

Kinetics and Mechanism of the Oxidation of Dithionate ion by  $N,N'$ -ethylenebis- [Salicylideneiminato] iron (III) Complex in aqueous perchloric acid medium.

\*P.O. Ukoha, J.N. Asegbeloyin, C. Alioke and O.T. Ujam

Coordination Chemistry and Inorganic Pharmaceutics Unit

Department of Pure and Industrial Chemistry

University of Nigeria, Nsukka

Enugu State, Nigeria

[Received: 30<sup>th</sup> July 2009; Accepted: 9<sup>th</sup> September 2009]

**Abstract**

The kinetics of the oxidation of dithionate ion,  $S_2O_6^{2-}$ , by  $N,N'$ -ethylenebis [salicylideneiminato] iron (III) complex ion,  $[FeSalen(H_2O)_2]^+$ , has been investigated at 28.5°C over aqueous perchloric acid concentration range of  $0.05 \geq [H^+] \geq 0.001 \text{ mol/dm}^3$ . Reduction of  $[FeSalen(H_2O)_2]^+$  was followed spectrophotometrically at 515nm. Spectrophotometric titration indicated that two moles of the oxidant was consumed for every mole of the reductant that was oxidized. Under pseudo-first order conditions of a large excess of dithionate ion, the rate of reaction increased with increase in concentration of dithionate ion but was invariant with variation in the concentration of the oxidant. The reaction is first order with respect to dithionate ion but zeroth-order with respect to  $[FeSalen(H_2O)_2]^+$  giving the rate as  $-\frac{1}{2} \frac{d[FeSalen]}{dt} = K [S_2O_6^{2-}][H^+]$ . The rate constant has a value of  $1.92 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

**Keywords:** kinetics, mechanism, oxidation, dithionate,  $N,N'$ -ethylenebissalicylideneiminato.

**Introduction**

The chemistry of mononuclear and dinuclear iron (III) complexes has continued to receive a lot of attention for years [1-3]. This is due mainly to the fact that iron plays a key role in physiological processes [4-6]. Redox processes involving iron (III) has been followed with keen interest especially as regards biomimetic processes involving haeme and non-haeme iron (III) complexes [7-10]. In this regard iron (III)-imine complexes have received special attention. In line with this thinking our previous efforts centred on the reduction of  $\mu$ -oxobridged iron (III) complex,  $[(FeHEDTA)_2O]^{2-}$ , with ascorbic acid[11], mercaptoacetic acid[12], mercaptoethylamine and mercaptoethanol[13]. Reactions of the oxobridged dimer with the thiols, mercaptoethanol, mercaptoacetic acid and mercaptoethylamine were found to follow the outer-sphere electron transfer mechanism for the mercaptoethylamine and mercaptoacetic acid and possible proton coupled electron transfer pathway for mercaptoethanol reaction[12,13]. Also the reaction of L-ascorbic acid with the complex dimer was found to have inverse acid dependence and followed outer-sphere mechanism[11].

Dithionate ion has been observed as a byproduct of the oxidation reactions of S(IV) and also in Fe(III)-sulfite ion redox processes[14-15]. The growing interest in the redox dynamics of dithionate ion centers more on the great potentials of Ce(IV)/Ce

(III)/ $S_2O_6^{2-}$ /S(IV) redox systems as an analytical tool[16]. Also the widespread analytical uses of Ce(IV)-S(IV) chemiluminescence phenomenon is narrowing the search light on the reactions of dithionate ion. Recently kinetic data have been published on the interactions of  $S_2O_6^{2-}$  with some oxoanions and metal ions[17]. The results suggest apparent inertness of  $S_2O_6^{2-}$  at low temperatures[17]. We present in this report kinetic and mechanistic studies on the oxidation of dithionate ion by  $N,N'$ -bis[Salicylideneiminato]iron(III) complex. We seek to gain insight into the redox behaviour of this reductant with this hitherto uninvestigated Fe (III) complex. The results we hope will compliment the existing data on the interaction of iron (III) containing enzymes with oxoanions.

**Experimental Section**

Bis(Salicylidene)ethylenediamine (denoted by Salen) was synthesized and characterized according to literature methods[17-18].  $N,N'$ -ethylenebis(Salicylideneiminato) iron(III) complex,  $[Fe(Salen)(H_2O)_2]^+$ , herein after referred to as FeSalen was prepared following the methods of Tsukahara and Yamamoto[19]. The ligand and complex were characterized via UV-visible and infrared spectroscopy. Selected FTIR absorption peaks (nujol,  $\text{cm}^{-1}$ ) for the ligand are: 3424.2(br,  $\nu$ -(OH), phenols); 2996.9 -

\*Correspondence author: piusukoha@yahoo.com



2738.1 (vs.m:  $\nu$ (aromatic ring); 1637.2 (vs,  $\nu$ (C = N); 1530.2 (s,  $\nu$ (C - N); UV-Vis (EtOH)  $\lambda_{\text{max}}$ /nm; 285, 371, 386. MP/°C: 125 - 126, yield: 89%.

Selected FTIR absorption peaks (nujol,  $\bar{\nu}$ /cm<sup>-1</sup>) for the complex are: 3450 (w,  $\nu$ H<sub>2</sub>O); 2921.34 (s,  $\nu$ C - H, aromatic); 1629.89 (s,  $\nu$ C = N); 1451.31 (s,  $\nu$ (C - N); 1136 - 1034.46 (s,  $\nu$ (C - O); 505 (m,  $\nu$ M - O), 425 (m,  $\nu$ M - N). MP/°C: 248 dec. yield: 92% UV-VIS (EtOH)  $\lambda_{\text{max}}$ /nm; = 385, 485, 515, 710sh. Sodium dithionate (BDH, GPR) was of analytical grade and was used as supplied. Reagent grade HClO<sub>4</sub> and NaClO<sub>4</sub> were used to adjust the acidity and ionic strength (0.008mol dm<sup>-3</sup>) of the reaction media. Doubly deionized water, ultra-filtered and freshly redistilled in the presence of alkaline MnO<sub>4</sub> solution in all glass still, was used to prepare all solutions unless otherwise indicated. UV-Vis spectra were recorded as ethanol solutions on UNICO-2102 and on JENWAY 6405 UV/Vis spectrophotometers. FTIR data of the ligand and complex were obtained as nujol on Termo Electron Corporation IR 100 Series. Absorbance of reaction solutions were obtained on Milton Roy Spectronic 21D spectrophotometer.

### Kinetic Measurements

Rate data for the disappearance of iron (III) complex in the oxidation of dithionite ion (S<sub>2</sub>O<sub>6</sub><sup>2-</sup>) was obtained as the decrease in absorbance at 515nm. At this wavelength, neither the reductant nor the products of the reaction have any significant absorption. The reactions were conducted under pseudo-first-order conditions with the reductant in large excess over the complex. Under such conditions, kinetic curves were exponential and rate constants were obtained from logarithmic plots of absorbance differences (ln (A<sub>t</sub>-A<sub>∞</sub>) against time. Pseudo-first-order rate constants were determined from the slopes of above plots based on the relation;

$$\ln (A_t - A_\infty) = k_o t + \ln (A_\infty - A_o)$$

A<sub>∞</sub> = final absorbance, A<sub>t</sub> = absorbance at time t, A<sub>o</sub> = initial absorbance and k<sub>o</sub> = pseudo-first-order rate constant) as reported elsewhere [12-13]. Specific rates for replicate runs are reproducible to within ± 5%.

The presence of free radicals was detected by monitoring gel formation by acrylamide in partially reacted reaction mixture in excess methanol as solvent [12]. The stoichiometries for the reactions were obtained by spectrophotometric titration under the following conditions: Concentration of FeSalen was kept constant at 2.0 x 10<sup>-4</sup> mol dm<sup>-3</sup> at [H<sup>+</sup>] =

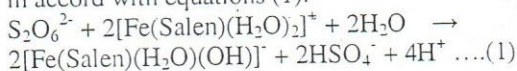
0.001 mol dm<sup>-3</sup>, I = 0.02 mol dm<sup>-3</sup> (NaClO<sub>4</sub>) and concentration of the reductant varied between 2 x 10<sup>-5</sup> to 3 x 10<sup>-3</sup> mol dm<sup>-3</sup> at T = 28.5 ± 0.1°C. Final absorbances (A<sub>∞</sub>) of the separate reaction solutions were plotted against mole ratio, [FeSalen]/[red.] and the stoichiometries derived from the points of inflexion on the curves.

### Results and Discussion

Following Job's continuous variation method [19], the metal-ligand mole ratio for the complex was established to be 1:1. From the electronic and infra red spectral data of the ligand and complex as presented above and in line with other published reports the complex is represented as [FeSalen(H<sub>2</sub>O)<sub>2</sub>]<sup>+</sup> where the metal has an octahedral geometry [15,19].

### Stoichiometry

Spectrophotometric titration showed that one mole of the reductants was consumed for every two moles of the complex that was reduced. These observations are in accord with equations (1).



Presence of SO<sub>4</sub><sup>2-</sup> as one of the products was ascertained by the formation of white precipitate with Ba(ClO<sub>4</sub>)<sub>2</sub> or with BaCl<sub>2</sub> in HCl medium [20]. Reduction of the Fe(III) complex to Fe(II) was confirmed by the reaction of acidified (HCl) solution of the completed reaction mixture with freshly prepared potassium hexacyanoferrate (II) or with freshly prepared potassium hexacyanoferrate (III) as described elsewhere [12,13].

### Kinetics

Pseudo-first-order decays were linear to greater than 85% extent of reaction for the reaction indicating first order dependence. Pseudo-first-order and second order rate constants are displayed in Table 1.

At [S<sub>2</sub>O<sub>6</sub><sup>2-</sup>] varied between 5.0 x 10<sup>-3</sup> to 1.0 x 10<sup>-1</sup> mol dm<sup>-3</sup> with the [H<sup>+</sup>] at 1 x 10<sup>-3</sup> mol dm<sup>-3</sup>, I = 0.002M (NaClO<sub>4</sub>) and T = 28.5 ± 0.2°C, the pseudo-first order rate constants increased linearly with increase in concentration of dithionite as seen in Table 1. Plot of logk<sub>obs</sub> against log[S<sub>2</sub>O<sub>6</sub><sup>2-</sup>] (r = 0.90), gave a slope of 1.10, which agrees to first-order dependence of rate of reaction on [S<sub>2</sub>O<sub>6</sub><sup>2-</sup>], (Fig 1). Variation of [FeSalen] between 1.0 x 10<sup>-4</sup> and 5.0 x 10<sup>-4</sup> mol dm<sup>-3</sup> at constant [S<sub>2</sub>O<sub>6</sub><sup>2-</sup>] where I = 0.02M (NaClO<sub>4</sub>) and T = 28.5°C, pseudo-first-order rate constants did not vary with change in [FeSalen]. The rate constants remained

within  $3.0 \times 10^{-3} \pm 3.0 \times 10^{-4} \text{ s}^{-1}$  (Table 2). This infers zeroth order dependence of the rate of the dithionate reaction on the concentration of the oxidant. Similar observations had been reported for the reactions of dithionate with  $\text{IO}_3^-$ , Cr (VI) and Ce (IV)[17].

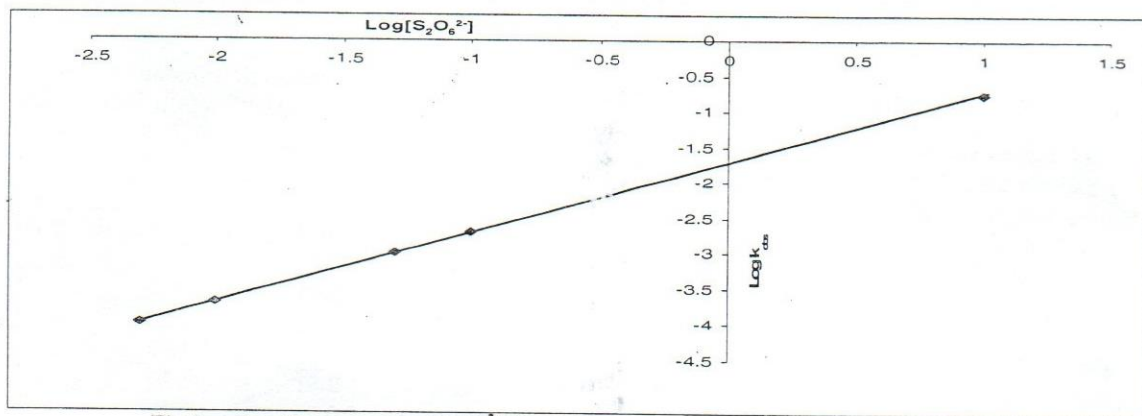
The rate constants,  $k$  were evaluated by dividing  $k_{\text{obs}}$  by concentration of reductant and  $k$  value is

about  $1.92 \times 10^{-2} \pm 1.7 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . Within the context of the above results the rates of  $\text{S}_2\text{O}_6^{2-}$  reaction with FeSalen could be given as equation(2).

$$-\frac{1}{2} \frac{d[\text{FeSalen}]}{dt} = k_o [\text{S}_2\text{O}_6^{2-}] \dots \dots \dots (2)$$

**Table 1: Pseudo-first order and second order rate constants for the reaction of  $\text{S}_2\text{O}_6^{2-}$  and FeSalen at  $[\text{FeSalen}] = 1 \times 10^{-4} \text{ mol dm}^{-3}$   $T = 28.5^\circ\text{C}$**

$10^3[\text{S}_2\text{O}_6^{2-}]/(\text{mol dm}^{-3})$	$10^3[\text{H}^+]/\text{mol dm}^{-3}$	$I/\text{mol dm}^{-3} (\text{NaClO}_4)$	$10^3 k_{\text{obs}}/\text{s}^{-1}$	$10^3 k_2(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$
5.0	1.0	0.002	0.099	1.98
10.0	1.0	0.002	0.192	1.92
50.0	1.0	0.002	0.930	1.86
100.0	1.0	0.002	1.982	1.98
50.0	0.1	0.09	0.422	0.84
50.0	10.0	0.09	6.910	13.82
50.0	30.0	0.09	7.920	15.80
50.0	50.0	0.09	9.120	18.18
1.0	0.10	0.002	23.0	-
1.0	0.10	0.005	3.10	-
1.0	0.10	0.008	no rxn	-
1.0	0.10	0.091	no rxn	-



**Fig 1:  $\text{Log } k_{\text{obs}}$  versus  $\text{log } [\text{S}_2\text{O}_6^{2-}]$  for the oxidation of  $\text{S}_2\text{O}_6^{2-}$  by  $[\text{Fe}(\text{Salen})(\text{H}_2\text{O})_2]^+$**

### Acid Dependence

The effect of  $[\text{H}^+]$  on the reaction kinetics was investigated by varying concentrations of  $\text{HClO}_4$

within the range  $1 \times 10^{-5}$  to  $5.0 \times 10^{-2} \text{ mol dm}^{-3}$  at  $I = 0.09 \text{ mol dm}^{-3} (\text{NaClO}_4)$ ,  $[\text{S}_2\text{O}_6^{2-}] = 0.05 \text{ mol dm}^{-3}$ ,  $[\text{FeSalen}] = 1 \times 10^{-4} \text{ mol dm}^{-3}$  and  $T = 28.5^\circ\text{C}$ .

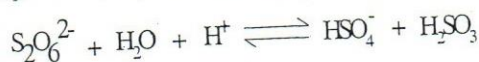


Under these conditions, the rate of the reactions increased with increase in concentration of  $H^+$ .  
**Table 2: Rate constants for the reaction of FeSalen and  $[S_2O_6^{2-}]$  at  $[S_2O_6^{2-}] = 0.01 \text{ mol dm}^{-3}$ ,  $I = 0.02 \text{ mol dm}^{-3}$  ( $NaClO_4$ )  $[H^+] = 0.01 \text{ mol dm}^{-3}$  and  $\lambda = 515\text{nm}$**

$[FeSalen]/\text{mol dm}^{-3}$	$k_{obs}/s^{-1}$
$1 \times 10^{-4}$	0.00310
$2 \times 10^{-4}$	0.00280
$3 \times 10^{-4}$	0.00281
$5 \times 10^{-4}$	0.00285

The enhancement of the rate of reaction with increase in  $[H^+]$  is interpreted to mean a preproportionation step being involved in the reaction. Under this condition, dithionate reaction with FeSalen showed increase in rate with increase in

concentration of  $[H^+]$ . This acid catalysis has been interpreted to be arising from a pre-equilibrium step before the electron transfer reaction. The reaction results in the formation of sulphurous acid (equation 3) which is the main reducing agent:



$$\text{Rate} = k_H[S_2O_6^{2-}][H^+] \quad \text{..... (4)}$$

Acid dependent rate constants are shown in Table 1 and the acid dependent paths of the reaction is given as  $k_H = a + b[H^+]$ . From the least square fits ( $r = 0.89$ ), for plot of  $k_2$  against  $[H^+]$  (Fig. 2) the value of  $a = 0.128 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  with  $b = 1.0 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ .

### Effect of Ionic Strength

Ionic strengths of the reaction media were varied from 0.002 to 0.091  $\text{mol dm}^{-3}$  using various portions of  $NaClO_4$  at  $[FeSalen] = 1 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[reductant] = 0.001 \text{ mol dm}^{-3}$ ,  $T = 28.5^\circ\text{C}$  and  $\lambda = 515\text{nm}$ . Results as shown in Table 1 indicate

that the rate of reaction decreased with increase in ionic strength (Table 1) and at  $I = 0.09$  no significant reaction took place for more than 10 hours. This negative primary salt effect is not unconnected with the fact that the rate determining step for this reaction involves interaction of  $S_2O_6^{2-}$  and  $H^+$  as indicated earlier. This purely is a medium effect.

### Effect of Dielectric Constant (D)

At other parameters kept constant dielectric constant of the reaction media was varied by adding varying portions of propan-2-one- $H_2O$  mixture. Results in Table 3 show increase in rate of reaction as dielectric constant decreased. Plot of  $\ln k$  versus  $1/D$  gave a positive slope, and in accord with the relation, According to the equation

$$\ln k = \ln k_0 - \frac{Z_A Z_B e^2}{DKTr_{\pm}}$$

It is indicative of a reaction between redox partners of opposite sign. The effect of  $D$  on the rate of reaction suggests that interaction between  $S_2O_6^{2-}$  and  $H^+$  is the rate determining step of the reaction[18].

### Effect of Added Anions

Catalytic effect of added anions was investigated by adding varying concentrations of chloride and ethanoate anions in the range of 0.001 to 0.005  $\text{mol dm}^{-3}$  separately to the reaction media with other (3) parameters remaining invariant.

**Table 3: Effect of dielectric constant  $D$  – on the rate of reaction of  $S_2O_6^{2-} = 0.010 \text{ mol/dm}^3$ ,  $[H^+] = 0.10 \text{ mol/dm}^3$ ,  $I = 0.02 \text{ mol/dm}^3$ ,  $[FeSalen] = 1 \times 10^{-4} \text{ mol/dm}^3$  and  $T = 28.5^\circ\text{C}$ .**

Dielectric constant	$10^3 k_{obs} / s^{-1}$	$10^2 k_2 / \text{dm}^3 \text{ mol}^{-1} \text{ s}$
68.10	7.95	19.5
72.24	2.76	27.6
77.15	1.32	13.2
80.06	0.81	8.06
83.12	0.75	7.50

The results in Table 4 show a decrease in rate with increase in concentration of the anions. This is suggestive of absence of inner-sphere reaction path for the reaction[13]. It also indicates likely operation of outer-sphere reaction path for the

reaction. Michaelis-Menten-type plot of  $1/k_{obs}$  versus  $1/[S_2O_6^{2-}]$  for the reaction was linear with no significant intercept(-0.01), (Fig 3). This is in accord with reactions occurring by the outer-sphere path.

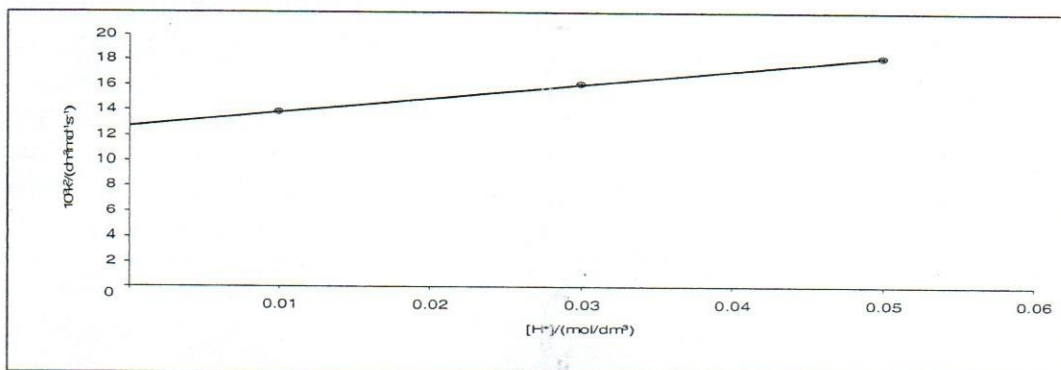


Fig 2: Dependence of  $k_2$  on  $[H^+]$  for the oxidation of  $S_2O_6^{2-}$  by  $[Fe(Salen)(H_2O)_2]^+$

Table 4: Effect of anions on the rate of reaction at  $S_2O_6^{2-} = 0.10 \text{ mol / dm}^3$ ,  $[H^+] = 0.10 \text{ mol / dm}^3$ ,  $I = 0.008 \text{ mol / dm}^3$  ( $NaClO_4$ ),  $(FeSalen) = 1 \times 10^{-4} \text{ mol / dm}^3$ .  $T = 28.5^\circ C$

Conc. of anion (mol /dm <sup>3</sup> )	10 <sup>3</sup> k <sub>obs</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> )	
	Cl <sup>-</sup>	CH <sub>3</sub> COO <sup>-</sup>	Cl <sup>-</sup>	CH <sub>3</sub> COO <sup>-</sup>
0.001	0.80	0.71	0.80	0.71
0.003	0.70	0.60	0.70	0.60
0.005	0.65	0.52	0.65	0.52

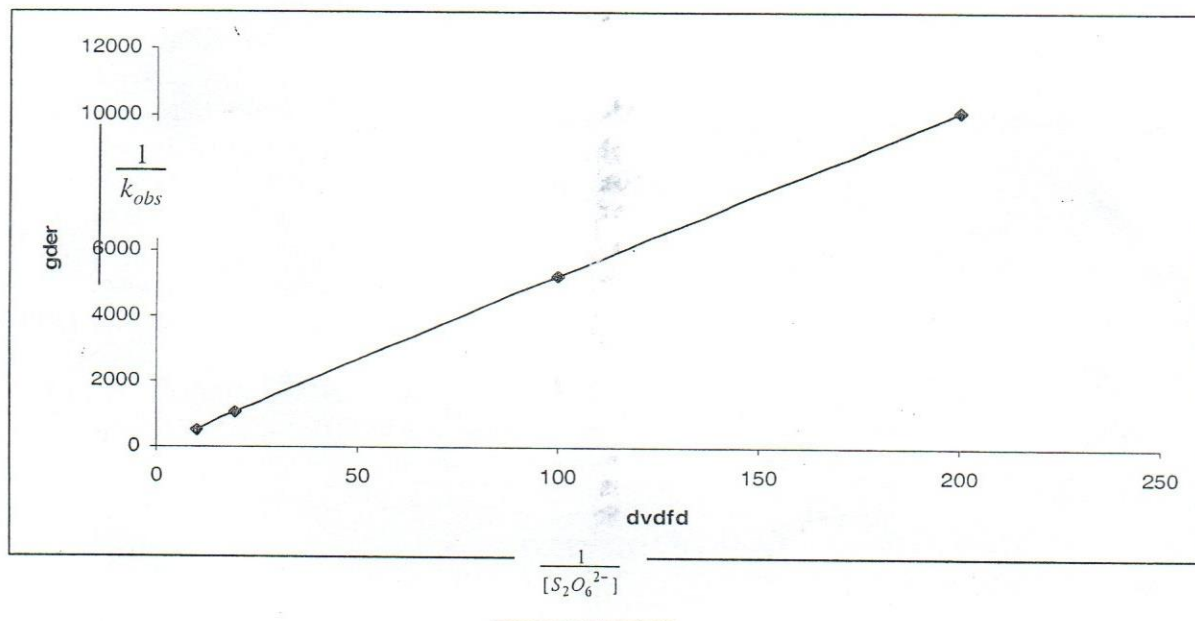


Fig 3: Michaelis-Menten type plot



## Temperature Dependence

It was observed that at low temperatures oxidation of dithionate was extremely slow. We decided to investigate the effect of temperature on the oxidation of dithionate by FeSalen. The temperature of the reaction was varied from 28.5°C to 70°C while other parameters were kept constant. From the results in Table 5 it is evident that the rate of reaction increased with increase

in temperature. From the plots of  $\ln k_2$  against  $1/T$  and  $\ln\left(\frac{k_2}{T}\right)$  against  $1/T$  activation parameters

$\Delta H^\ddagger$ ,  $\Delta S^\ddagger$  and  $E_a^\ddagger$  were determined (Table 6). The negative value of  $\Delta S^\ddagger$  is probably indicative of an associatively activated process[19].

## Reaction Mechanism

In consideration of the stiochiometries, acid-dependence, effect of ionic strength, effect of dielectric constant, catalysis, the Michaelis-Menten-type plot and the fact that the  $\lambda_{\max}$  of the reaction did

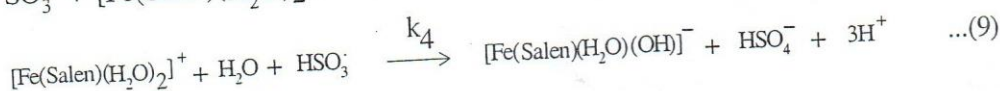
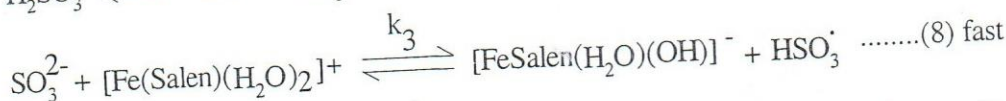
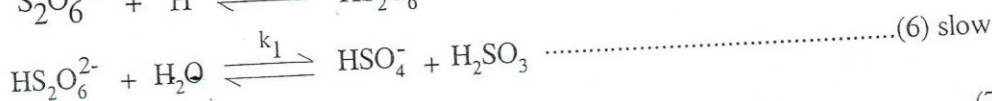
**Table 5: Temperature dependent rate constants and activation parameters for the  $S_2O_6^{2-}/FeSalen$  reaction**

Temp/K	303	308	333	343
$k_2/(\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})$	0.144	0.152	0.160	0.171

not change significantly on scanning the reaction mixtures a few minutes into the reaction, the following mechanistic scheme has been proposed for the reaction

**Table 6: The activation parameters for the  $S_2O_6^{2-}/FeSalen$  reaction**

$E_a^\ddagger / \text{kJ/mol}^{-1}$	$\Delta H^\ddagger / (\text{kJ/mol}^{-1})$	$\Delta S^\ddagger / (\text{Jmol}^{-1} \text{K}^{-1})$
2.77	3.08	-205.01



$$\text{Rate} = \frac{-d[S_2O_6^{2-}]}{dt} = K[S_2O_6^{2-}][H^+] \dots\dots\dots(10)$$

$$\text{Rate} = K[S_2O_6^{2-}][H^+] + k_1[HS_2O_6][H_2O] \dots\dots\dots(11)$$

Following steady state approximation,

$$[HS_2O_6] = K[S_2O_6^{2-}][H^+] - k_1[HS_2O_6][H_2O] = 0 \dots\dots\dots(12)$$

$$[HS_2O_6] = \frac{K[S_2O_6^{2-}][H^+]}{k_1[H_2O]} \dots\dots\dots(13)$$

$$\text{Rate} = K[S_2O_6^{2-}][H^+] + \frac{kK[S_2O_6^{2-}][H^+][H_2O]}{k_1[H_2O]} \dots\dots\dots(14)$$

$$2K[S_2O_6^{2-}][H^+] \dots\dots\dots(15)$$

$$\frac{-d[S_2O_6^{2-}]}{dt} = 2K[S_2O_6^{2-}][H^+] \dots \dots \dots (16)$$

K is likely to have a very small value since protonation of dithionate was not observed to operate significantly under the acid conditions of this reaction at low temperatures.  $H_2SO_3$ , which is the product of the hydrolysis, is more reactive than  $S_2O_6^{2-}$  or  $HS_2O_6^-$ . It undergoes reaction readily with the oxidant. Therefore the rate determining step for the reaction is the combined steps of (5) and (6). The acid mediated disproportionation of the dithionate is the key step in its oxidation [17].

### Acknowledgment

The authors wish to thank the staff of Science Laboratory Technology Department, Instrument Unit, Kaduna State Polytechnic, Zaria, Nigeria, for running the spectra of the ligand and complex.

### References

1. T.R. Weaver, T.J. Meyer, A.S.Adeyemi, G.M. Brown, R.P. Ecberg, W.E. Hatfield, E.C.Johnson, R.W. Murray, and D. Unterek, (1975), Chemically significant interactions between ions in oxobridged complexes of ruthenium (III) *J. Am. Chem. Soc.*, 97, 3039.
2. K.S. Murray (1974), Binuclear oxo-bridge iron (III) complexes *Coord. Chem Rev.*, vol 12, Issue 1, pp1- 35.
3. O.B. Fernandez, I.M. Lorkovic, and C.P. Ford (2004): Mechanisms of ferriheme reduction by nitric oxide : nitrite and general base catalysis. *Inorg. Chem.*, 43, 5393.
4. S. Herold (2004): The outer-sphere oxidation of nitrosyliron (II) hemeghobin by peroxynitrite leads to the release of nitrogen monoxide *Inorg. Chem.*, 43, 3783.
5. I.A. Cohen, (1969): The dimeric nature of hemin hydroxides . *J. Am. Chem. Soc.*, 91, 1980.
6. W.M. Reiff, G.J. Long and W.A.Baker (1968): Nature of the spin states in some binuclear iron (III) complexes. *J. Am. Chem. Soc.*, 90, 6347.
7. A. Brausam and R. Van Eldik (2004): Further mechanistic information on the reaction between Fe(III) (EDTA) and hydrogen peroxide: observation of a second step and importance of pH . *Inorg. Chem.*, 43, 5351.
8. Z. Smelkal, F. Biezina, Z. Sindelar and R. Klicka (1996): Binuclear iron (III) – iron (III) complexes with teradentate Schiff base N,N'- bis(salicylidene) ethylenediamine and dicarboxylic acids or dithiooxamide as bridging ligands. *Transition Met. Chem.*, 21, 49.
9. A.R. Henderson, (1995): Inorganic Reaction Mechanisms: the Bioinorganic – Organometallic Interface. *J. Chem. Soc. Dalton Trans.*, 503.
10. R.R. Tirureedhula, V. Parvataneni, and S.A.D. Lanka (1995): Mechanism of oxidation of DL- methionine by iron(III)-1,2-bipyridyl in perchloric acid – A kinetic study. *Transition Met. Chem.*, 20, 170
11. P.O. Ukoha and J.F Iyun (2002): Oxidation of L-ascorbic acid by  $enH_2[(FeHEDTA)_2O].6H_2O$  in aqueous Medca. *J. Chem. Soc. Nigeria*, 27, 119.
12. P.O. Ukoha and J.F Iyun. (2005):Mechanism of the Oxidation of 2-Mercaptoacetic acid by  $enH_2[(FeHEDTA)_2O].6H_2O$  in aqueous acid Medium. *Chem.Class Journal*, 2 . 119.
13. P.O. Ukoha and J.F Iyun (2001): Kinetics of reduction of an Iron(III) Complex Ion by  $\beta$ -Mercaptoethanol and  $\beta$ -



- Mercaptoethylamine in Perchloric acid Medium *J. Chem. Soc. Nigeria*, 26, 163.
14. H. Basset and A.J. Henry (1935): *J. Chem. Soc.*, 914.
  15. C. Brandt and R. van Eldik, (1995): Transition metal-catalysed oxidation of sulphur (IV) oxides. Atmospheric-relevant processes and mechanism. *Chem. Rev.*, 95(1), 119.
  16. K. Takeuchi and T. Ibusuki (1995): Determination of traces of hydrogensulfite by Chemiluminescence with cerium (IV) sulfate as the reagent. *Anal. Chem. Acta.*, 174, 359.
  17. G. Lente and I. Fabian (2004): Effect of dissolved oxygen on the oxidation of dithionate ion. Extremely unusual kinetic traces. *Inorg. Chem.*, 43, (13), 4019.
  18. N. Sonoyama, O. Kasarawa, and Y. Kaizu (1995): *J. Chem. Soc. Faraday. Trans.*, 91, 437.