

---

---

## Kinetic Approach to the Mechanism of the Redox Reaction of Ethylenediaminetetraacetatoferrate(III) Complex and Thioglycolic Acid in Bicarbonate Buffer Medium

By

**\*I. U. Nkole, \*\*A. D. Onu, \*C. R. Osunkwo, and \*O. S. Idris**

\*Department of Chemistry, Ahmadu Bello University, Zaria, Nigeria

\*\*Department of Chemistry, Federal University of Education, Zaria, Nigeria

\*Email: [nkoleikechukwu@gmail.com](mailto:nkoleikechukwu@gmail.com)

---

---

### ABSTRACT

*The kinetic approach of the reduction of ethylenediaminetetraacetatoferrate(III) complex (hereafter  $[Fe(III)EDTA]^-$ ) by thioglycolic acid (hereafter TSH) in bicarbonate buffer medium have been studied under the following conditions:  $T = 28 \pm 1^\circ C$ , Ionic Strength,  $I = 0.2 \text{ mol dm}^{-3}$  ( $KNO_3$ ),  $pH = 7.5$  and  $\lambda_{max} = 470 \text{ nm}$ . The ratio from the stoichiometric study conforms to the equation  $2[Fe(III)EDTA]^- + 2TSH \rightarrow 2[Fe(II)EDTA]^{2-} + TSST + 2H^+$ . The reaction rate varied linearly to the first power of the concentrations of the oxidant and reductant and displayed dependence on pH of the reaction medium. The reaction was sensitive to the change in ionic strength of the medium suggesting an interaction of charged species at the activated complex. The Michaelis-Menten plot of  $1/k_{obs}$  versus  $1/[TSH]$  was linear with zero intercepts which suggested an absence of intermediate complex. Pieces of evidences in this paper showed that the reaction occurred via the outer-sphere mechanism.*

**Keywords:** Ethylenediaminetetraacetatoferrate(III) complex, Kinetics, Mechanism, Reduction, Thioglycolic acid, pH

### INTRODUCTION

Electron transfer reactions are one of the frontier research areas in the inorganic chemistry of iron complexes [1] [2], and the use of thiols as reductants on iron complexes are gaining more interest in biological systems. Thioglycolic acid is involved in some life's vital processes and its varied utilities include metals recovery [3], leather processing [4], wheel cleaning solutions [5], hair formulation treatment [6], and heavy metal passivator [7]. The kinetics and mechanisms of its reaction with transition metal complexes, which revealed the formation of dithiodiglycolic acid and the role of specific free radical species [8], have received considerable attention [9] [10]. The reactions have been studied under acidic [11] [12] [13] and aqueous [14] [15] media and the mechanism of reactions established in addition to other kinetic parameters are evaluated. Ethylenediaminetetraacetatoferrate(III) complex has application in gas desulfurization

processes (SulFerox process) based on the reports [16] [17] [18], and its structure and composition have been characterized [19] [20].

This study is a further effort in the general interest of the electron transfer reaction of this useful substrate and the complex. It is hoped that the data from this study will shed more light on the mechanism of reaction of the oxidant in terms of outer- and inner-sphere mechanism.

## EXPERIMENTAL

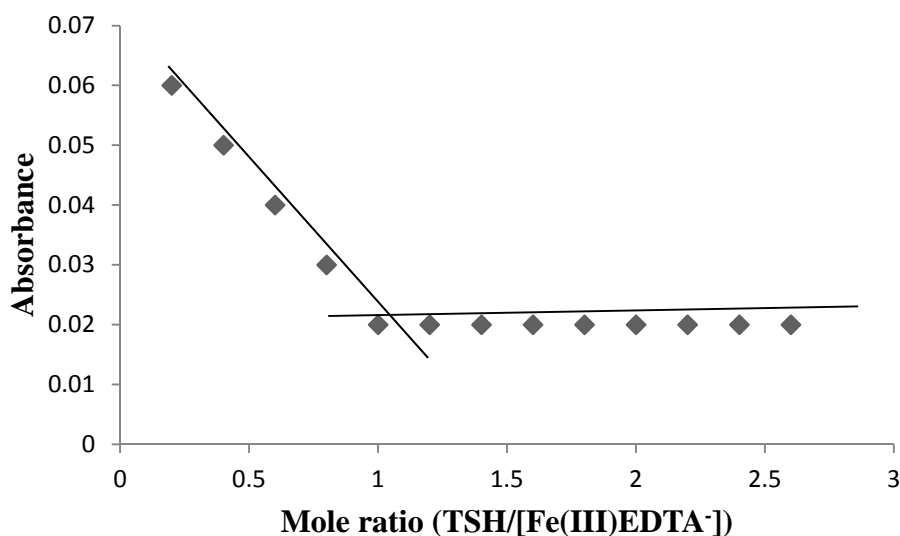
The  $[\text{Fe(III)EDTA}]^-$  complex was prepared according to the method of Xiao-juan [21] and was characterized using UV/Visible spectrophotometer (Cary 300 series Agilent Technologies, China). The UV/Visible spectrum of  $[\text{Fe(III)EDTA}]^-$  was scanned between ranges of 300 – 800 nm and gave  $\lambda_{\text{max}}$  of 308 and 470 nm.

Standard solution ( $0.05 \text{ mol dm}^{-3}$ , 1.21 g) of ferric nitrate (Sigma-Aldrich, USA) and  $0.05 \text{ mol dm}^{-3}$  (1.68 g) of EDTA (Sigma-Aldrich, USA) was prepared and added up to a ratio of chelant /  $\text{Fe}^{3+} = 1:1$ .  $\text{KNO}_3$  (BDH, London) was used to maintain ionic strength. The complex stock solution had a concentration of about  $0.05 \text{ mol dm}^{-3}$ . Prior to use, the solution's pH is adjusted to 7.5 with bicarbonate buffer solution.

A  $1.5 \text{ mol dm}^{-3}$  stock solution of thioglycolic acid (molecular weight =  $92.112 \text{ g mol}^{-1}$ , percentage purity = 98 %, density =  $1.325 \text{ g cm}^{-3}$ ) was prepared by diluting 5.32 ml of thioglycolic acid (Sigma-Aldrich, USA) in a  $50 \text{ cm}^3$  volumetric flask and topped up to the mark.  $0.2 \text{ mol dm}^{-3}$  stock solutions of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and sodium bicarbonate ( $\text{NaHCO}_3$ ) were prepared by dissolving 2.12 g and 1.68 g with distilled water in  $100 \text{ cm}^3$  volumetric flask and topped up to the mark respectively. A  $0.1 \text{ mol dm}^{-3}$  stock solution of potassium permanganate (molecular weight =  $157.94 \text{ g mol}^{-1}$ ) was prepared by dissolving 0.39 g of potassium permanganate (Merck, USA) in a  $25 \text{ cm}^3$  volumetric flask and topped up to the mark.

### Stoichiometric Studies

The stoichiometry of the reaction was determined by spectrophotometric titration using the mole ratio method [22] [23]. The concentration of  $[\text{Fe(III)EDTA}]^-$  was kept constant at  $0.001 \text{ mol dm}^{-3}$  while that of [TSH] was varied at least 10 folds above. The reactions were allowed to go to completion at constant pH and ionic strength ( $0.2 \text{ mol dm}^{-3}$ ). The absorbances of the solutions were taken at 470 nm. The mole ratio was determined from the plot of absorbance versus mole ratio [TSH]:  $[\text{Fe(III)EDTA}]^-$  (Figure 1).



**Figure 1:** Stoichiometric Plot of the reaction of  $[\text{Fe(III)EDTA}]^-$  and TSH at  $[\text{Fe(III)EDTA}]^- = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $I = 0.2 \text{ mol dm}^{-3}$  ( $\text{KNO}_3$ ),  $[\text{TSH}] = (2.0 - 2.6) \times 10^{-3} \text{ mol dm}^{-3}$ ,  $\text{pH} = 7.5$ ,  $\lambda_{\text{max}} = 470 \text{ nm}$ , and  $T = 28 \pm 1^\circ\text{C}$

### ***Kinetic Measurements***

The rates of the reactions were studied under pseudo-first order condition by monitoring the change in absorbance of  $[\text{Fe(III)EDTA}]^-$  at 470 nm on Sherwood Colorimeter 254 at constant pH, ionic strength, and temperature. The plots of  $\log(A_t - A_\infty)$  versus time were obtained (Figure 2). From the slope of the plots the pseudo-first order rate constants,  $k_{\text{obs}}$ , were determined. The second order rate constant ( $k_2$ ) was determined as  $k_{\text{obs}}/[\text{Reductant}]$ . The results are presented in Table 1. The effects of pH, the ionic strength ( $I$ ) and the dielectric constant ( $D$ ) on the rate was investigated with 6 – 10, 0.3 – 1.0  $\text{mol dm}^{-3}$  ( $\text{KNO}_3$ ) and 70.1 – 80.1 respectively while all other conditions are kept constant.

### ***The Effect of Added Ions on the Reaction Rate***

The effect of added ions  $X$  ( $X = \text{SO}_4^{2-}$  and  $\text{Na}^+$ ) on the reactions was investigated for  $[X] = (1.0 - 21.0) \times 10^{-3} \text{ mol dm}^{-3}$ . The concentration of all other reactants was kept constant at  $I = 0.2 \text{ mol dm}^{-3}$  ( $\text{KNO}_3$ ).

### ***Free Radical Test***

The generation and participation of free radicals in the course of the reaction were investigated by adding 3  $\text{cm}^3$  of 0.28  $\text{mol dm}^{-3}$  acrylamide solution to a partially reduced

reaction mixture followed by addition of excess methanol. A control experiment was carried out by adding acrylamide solution to separate solution of  $[\text{Fe(III)EDTA}]^-$  and TSH.

### Temperature Dependence

The effect of temperature on the reaction rate was investigated to ascertain the thermodynamic parameters of the reaction medium by using Eyring's plot of  $\ln(k_2/T)$  versus  $1/T$ , wherein enthalpy of activation  $\Delta H^\ddagger$  is obtained from the slope, entropy of activation  $\Delta S^\ddagger$  is from the intercept and Gibbs free energy  $\Delta G^\ddagger$  is from the equation;

$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$ . The Eyring's equation is given as;

$$\ln\left(\frac{k_2}{T}\right) = \ln\left(\frac{K_b}{h}\right) + \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT} \quad (1)$$

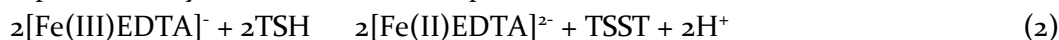
### Product Analysis

The UV/Visible spectrum of the reaction product was scanned between wavelength ranges of 300 - 800 nm gave a  $\lambda_{\text{max}}$  of 520 nm, which is characteristic of the Fe(II) product [24] [25], and the appearance of a brown solution that turns into soil brown precipitate on standing after some seconds reveals the presence of Fe(II) product [26]. Investigations of the formation of disulfide at the completion of the reaction were done by extracting the mixture six times with diethyl ether and the combined ether extracts were washed and dried with anhydrous  $\text{Na}_2\text{SO}_4$  and left overnight to dry. The appearance of crystals suggested that the products of reaction included disulfide [27] [28].

## RESULTS AND DISCUSSION

### Stoichiometry

The spectrophotometric titrations showed oxidant - reductant ratio of 1:1 represented by the stoichiometric equation;



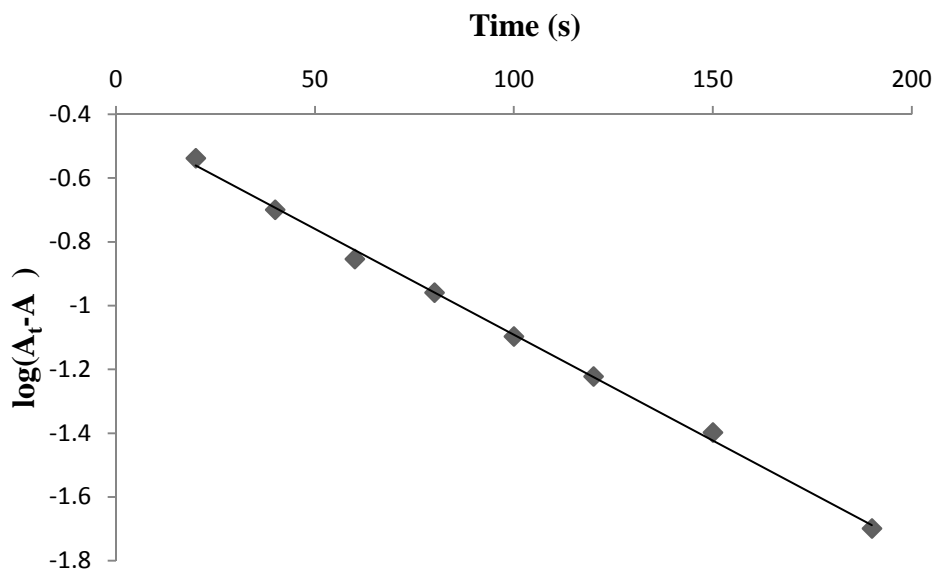
Similar stoichiometry has been documented for the reaction involving thioglycolic acid [9] [10] [29].

### Kinetic Study

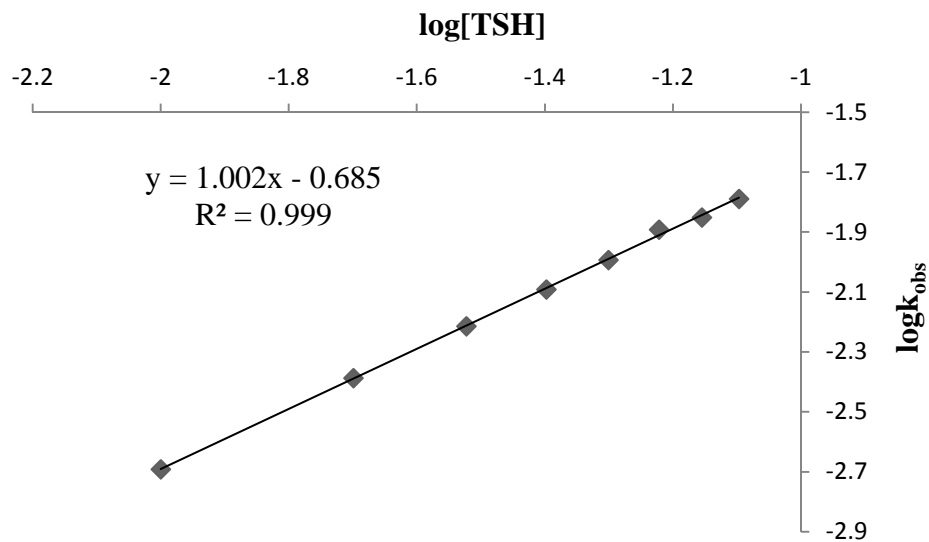
The pseudo-first order plot was linear for about 95 % of the reaction time (Figure 2) and the slope of 1.002 was obtained from the logarithmic plot of  $k_{\text{obs}}$  versus [TSH]. The results show the reaction is first-order in  $[\text{Fe(III)EDTA}]^-$  and [TSH] respectively and second order overall. Similar order has been reported for TSH reactions by the earlier researchers [9] [30] [31].

**Table 1:** Pseudo-first and Second Order Rate Constants for the Reaction of  $[\text{Fe(III)EDTA}]^-$  and TSH at  $[\text{Fe(III)EDTA}^-] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $I = 0.2 \text{ mol dm}^{-3}$  ( $\text{KNO}_3$ ),  $\text{pH} = 7.5$ ,  $T = 28 \pm 1^\circ\text{C}$  and  $\lambda_{\text{max}} = 470 \text{ nm}$

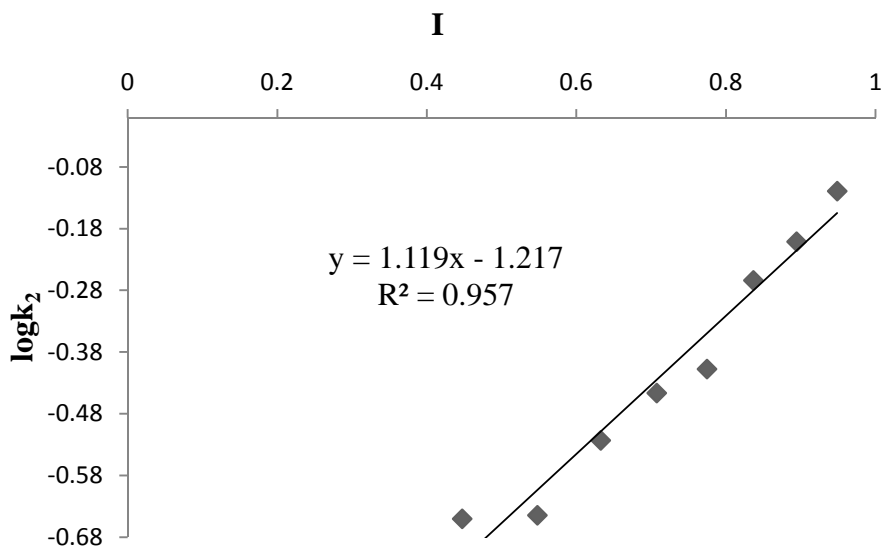
$10^2[\text{TSH}], \text{ mol dm}^{-3}$	pH	$I, \text{ mol dm}^{-3}$	$10^3k_{\text{obs}}, \text{ s}^{-1}$	$10^4k_2, \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
1.0	7.5	0.2	2.03	2.03
2.0	7.5	0.2	4.09	2.05
3.0	7.5	0.2	6.09	2.03
4.0	7.5	0.2	8.09	2.02
5.0	7.5	0.2	10.2	2.03
6.0	7.5	0.2	12.8	2.14
7.0	7.5	0.2	14.1	2.01
8.0	7.5	0.2	16.2	2.03
6.0	6.0	0.2	3.27	0.55
6.0	6.5	0.2	7.42	1.24
6.0	7.0	0.2	4.81	0.80
6.0	7.5	0.2	12.8	2.14
6.0	8.0	0.2	11.4	1.89
6.0	8.5	0.2	6.40	1.07
6.0	9.0	0.2	6.61	1.10
6.0	9.5	0.2	2.07	0.35
6.0	7.5	0.2	12.8	2.14
6.0	7.5	0.3	13.6	2.27
6.0	7.5	0.4	17.9	2.99
6.0	7.5	0.5	21.5	3.58
6.0	7.5	0.6	23.5	3.92
6.0	7.5	0.7	32.7	5.45
6.0	7.5	0.8	37.8	6.29
6.0	7.5	0.9	45.6	7.59



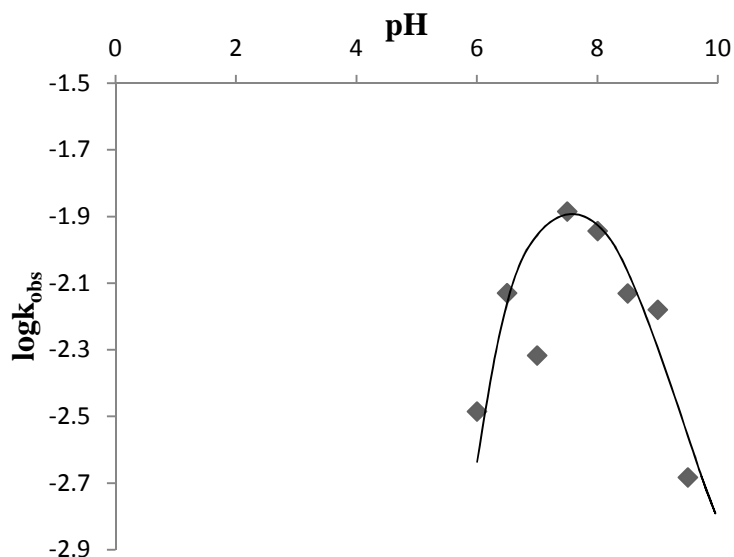
**Figure 2:** Typical Pseudo-first Order Plot for the reaction of [Fe(III)EDTA]<sup>-</sup> and TSH at [Fe(III)EDTA]<sup>-</sup> = 1.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>, [TSH] = 6.0 × 10<sup>-2</sup> mol dm<sup>-3</sup>, I = 0.2 mol dm<sup>-3</sup> (KNO<sub>3</sub>), pH = 7.5, T = 28 ± 1°C, and λ<sub>max</sub> = 470 nm



**Figure 3:** Plot of log k<sub>obs</sub> versus log [TSH] for the reaction of [Fe(III)EDTA]<sup>-</sup> and TSH at [Fe(III)EDTA]<sup>-</sup> = 1.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>, [TSH] = (1.0 - 8.0) × 10<sup>-2</sup> mol dm<sup>-3</sup>, I = 0.2 mol dm<sup>-3</sup> (KNO<sub>3</sub>), pH = 7.5, T = 28 ± 1°C, and λ<sub>max</sub> = 470 nm



**Figure 4:** Plot  $\log k_2$  versus  $\sqrt{I}$  for the reaction of  $[\text{Fe(III)EDTA}]^-$  and TSH at  $[\text{Fe(III)EDTA}]^- = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{TSH}] = 6.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = (0.2 - 1.0) \text{ mol dm}^{-3}$ ,  $\text{pH} = 7.5$ ,  $T = 28 \pm 1^\circ\text{C}$ , and  $\lambda_{\text{max}} = 470 \text{ nm}$



**Figure 5:** Plot of  $\log k_{\text{obs}}$  versus  $\text{pH}$  for the reaction of  $[\text{Fe(III)EDTA}]^-$  and TSH at  $[\text{Fe(III)EDTA}]^- = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{TSH}] = 6.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.2 \text{ mol dm}^{-3} (\text{KNO}_3)$ ,  $T = 28 \pm 1^\circ\text{C}$ , and  $\lambda_{\text{max}} = 470 \text{ nm}$

### ***Effect of change in ionic strength and dielectric constant of reaction medium on reaction rate***

Variation of the ionic strength of the reaction medium from 0.3 – 1.0 mol dm<sup>-3</sup> (KNO<sub>3</sub>) led to increase in the rate of the reaction (Table 1). This suggests the interaction of like-charged species prior to electron transfer. This is reinforced by the effect of change in the dielectric constant, D, from 70.1 - 80.1 on the rate of the reaction. It was observed that the reaction rate decreased as D decreases.

### ***Effect of pH on reaction rate***

Results obtained from the pH-dependent study showed that change in pH (6.0 – 10.0) affected the reaction rate (Table 1). There is a marked reactivity increase in pH from 6.0 to 7.5 and a decrease from 7.5 to 10.0. Indicative of deprotonation of thioglycolic acid at pH 7.5 prior to the formation of the activated complex [9] [32] [33]. A plot of log k<sub>obs</sub> versus pH also reveals this optimum reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup> (Figure 5).

### ***Effect of added ions on reaction rate***

The change in concentrations of the added anion (SO<sub>4</sub><sup>2-</sup>) decreased the rate of the reaction and the cation (Na<sup>+</sup>) increased the reaction rate (Table 2). The catalysis by these ions suggests that the reaction occurs by outer-sphere mechanism, as the reactant species at the activated complex are like-charged and the solvent molecules near this complex are subject to strong electrostatic forces.

### ***Detection of free radicals***

The free radicals formation were positive in the reduction of [Fe(III)EDTA]<sup>-</sup> by TSH. This agrees with a work reported earlier [8].

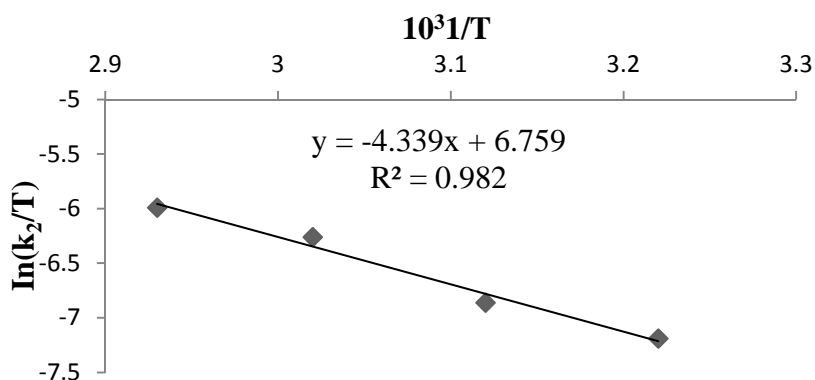
**Table 2:** Effect of Added Anion and Cation to the reaction Medium on the Rate Constants for the Reduction of [Fe(III)EDTA]<sup>-</sup> by TSH at [Fe(III)EDTA<sup>-</sup>] = 1.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>, [TSH] = 6.0 × 10<sup>-2</sup> mol dm<sup>-3</sup>, I = 0.2 mol dm<sup>-3</sup> (KNO<sub>3</sub>), pH = 7.5, T = 28 ± 1°C, and λ<sub>max</sub> = 470 nm

ION	10 <sup>3</sup> [Ion]	10 <sup>3</sup> k <sub>obs</sub>	10 <sup>2</sup> k <sub>2</sub>	ION	10 <sup>3</sup> [Ion]	10 <sup>2</sup> k <sub>obs</sub>	10 <sup>1</sup> k <sub>2</sub>
	mol dm <sup>-3</sup>	s <sup>-1</sup>	dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>		mol dm <sup>-3</sup>	s <sup>-1</sup>	dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>
SO <sub>4</sub> <sup>2-</sup>	0.00	12.8	21.4	Na <sup>+</sup>	0.00	1.28	2.14
	1.0	8.76	14.60		1.0	5.59	9.33
	3.0	7.21	12.18		3.0	8.04	13.39
	9.0	7.13	11.89		9.0	8.52	14.20
	12.0	6.96	11.61		12.0	9.81	16.40
	15.0	6.82	11.37		15.0	9.88	16.47
	18.0	5.26	8.76		18.0	11.8	19.61
21.0	3.98	6.64	21.0	12.9	21.46		



### Effect of temperature on reaction rate

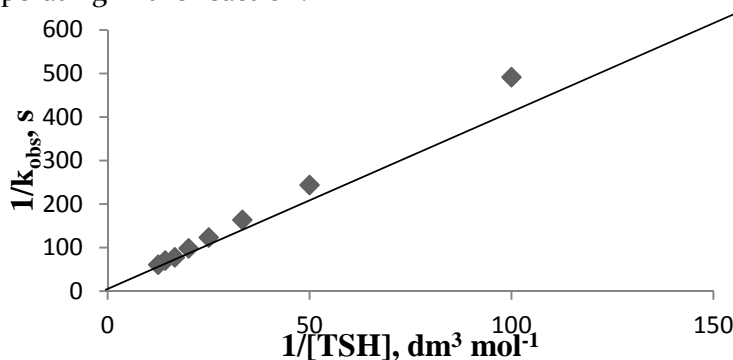
The plot of  $\ln(k_2/T)$  versus  $1/T$  based on Eyring-Polanyi equation was linear with an intercept at 6.759 and the slope is -4339 (Figure 6). The activation parameters ( $\Delta S^\ddagger = -141.35 \text{ Jmol}^{-1}\text{K}^{-1}$  &  $\Delta H^\ddagger = +36.07 \text{ kJmol}^{-1}$ ) revealed that the solvent molecules are reorganized within the activated complex resulting to decrease in entropy of the system. However, activation energy is needed to overcome electrostatic repulsion between the ions of like charge and to shorten bonds so that they are equivalent in the transition state and to alter the solvent sphere around the complex. This is supported by previous reports [34] [35].



**Figure 6:** Plot of  $\ln(k_2/T)$  versus  $1/T$  for the reaction of  $[\text{Fe(III)EDTA}]^-$  and TSH at  $[\text{Fe(III)EDTA}^-] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{TSH}] = 6.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.2 \text{ mol dm}^{-3}$  ( $\text{KNO}_3$ ),  $\text{pH} = 7.5$  and  $\lambda_{\text{max}} = 470 \text{ nm}$

### Michaelis-Menten plot

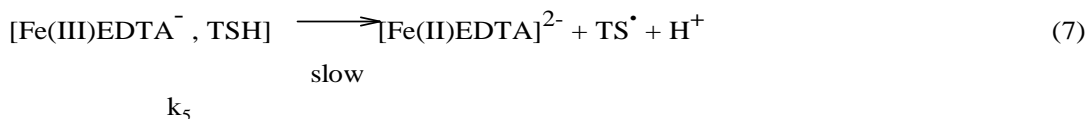
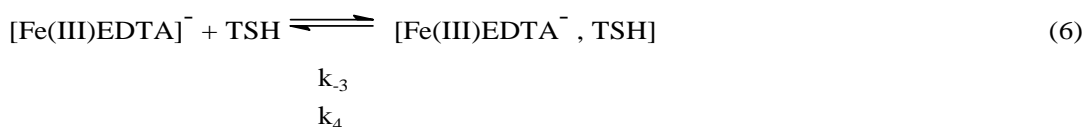
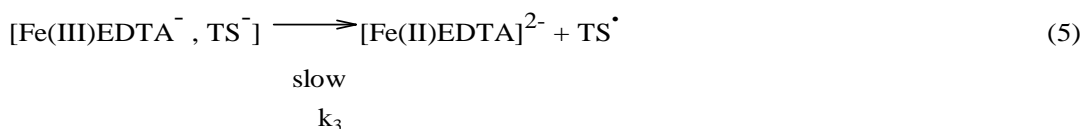
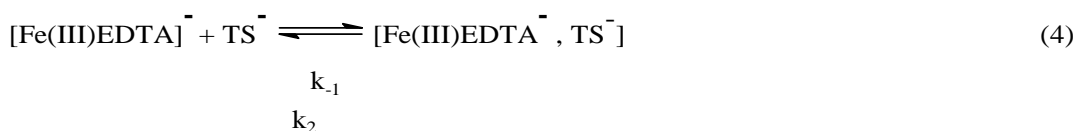
Michaelis-Menten plot of  $1/k_{\text{obs}}$  versus  $1/[\text{TSH}]$  was linear without any appreciable intercept (Figure 7). This confirms the absence of stable intermediate, but probably the formation of ion-pair [36]. The above facts reinforce the suggestion that outer-sphere mechanism is operating in the reaction.



**Figure 7:** Michaelis-Menten Plot of  $1/k_{\text{obs}}$  versus  $1/[\text{TSH}]$  for the Reduction of  $[\text{Fe(III)EDTA}]^-$  by TSH

The choice of the mechanism is supported by;

- I. The Michaelis-Menten plot which has no intercept
- II. Catalysis of reaction by added ions
- III. The first order in the rate law obtained for each reactant species is known to be appropriate for reactions occurring by the outer-sphere mechanism [22].



Therefore,

$$\text{Rate} = k_2[\text{Fe(III)EDTA}^-, \text{TS}^-] + k_4[\text{Fe(III)EDTA}^-, \text{TSH}] \quad (9)$$

From equation 4;

$$[\text{Fe(III)EDTA}^-, \text{TS}^-] = k_{-1}[\text{Fe(III)EDTA}^-][\text{TS}^-] \quad (10)$$

Substituting equation 10 into equation 9;

$$\text{Rate} = k_2 k_{-1} [\text{Fe(III)EDTA}^-][\text{TS}^-] + k_4 [\text{Fe(III)EDTA}^-, \text{TSH}] \quad (11)$$

From equation 3;

$$[\text{TS}^-] = \frac{K_1 [\text{TSH}]}{[\text{H}^+]} \quad (12)$$

Substituting equation 12 into equation 11;

$$\text{Rate} = \frac{K_1 k_2 k_{-1} [\text{Fe(III)EDTA}^-][\text{TSH}]}{[\text{H}^+]} + k_4 [\text{Fe(III)EDTA}^-, \text{TSH}] \quad (13)$$

Also, from equation 6;

$$[\text{Fe(III)EDTA}^- , \text{TSH}] = k_{-3}[\text{Fe(III)EDTA}^-][\text{TSH}] \quad (14)$$

Substituting equation 14 into equation 13;

$$\text{Rate} = \frac{K_1 k_2 k_{-1} [\text{Fe(III)EDTA}^-][\text{TSH}]}{[\text{H}^+]} + k_4 k_{-3} [\text{Fe(III)EDTA}^-][\text{TSH}] \quad (15)$$

$$\text{Rate} = (K_1 k_2 k_{-1} [\text{H}^+]^{-1} + k_4 k_{-3}) [\text{Fe(III)EDTA}^-][\text{TSH}] \quad (16)$$

$$\text{Rate} = k [\text{Fe(III)EDTA}^-][\text{TSH}] \quad (17)$$

which conforms to the experimental rate law,  $k = K_1 k_2 k_{-1} [\text{H}^+]^{-1} + k_4 k_{-3}$

## CONCLUSION

The kinetics of the electron transfer reaction of  $[\text{Fe(III)EDTA}]^-$  complex with thioglycolic acid was studied and established in buffer solution (pH = 7.5) at constant ionic strength ( $0.2 \text{ mol dm}^{-3}$ ) using  $\text{KNO}_3$ . The mole ratio of oxidant: reductant is 1:1. The reaction was first order with respect to  $[\text{Fe(III)EDTA}^-]$  and  $[\text{TSH}]$ . The reaction rate was faster at the pH 7.5 where deprotonation of the thioglycolic acid took place. The reaction was sensitive to change in ionic strength of the reaction medium, indicating the presence of like-charged reactant species in the activated complex. The zero intercept obtained from the Michaelis-Menten plot indicates lack of stable intermediate. Pieces of evidences from this study showed that the reaction occurred via outer-sphere mechanism and a plausible mechanistic pathway which explained the experimental data was proposed.

## Acknowledgments

The authors are grateful to Department of Chemistry, Ahmadu Bello University Zaria for her assistant in this research.

## REFERENCES

- [1] Fukuzumi, S. (2003). New Perspective of Electron Transfer Chemistry. *Organic Biomolecular Chemistry*, 1: 609 – 620. <http://dx.doi.org/10.1039/B300053B>.
- [2] Tuite, E. Benniston, A. and Harriman, A. (2002). Electron Transfer in Chemistry. *Journal of Chemical Society, Perkin Transition*, 1(17): 2028 – 2030.
- [3] Luptakova, A., Ubaldini, S., Macingova, E., Fornari, P. and Giuliano, V. (2012). Application of Physical-chemical and Biological-chemical Methods for Heavy Metal Removal from Acid Mine Drainage. *Process Biochemistry*, 47(11): 1633 – 1639. <http://dx.doi.org/10.1016/j.procbio.2012.02.025>.
- [4] Thanikaivelan, P., Rao, J., Nair, B. and Ramasami, T. (2005). Recent Trends in Leather Making: Processes, Problems, and Pathways. *Critical Rev. Environmental Science Technology*, 35: 37 – 79. <http://dx.doi.org/10.1080/10643380590521436>.

- [5] Fujii, S. Yosida, H. and Hagihara, T. (2003). Polishing Composition. *US Patent*. US20030041526A1.
- [6] Sivasubramian, S., Manoha, B.M., Rajaram, A. and Puvanakrishnan, R. (2008). Eco-friendly Lime and Sulfide Free Enzymatic Dehairing of Skins and Hides using a Bacterial Alkaline Protease. *Chemosphere*, 70(6): 1015 – 1024. <http://dx.doi.org/10.1016/j.chemosphere.2007.09.036>.
- [7] Wiklund, P., Levin, M. and Pahlavanpour, B. (2007). Copper Dissolution and Metal Passivators in Insulating Oil. *IEEE Electrical Insulator Magazine*, 23(4): 1.
- [8] Özeroglu, C. and Erdogan, S. (2005). Oxidative polymerization of Acrylamide in the Presence of Thioglycolic Acid. *Central European Journal of Chemistry*, 3(4): 705 – 720. <https://doi.org/10.2478/BF02475198>.
- [9] Saha, B., Meiling, H. and Stanbury, D.M. (2002). Reduction of Octacyanomolybdate(V) by Thioglycolic Acid in Aqueous Media. *Inorganic Chemistry Journal*, 41, 5538 – 5543. <http://dx.doi.org/10.1021/ico25702z>.
- [10] Sun, J. and Stanbury, D.M. (2002). Kinetics and Mechanism of Oxidation of Thioglycolic Acid by Hexachloroiridate(IV). *Journal of Chemical Society, Dalton Transition*, 785 – 791. <http://dx.doi.org/10.1039/b105951n>.
- [11] Ukoha, P.O. and Ibrahim, E. (2004). Mechanism of the Oxidation of  $\beta$ -Mercaptoacetic Acid by Trioxiodate(V) in Aqueous Acid Medium. *Chemclass Journal*, 138 – 141.
- [12] Sami, P., Venkateshwari, K., Mariselvi, N., Sarathi, A. and Rajasekaram, K. (2009). Studies on Electron Transfer Reaction of Heteropoly 11-tungstophosphovanadate(V) by L-cysteine and Thioglycolic Acid in Aqueous Acid Medium. *Transition Metal Chemistry*, 34: 733 – 737. <http://dx.doi.org/10.1007/s11243-009-9255-3>.
- [13] Demirhan, F., Taban, G., Baya, M., Dinoi, C., Daran, J. and Poli, R. (2006). Reduction of  $[Cp^*_2Mo_2O_5]$  by Thioglycolic Acid in an Aqueous Medium: Synthesis and Structure of  $\{[Cp^*_2Mo(\mu-SCH_2COO)]_2(\mu-5)\}$ . *Journal of Organometallic Chemistry*, 691: 648 – 654. <http://dx.doi.org/10.1016/j.jorganchem.2005.10.006>.
- [14] Ghosh, G.K., Misra, K., Baskim, M., Linert, W. and Moi, S.C. (2013). Kinetics and Mechanism of the Interaction of di- $\mu$ -hydroxo-bis(1,10-phenanthroline)dipalladium(II) Perchlorate with Thioglycolic Acid and Glutathione in Aqueous Solution. *Journal of Solution Chemistry*, 42: 526 – 543. <http://dx.doi.org/10.1007/s10953-013-9973-1>.
- [15] Gangopahyay, S., Ali, M., Dutta, A. and Banerjee, P. (1994). Oxidation of Thioglycolic Acid and Glutathione by (trans-cyclohexane-1, 2-diamine-N,N,N<sub>1</sub>,N<sub>1</sub>-tetraacetato)manganese(III) in Aqueous Media. *Journal of American Chemical Society. Dalton Transition*, 3: 841 – 845. <http://dx.doi.org/10.1039/DT9940000841>.

- [16] Diez, M.C., Pouleurs, D., Navia, R. and Vidal, G. (2005). Effect of EDTA and Fe-EDTA Complex Concentration on TCF Kraft Mill Effluent Degradability. Batch and Continuous Treatments. *Water Research*, 39: 3239 - 3246. <http://dx.doi.org/10.1016/j.watres.2005.05.046>.
- [17] Demmink, J.F., Van Gils, I.C.F. and Beenackers, A.A.C.M. (1997). Absorption of Nitric Oxide into Aqueous Solutions of Ferrous Chelates Accompanied by Instantaneous Reactions. *Industrial & Engineering of Chemistry Research*, 36, 4914 - 4927. <http://dx.doi.org/10.1021/ie9702800>.
- [18] Nagl, G.J. (1997). Controlling H<sub>2</sub>S Emissions. *Chemical Engineering*, 125 - 131.
- [19] Beale, S.I. (1971). A Simple Method for Synthesis of Ferric Ethylenediaminetetraacetate in a Pure and Stable Form. *Plant Physiology*, 48: 228.
- [20] Sivasubramanian, V.K., Ganesan, M., Rajagopal, S. and Ramaraj, R. (2002). Iron (III)-Salen Complexes as Enzyme Models: Mechanistic Study of Oxo(salen)iron Complexes Oxygenation of Organic Sulfides. *Journal of Organic Chemistry*, 67: 1506 - 1514. <http://dx.doi.org/10.1021/j00108780>.
- [21] Xiao-juan, Y., Lin, Y., Li, D., Xiang-Li, L. and Wei-Kang, Y. (2011). Kinetics of the [Fe(III)-EDTA]<sup>-</sup> Reduction by Sulfite under the Catalysis of Activated Carbon. *Journal of American Chemical Society*. 25: 4248 - 4255. <http://dx.doi.org/10.1021/ef2006063>.
- [22] Onu, A.D., Iyun, J.F. and Idris, O.S. (2015). Kinetics and Stoichiometry of the Reduction of Hydrogen Peroxide by an Aminocarboxylatecobaltate(II) Complex in Aqueous Medium. *Science Research Publishers*, 5: 75 - 82. <http://dx.doi.org/10.4236/ojic.2005.54009>.
- [23] Mamman, S. and Iyun, J.F. (2007) Kinetics and Mechanisms of the Reactions of Benzenediols with Binuclear Oxalato-cobaltate (III) Complex. *International Journal of Pure and Applied Chemistry*, 2, 407 - 413.
- [24] Iyun, J.F. (2004). The Oxidation of some Tris-(diimine) iron (II) and Tris-(substituted diimine) iron (II) Complexes by Aqueous Acidic Bromine Solution. An Assessment of the Marcus Model for Non - Complimentary Reactions. *ChemClass Journal*. 59 - 63.
- [25] Idris, S.O., Iyun, J.F. and Agbaji, E.B. (2008). Kinetics and Mechanism of Oxidation of Thiosulfate Ion by Tetrakis (2, 2-Bipyridine)- $\mu$ -oxodiiron (III) Ion in Aqueous Acidic Medium. *ChemClass Journal*, 103 - 108.
- [26] Stephen, M. (1997). *Identification of Iron (II) and (III) Cations by Precipitation Reactions*. Retrieved from <http://www.marz-kreations.com/Chemistry/Cation-ID/162k-Iron.html>

- [27] McAuley, A. and Gomwalk, U.D. (1969). Metal Ion Oxidations in Solution. Part VI. Oxidation of Thiourea and its N-Substituted Derivatives by Cobalt (III). *Journal of Chemical Society (A)*, 977 – 2951.
- [28] Ayoko, G.A. and Olatunji, M.A. (1982). Oxidation of L-cysteine, Mercaptoacetic Acid and  $\beta$ -mercaptoethylamine by 12-tungstocobaltate (III). *Polyhedron*, 2(7): 577 – 582.
- [29] Dutta, A., Basudeb, S., Mohammad, A. and Pradyot, B. (1997). Kinetics of Oxidation of Thioglycolic and Thiomalic Acids by a Nickel (III) Oxime-Imine Complex. *Journal of Chemistry Research (S)*, 186 - 187.
- [30] Sun, J. and Stanbury, D.M. (2002). Kinetics and Mechanism of Oxidation of Thioglycolic Acid by Hexachloroiridate (IV). *Journal of Chemical Society, Dalton Transition*, 785 – 791.
- [31] Claudio, B., Edoardo, M. and Patrizia, A. (1983). Kinetics and Mechanisms of Complex Formation and Redox Reactions of Iron (III) with Mercaptocarboxylic Ligands in Acid Perchlorate Media. *Transition Metal Chemistry*, 8: 40 – 45.
- [32] Zueva, T.S, Protopopov, E.V. and Ivanov, I.A. (1990). Role of Thiols (Cysteine and Thiourea) in the Mechanism of the Periodic Decomposition Reaction of Hydrogen Peroxide by Potassium Iodate in an Acid Medium. *TERCAXA* 26: 51 – 56.
- [33] Salem, I.A. and Gemeay, A.H. (1996). Kinetics and Mechanism of the Oxidation of L-Ascorbic Acid by the N, N'-ethylenebis (salicylideneiminato) manganese (III) Complex in Aqueous Solution. *Transition Metal Chemistry*, 21: 130 – 134.
- [34] Housecroft, C.E. and Sharpe, A.G. (2005). Inorganic Chemistry. *Pearson Education Limited*, Second Edition. 766 – 799. ISBN: 0130-39913-2.
- [35] Pryztas, T.J. and Sutin, N. (1973). Kinetics Studies of Anion – Assisted Outer-sphere Electron Transfer Reactions. *Journal of American Chemical Society*, 95: 5545.
- [36] Osunlaja, A.A., Idris, S.O. and Iyun, J.F. (2012). Mechanism of the Reduction of Methylene Blue by Thiourea in Aqueous Acid Medium. *International Journal of ChemTech Research*, 4(2): 609 – 617.