. In this paper, we have investigated the kinetics and mechanisms of the oxidation of thiosulphate by Potassium trisoxalatoferrate(III) in aqueous hydrochloric acid medium.

### Experimental

### Materials and reagents

The complex,  $K_3[Fe(C_2O_4)_3]$ .3H<sub>2</sub>O was synthesized according to a known procedure involving the direct reaction of potassium oxalate monohydrate and iron(III)chloride hexahydrate and standardized as reported in the literature [10].



Sodium chloride (BDH, analar) stock solution was prepared without further purification or standardization and used to maintain the ionic strength at 0.4 mol dm<sup>-1</sup> while HCl was used to investigate the effect of hydrogen ions on the rate of the reaction. All other chemicals were used as supplied.

## **Stoichiometric Studies**

The stoichiometry of the reaction was determined by spectrophotometric titration using the mole ratio method. Solutions containing known concentrations of  $[Fe(C_2O_4)_3^{3-}]$  and varying concentrations of  $S_2O_3^{2-}$  (0.099-0.396) mol dm<sup>3</sup> were reacted at  $[H^+] = 0.02$  mol dm<sup>-3</sup> and I = 0.4 mol dm<sup>-1</sup> (NaCl) and allowed to stand for 24 hours for the reaction to go to completion. The absorbance of the solutions was measured at 420nm and the stoichiometry was evaluated from the plot of absorbance versus mole ratio.

### **Kinetic Measurements**

All kinetic runs were performed under pseudo-first order conditions with the concentration of  $S_2O_3^{2-}$  in at least 10 fold excess over that of  $[Fe(C_2O_4)_3^{3-}]$ . The rate of reaction was monitored by measuring the rate of decrease in absorbance of the mixture at 420nm using a Seaward photoelectric colorimeter [AE-11D] at 27.0±1.0 °C,  $[H^+] = 0.02 \text{ mol dm}^{-1}$  and  $I = 0.4 \text{mol dm}^{-1}$  (NaCl) unless otherwise stated.

Pseudo-first order rate constants were obtained from plots of  $log(A_t-A_{\infty})$  versus time.

### **Results and Discussion**

### Stoichiometry

The results of the spectrophotometric titration indicated a 1:2 Stoichiometry and the overall reaction is given by:  $[Fe(C_2O_4)_3]^{3-} + 2S_2O_3^{2-} + H^+ \longrightarrow [Fe(C_2O_4)_3]^{4-} + S_4O_6^{2-} + Other products.....(1)$ 

# **Product Analysis**

 $SO_3^{2-}$  was identified by chemical test by addition of BaCl<sub>2</sub> solution which gave a white precipitate which dissolved in excess dilute hydrochloric acid to give a colourless solution. Also, the solution decolourized KMnO<sub>4</sub> solution, all indicating that one of the products was  $SO_3^{2-}$ .

### **Determination of Order**

Pseudo-first order plots of  $\log(A_t-A_{\infty})$  versus time were linear for greater than 80% extent of the reaction indicating first order with respect to  $[Fe(C_2O_4)_3^{3-}]$ . Values of the observed rate constants are given in Table 1. A plot of log  $k_1$  versus log  $[S_2O_3^{2^-}]$  was linear. The slope of 1.02 signifies first order in  $[S_2O_3^{2^-}]$ , shown in figure 1. This was also confirmed by plotting  $k_1$  versus  $[S_2O_3^{2^-}]$  which gave a straight line passing through the origin (figure 2). The second order rate constants,  $k_2$  was obtained from  $k_2 = k_1/[S_2O_3^{2^-}]$  were found to be fairly constant (Table 1). The rate law is given by equation (2):



Figure 1: Plot of Log  $k_1$  versus Log  $[S_2O_3^{2^2}]$  for the redox reaction between  $[Fe(C_2O_4)_3^{3^2}]$  and  $S_2O_3^{2^2}$ 





Figure 2: Plot  $k_1$  versus  $[S_2O_3^{2^-}]$  for the redox reaction between  $[Fe(C_2O_4)_3^{3^-}]$  and  $S_2O_3^{2^-}$ 

### **Acid Dependence**

The acid dependence on the rate of this reaction was investigated at constant  $[Fe(C_2O_4)_3^{3-}]$ ,  $[S_2O_3^{2-}]$  and ionic strength of 0.4 mol<sup>-1</sup> dm<sup>-3</sup> (NaCl),  $[H^+] = (2.0-14.0) \times 10^{-3}$  mol dm<sup>-3</sup> at  $27.0 \pm 1.0^{\circ}$ C. A least square plot of k<sub>2</sub> versus  $[H^+]$  was found to be linear

(r =0.96, figure 3). The slope of 1.3 indicates first order in  $[H^+]$  and the relationship represented by:

 $k_2 = a + b [H^+]$  ......(3)

a = 0.402 s<sup>-1</sup> and b = 1.26 dm<sup>6</sup> mol<sup>2</sup> s<sup>-1</sup>. The rate equation for the reaction can therefore be written as:  $\frac{-d[Fe(C_2O_4)_3^{3^-}]}{dt} = a + b\{[H^+]\}[Fe(C_2O_4)_3^{3^-}][S_2O_3^{2^-}]$ .....(4)

The equation suggests that the reaction occurs via acid dependent and acid independent pathways. It has been reported that redox reactions of many oxoanions are strongly acid dependent [12-13]. Under the present experimental conditions, therefore, it is reasonable to postulate that  $S_2O_3^{-2-}$  reacts reversibly with H<sup>+</sup> in a first step to give  $S_2O_3^{-2-}$  and  $S_2O_3^{-2-}$  which then reacts individually with  $[Fe(C_2O_4)_3]^{3-}$  in two separate slow steps to give the products.

$[S_2O_3^{2}]$	$10^{3}[H^{+}]$	I, (NaCl),	$10^{2}[k_{2}]$
Mol dm <sup>-3</sup>	mol dm <sup>-3</sup>	mol dm <sup>-3</sup>	dm <sup>-3</sup> mol <sup>-1</sup> s <sup>-1</sup>
0.099	10	0.4	7.3
0.149	10	0.4	6.78
0.198	10	0.4	7.2
0.248	10	0.4	7
0.297	10	0.4	7.58
0.347	10	0.4	6.34
0.396	10	0.4	7.21
0.248	2	0.4	28.8
0.248	4	0.4	30.4
0.248	6	0.4	30.7
0.248	8	0.4	31.1
0.248	10	0.4	38.4
0.248	12	0.4	56.9
0.248	14	0.4	78.7
0.248	10	0.4	4.73
0.248	10	0.48	5.71
0.248	10	0.56	6.73
0.248	10	0.64	7.03
0.248	10	0.72	7.48
0.248	10	0.8	7.84

Table 1: Second	order rate constants for the ox	xidation of $S_2O_3^{2-}$ by $[Fe(C_2O_4)_3^{3-}]$
$[Fe(C_2O_4)_3^{3-}] = 9.9 \times 10^{-3}$	$moldm^{-3}$ , $I=0.4 moldm^{-3}$ (NaC	Cl), T= 27.0 $\pm$ 1.0 °C and $\lambda$ =420 nm



X	10 <sup>2</sup> [x], moldm- <sup>3</sup>	$10^{3}$ k <sub>1</sub> , s <sup>-1</sup>	10 <sup>2</sup> k <sub>2</sub> , dm <sup>-3</sup> mol <sup>-1</sup> S <sup>-1</sup>
Zn <sup>2+</sup>	4	3.33	1.34
	6	3.62	1.46
	8	3.72	1.5
	10	4.08	1.65
	12	4.67	1.88
	14	4.97	1.93
NO <sub>2</sub>	4	3.18	1.28
	6	3.85	1.55
	8	4.04	1.63
	10	4.68	1.89
	12	5.09	2.05
	14	6.17	2.49

**Table 2:** Effect of added species on the second order rate constants for the oxidation of  $S_2O_3^{2-}$  by  $[Fe(C_2O_4)_3^{3-}]$  at  $[Fe(C_2O_4)_3^{3-}] = 9.9 \times 10^{-3} \text{ mol dm}^{-3}, [S_2O_3^{2-}] = 0.248 \text{ moldm}^{-3}, [H^+] = 0.01 \text{ moldm}^{-3}, I = 0.4 \text{ moldm}^{-3}(NaCl), T = 27.0 \pm 1.0 \text{ °C and } \lambda = 420 \text{ nm}.$ 

### Ionic Strength

The ionic strength was varied from (0.40 - 0.96) mol dm<sup>-3</sup> using NaCl. The rate of the reaction was found to increase with increase in ionic strength in the concentration range used. It is expected that the rate should vary with changes in ionic strength since the redox species are charged [14].

### **Dielectric constant**

The dielectric constant was varied by varying acetone/water concentration. It was observed that that the reaction rate was enhanced as a function of 1/D (D= dielectric constant). A plot of log k<sub>2</sub> versus 1/D gave a positive slope (figure 3). This indicates a positive- ion dipole reaction prior to the electron transfer [15].

### Effect of added species

The effects of added  $Zn^{2+}$  and  $NO_2^{-}$  on the rate of the reaction were studied. The values of the rate constants are shown in table 2. It was found that these species enhanced the reaction rate, which is suggestive that an outer- sphere mechanism is probably in operation. [16].

### Test for free radicals

Addition of acrylamide to partially reacted mixture did not give a gel in the presence of excess methanol, indicating the probable absence of free radicals in the reaction medium. On the other hand, free radicals could have been formed, but reacted so quickly that that this method could not detect it [17].

## Michaelis-Menten plot

Least squares analysis of  $1/k_1$  versus  $1/[S_2O_3^{2-}]$  gave a straight line with an insignificant intercept, suggesting the absence of intermediate complex formation, an indication that the reaction most probably proceeded by an outer-sphere pathway.



Figure 3: Plot of  $k_2$  versus 1/D for the oxidation of  $S_2O_3^{2-}$  by  $[Fe(C_2O_4)_3^{3-}]$ 



### **Reaction Mechanism**

The result of acid dependence suggests that the reaction occurs through an acid dependent pathway. The lack of cation and anion dependence of the rate of the reaction suggests that the intermediate is likely as a result of the union of the two reactants. The non detection of a radical intermediate may be due to the fact that it was formed so quickly that the method used could not detect it.

The proposed mechanism for the oxidation of  $S_2O_3^{2-}$  by  $[Fe(C_2O_4)_3^{3-}]$  is given in the scheme below. The mechanism is based on the Stoichiometry, kinetic studies as well as the known chemistry of thiosulphate. The existence of thiosulphate and trithionate radicals,  $(S_2O_3^{2-} \text{ and } S_2O_3^{-})$  ions in aqueous solutions are well documented in literature [17].

$$2S_{2}O_{3}^{2^{2}} + H^{+} \xrightarrow{k_{1}} S_{2}O_{3}^{2^{2}} + S_{2}O_{3}^{-} \text{ (fast)......(5)}$$

$$[Fe(C_{2}O_{4})_{3}^{3^{2}}] + S_{2}O_{3}^{2^{2}} \xrightarrow{k_{2}} [Fe(C_{2}O_{4})_{3}^{4^{2}}] + SO_{3}^{2^{2}} + \text{ other products ......(6)}$$

 $[\operatorname{Fe}(\operatorname{C}_{2}\operatorname{O}_{4})_{3}^{3^{-}}] + \operatorname{S}_{2}\operatorname{O}_{3}^{-} \xrightarrow{K_{3}} [\operatorname{Fe}(\operatorname{C}_{2}\operatorname{O}_{4})_{3}^{4^{-}}] + \operatorname{SO}_{3}^{2^{-}} + \text{other products .....(7)}$ For the intermediates in equation (5), Rate = k\_{1}[S\_{2}\operatorname{O}\_{3}^{2^{-}}] [H^{+}] - k\_{.1} [S\_{2}\operatorname{O}\_{3}^{2^{-}}] [S\_{2}\operatorname{O}\_{3}^{-}]
Applying the steady state scheme to this, Rate = k\_{1}[S\_{2}\operatorname{O}\_{3}^{2^{-}}] [H^{+}] - k\_{.1} [S\_{2}\operatorname{O}\_{3}^{2^{-}}] [S\_{2}\operatorname{O}\_{3}^{-}] = 0

$$[S_2O_3^{-}] = \frac{k_1[S_2O_3^{-2^-}][H^+]}{k_{-1}[S_2O_3^{-2^-}]} = \frac{k_1[H^+]}{k_{-1}} \qquad (8)$$

From equations (6) and (7) which are the rate determining steps, Rate = $k_2 [Fe(C_2O_4)_3^{3-}] [S_2O_3^{2-}] + k_3[Fe(C_2O_4)_3^{3-}] [S_2O_3^{-}]$  .....(9) Substituting equation (8) into (9) gives:

Rate = 
$$k_2 [Fe(C_2O_4)_3^{3-}] [S_2O_3^{2-}] + k_{-3} [Fe(C_2O_4)_3^{3-}] \cdot \frac{k_1[H^+]}{k_{-1}}$$

Under limiting pseudo-first order conditions,  $k_1 \ge k_1$  so the expression reduces to Rate =  $k_2 [Fe(C_2O_4)_3^{3-}] [S_2O_3^{2-}] + k_1k_{-3} [Fe(C_2O_4)_3^{3-}] [H^+]$ 

 $= (k_2 + k_1 k_3 [H^+]) [Fe(C_2 O_4)_3^{3-}] [S_2 O_3^{2-}] \dots (10)$ 

Equation (10) is analogous to equation (4) with  $k_2$ = a and  $k_1k_3$ = b, hence the proposed mechanism is plausible. In order to assign a pathway for the reaction, the following points were considered:

(a) The Michaelis-Menten plot of  $1/k_1$  versus  $1/[S_2O_3^{2^2}]$  gave an insignificant positive intercept indicating the absence of the formation of intermediates prior to the electron transfer, which is in favour of the outer-sphere pathway.

(b) The absence of gel formation after the addition of a solution of acrylamide to a partially oxidized reaction mixture suggests the absence of free radicals in this reaction, or the equilibrium constant for the formation of such radicals can be assumed to be negligible [18]. This is also in support of the outer-sphere pathway

(c) An enhancement of the reaction rate by added nirite. Anion catalysis/inhibition has been proposed to support outer-sphere mechanism in most redox reactions that have been studied [19, 20, 21].

Based on the above reasoning, the mechanism of this reaction has been rationalized on the basis of the outer-sphere pathway.

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