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Reduction of the Adipato-Bridged Binuclear Iron(III) Complex, [(Fesalen)$_2$adi] by Thioglycolic Acid: Kinetic and Mechanistic Study

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Abstract *Reduction of the binuclear iron (III) complex ion, [(Fesalen)$_2$adi] by β-mercaptoacetic acid was studied spectropotometrically at 495nm. Kinetic runs were obtained at 302K, under pseudo-first order conditions of a large excess of the reductant over the oxidant. At constant ionic strength, pseudo-first order rate constants increased with increase in concentration of the reductant and second rate constant were fairly invariant at 4.67x10^{-2}±0.017 dm^3 mol^{-1}s^{-1}. Within the acid concentration 0.001≤[H$^+$]≤0.15 mol dm^{-3} the rate of reaction increased with [H$^+$]. The results are consistent with the general rate law:*$\frac{-d[Fe_2adiH]}{dt} = (c + m[H^+])[Fe_2adi][Red]$. *Rate constant was not altered on varying ionic strength and dielectric constant of the reaction media.Addition of the small amounts of Mg^{2+} and CH$_3$COO$^-$ did not affect the rate of reaction. Least square fits of Michaelis-Menten type plot of* $\frac{1}{k_{obs}}$ *versus* $\frac{1}{[Red]}$ *was linear with intercept and analysis of products of reaction inferred formation of iron(III) and disulfides as products. The results point to plausible inner-sphere electron transfer path for the reduction of the iron(III) complex.*

Key Words:*Kinetics, mechanism, electron transfer, dinuclear iron(III) complex.*

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1.0 Introduction

Our quest to probe the redox properties of binuclear iron (III) species stems from our desire to gain insight into the dynamics of the actions of iron-based electron transfer enzymes (Atiga *et al.,* 2014; Ukoha *et al.,* 2015; Atiga *et al.,* 2015; Ukoha and Iyun, 2001; Ukoha and Iyun, 2005.). The drive is the established knowledge that the study of model compounds used as mimicsfor naturally occurring ones especially those havingphysciological activity is a great stride in chemistry, biochemistry, medicine and physiology (York and Bearden 1970; Okamara *et al.,* 1966; Fleischer *et al., 1969*).

In line with this thinking, study of some hitherto univestigated binuclear iron (III) complexes has been embarked on by our team. Redox characteristics of some first generation oxo-bridged complexes have been studied in aqueous media using thiols (Ukoha and Iyun, 2001; Ukoha and Iyun, 2005), and catechols(Idris *et al.,* 2005) and ascorbic (Ukoha and Iyun, 2002).

Results in literature show pathways ranging from outer-sphere, (Ukoha and Iyun, 2001; Ukoha and Iyun, 2005; Idris *et al.,* 2005; Ukoha and Iyun, 2002)to proton-coupled electron transfer (Ukoha and Iyun, 2001; Ukoha and Iyun, 2005).Insight from these results, though inconclusive, have been enriching.

Foray into redox dynamics of some second generation dioic acid-bridged binuclear complexes of iron(III) is very recent. Reduction of the adipic acid bridged iron (III) complex, Fe$_2$adi by oxosulfur anions (Atiga *et al.,* 2014; Ukoha *et al.,* 2015; Atiga *et al.,* 2015) threw up some strange kinetic traces and pointed to likely mediation ofredox potentials by span of the bridging molecule.

Also, oxidationof benzyl mercaptan and β-mercaptobenzothiazole as model thiols has been investigated (Ugwuanyi and Ukoha, 2015; Ugwuanyi and Ukoha, 2017). Whereas the reaction of thiobenzothiazole was first order on the reductant, benzyl mercaptan showed inverse first-order in its reaction with Fe_2adi(Ugwuanyi and Ukoha, 2015).

Reduction of [(Fe(Saloph))$_2$-μ-dicarpy] by some biomolecules has also been studied (Anidobu, 2013). This pyridenedicarboxylic bridged iron(III) dimer, at physiological pH was reduced by L-ascorbic acid to Fe (III) (Ukoha *et al.,* 2018) with second order rate constant of 0.07 $dm^3mol^{-1}s^{-1}$· The electron transfer route followed outer-sphere path mediated by the formation of ion-pair intermediates.

The present effort is a follow-up on the probe of the redox dynamics of these iron-enzyme mimics in order to gain insight into the electron transfer process. It is hoped that the data provided will help shed more light on the redox reaction kinetics of the iron(III) dimers, explain the implications of bridge span on electron transfer rate, give some guide on extent of Fe(III) orbital overlap and aid in solving the mysteries surrounding physiological process of some non-haeme proteins like haemerythrin.

2.0 Materials and Methods

Analytical grade thioglycolic acid, ethylenediamine, adipic acid, salicylaldehyde, methanol, sodium ethanoate, perchloric acid, ferric chloride, and sodium hydroxide were products of Aldrich-Sigma and BDH. They were used as supplied except otherwise state. Degassed, de-ionized water was used for kinetic investigations.

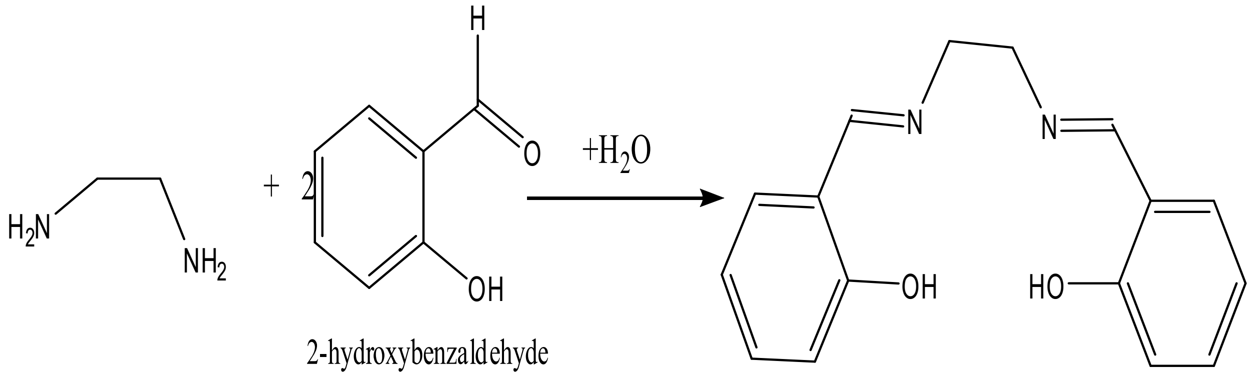
UV-Visible spectra were recorded on Jenway 6305 and Unico 2012 Spectrophotometers. Infra red data of the compounds were obtained in KBrpellets using Shimadzu 8000 FTIR Spectrophotometer. μ-Oxo-di [μ, μ^1-bis {salicylideneethylenediaminoiron(III)}], [(Fe-salen)$_2$adi] were prepared as reported elsewhere (Atiga *et al.,* 2014).

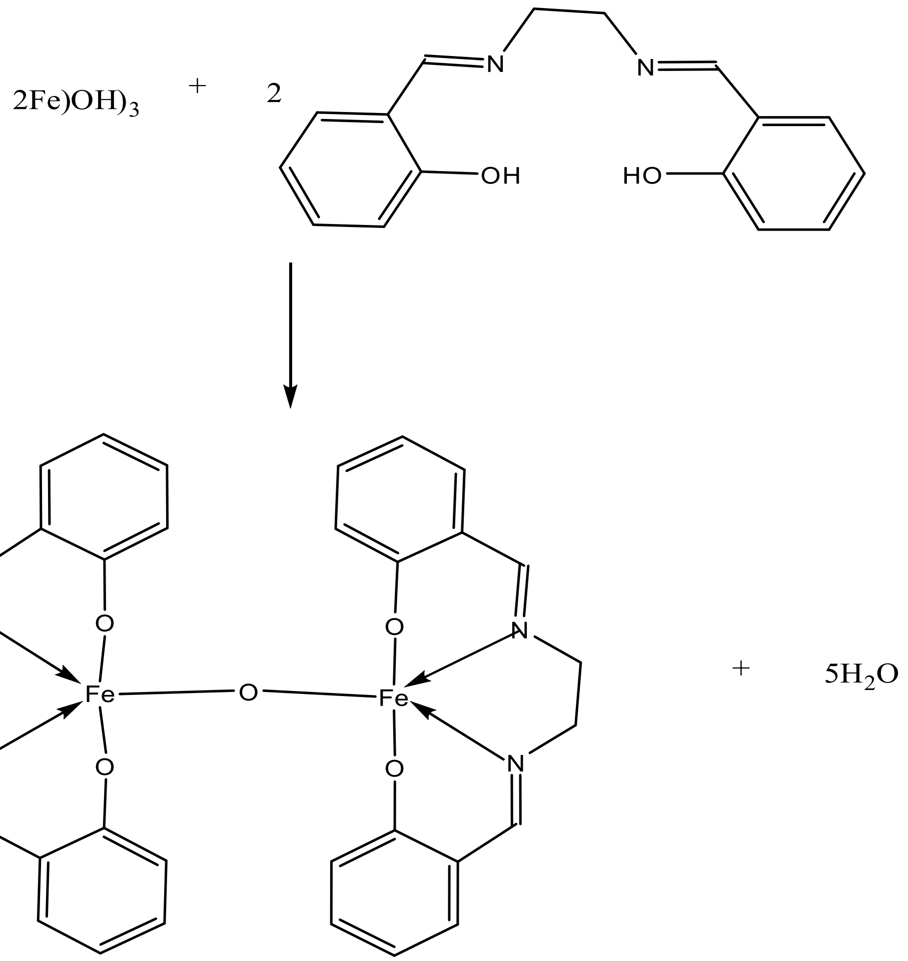
2.1 Syntheses of μ-[(Fe-salen)₂adi]

Methanolic solution (1.0mmol, 20 cm^3) of adipic acid was mixed with ethanolic suspension of [(Fe-salen)$_2$O] (0.76mm, 20cm^3). The mixture at constant stirring was refluxed for 30min until it turned black. The solid product formed was filtered, washed with ethanol and methanol and dried in a desicator. FTIR, UV-Visible data of the dimer matched literature reports (Smekal *et al.,* 1996; Smekal and Sindelar, 2004). Scheme1shows the preparation of the iron(III) dimer.

2.2 Stiochiometric determination

The determination of the stiochiometry of the reduction of [(Fe-salen)$_2$adi] by thioglycolic acid followed spectrophotometric titration method (Ukoha and Iyun, 2001). A constant concentration ($1x10^{-4}$ mol dm^{-3}) o [(Fe-salen)$_2$adi] was reacted separately with different concentrations ($5x10^{-5}$ – $1x10^{-4}$ mol dm^{-3}) of thioglycolic acid at μ = 0.011 mol dm^{-3} ($NaClO_4$), [H^+] = $1x10^{-3}$ mol dm^{-3} and T=302 K. The reaction mixtures were allowed to undergo complete reaction. Their absorbances (A_∞) at 495 nm (absorption maxima of the oxidant) were plotted against mole ratios of the reactants and the point of inflexion on the curve gave stoichiometry of the reaction.





Scheme 1: Synthesis of [(Fe-salen)$_2$O]

2.3 *Kinetic study*

Kinetic data for oxidation of thioglycolic acid by [(Fe-salen)$_2$adi] were generated at 495 nm by monitoring the decrease in the absorbance of the reacting mixture having confirmed that only the oxidant absorbed maximally at this wavelength. Thioglycolic acid and the products of reaction did not interfere under this condition. Pseudo-first order conditions were maintained with concentration of thioglycolic in at least 20-fold excess over that of the oxidant. Plot of absorbance difference ($\text{In}A_t - A_\infty$) against time yielded the pseudo-first order rate constant, k_{obs}, as slopes in accord with equation 1 as shown elsewhere (Ukoha *et al.,* 2010; Alioke *et al.,* 2012).

$(\mathit{In}A_t - A_\infty) = k_{obs}t + \text{In}\,(A_\infty - A_0)$ (1)

where A_∞ = final absorbance, A_t = absorbance at time t, A_0 = initial absorbance and k_{obs} = pseudo-first order rate constants. Specific rates were the mean of replicate runs and were consistent within ±5%.Gel formation on adding acrylamide to partially reacted reaction mixtures in methanol indicated presence of free radicals (Atiga *et al.,* 2014; Ukoha *et al.,* 2015). Dielectric constant and ionic strength of the reaction media were altered using propan-2-one and $NaClO_4$ respectively. Mg^{2+} and $CHCOO^-$ were used to investigate incidence of catalysis or not in the reaction.

3.0 Results and Discussion

Fitting of final absorbances of reaction mixture against mole ratios of reactants with respectto mole ratio method gave point of inflexion at approximately 1.01. This is indicative of the consumption of mole of thioglycolic acid per mole of the dimer reduced as shown in equation (2).

$2[(\text{Fe-salen})_2\text{adi}] + 2HSCH_2COOH + 2H^+ \rightarrow 2[(\text{Fe-salen})_2\text{adi}H_2]^+ + HOOCCH_2S\text{-}S\text{-}CH_2COOH$ (2)

Redox reactions of (Fe-salen)$_2$adi with some oxosulfur ions (Atiga *et al.,* 2014; Ukoha *et al.,* 2015; Atiga *et al.,* 2015) occurred in 1:1 stiochiometry as well as with benzene mercaptan, whereas reaction of

(Fe-salen)$_2$adi with 2-mercaptobenzothiazole followed 1:2 stiochiometry. The iron (III) dimer, [(Fe-salen)$_2$adi], was reduced to the iron (II) dimer, [(Fe-salen)$_2$adiH$_2$]$^+$, now stabilized by protonation of two of the azomethine nitrogen atoms. Addition of acidified K$_3$[Fe (CN)$_6$] solution to the reaction mixture on completion of reaction in the presence of excess of the reductant gave a deep blue-green precipitate indicating presence of Fe (II). The acidified completely reacted mixture gave a pale blue precipitate in the presence of 0.5 moldm^{-3} K$_4$[Fe (CN)$_6$] also indicating presence of Fe (II). The organic product was confirmed to be disulphide based on the method of McAuley and Gomwalk (Atiga *et al.,* 2014). The formation of iron (II) dimer instead of a monmeric species was investigated by Fourier Transform Infra red Spectroscopy. Comparism of the FTIR spectrum (Fig 1) of [(Fe-salen)$_2$adi] with that of the product [(Fe-salen)$_2$adiH$_2$]$^+$ (Fig 2) reveals interesting bands. V(C=0) of (Fe-salen)$_2$adi at 1702 cm^{-1} is retained in the product at 1727 cm^{-1} and V(C-0) of oxidant is retained in the product. Bands due to M-N or M-O vibration in the region 560 to 400cm^{-1} are also retained. However, a broad band around 3484cm^{-1} in the product is not found in (Fe-salen)$_2$adi. This band is assigned to $V(N - H)$ and indicates likely protonation of the C=N-groups in the Fe (II) product. It gives insight to the fact that the product is the iron (II) dimer, [(Fe-salen)$_2$adiH$_2$]$^+$. In the reactions of [(Fe-salen)$_2$adi] with dithionate ion(Atiga *et al.,* 2014), trioxosulfate (IV) (Atiga *et al.,* 2015) and dithionite (Ukoha *et al.,* 2015) ions. The iron(II) dimer was formed as product with intervening protonated oxidant species and retention of structure on completionof reaction.

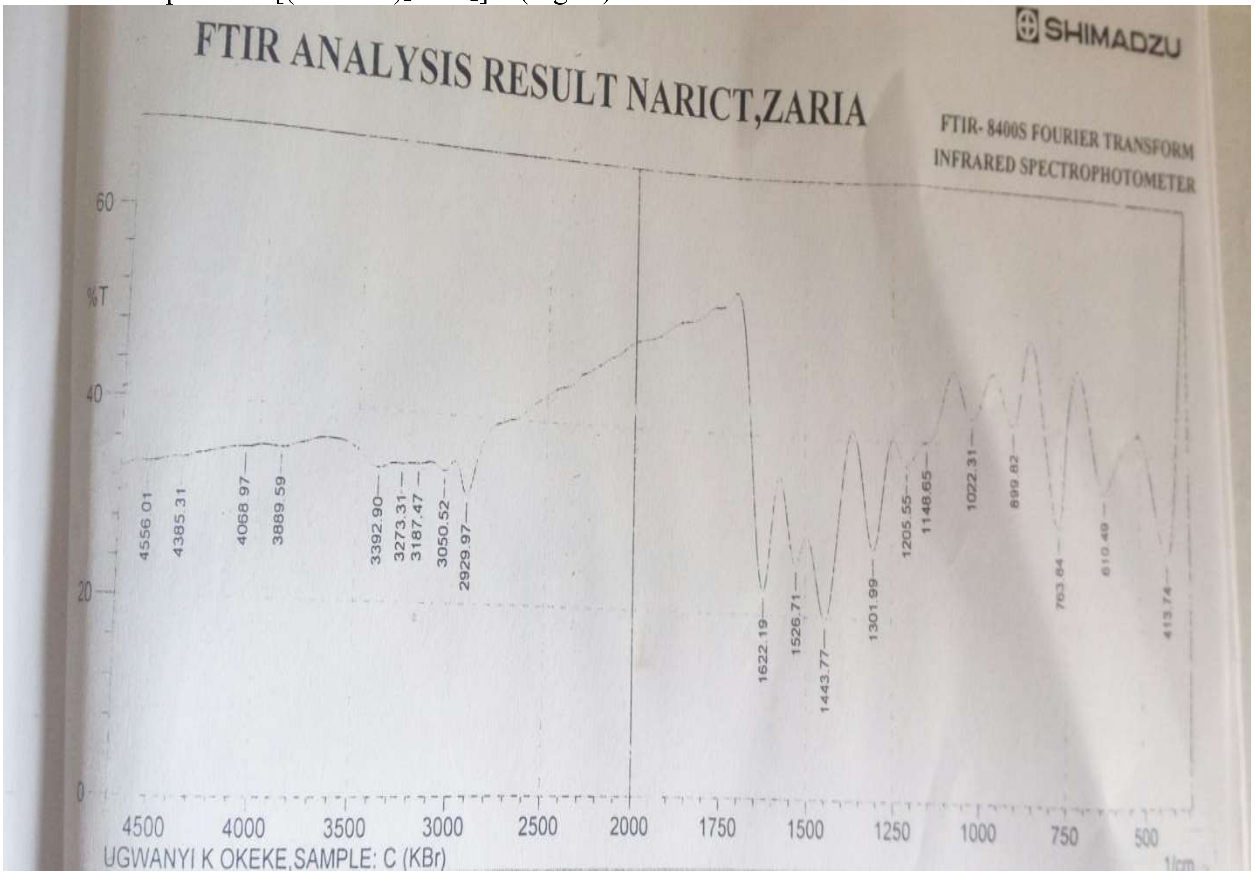


Fig. 1: FTIR Spectrum of [(Fe-salen)$_2$adi]

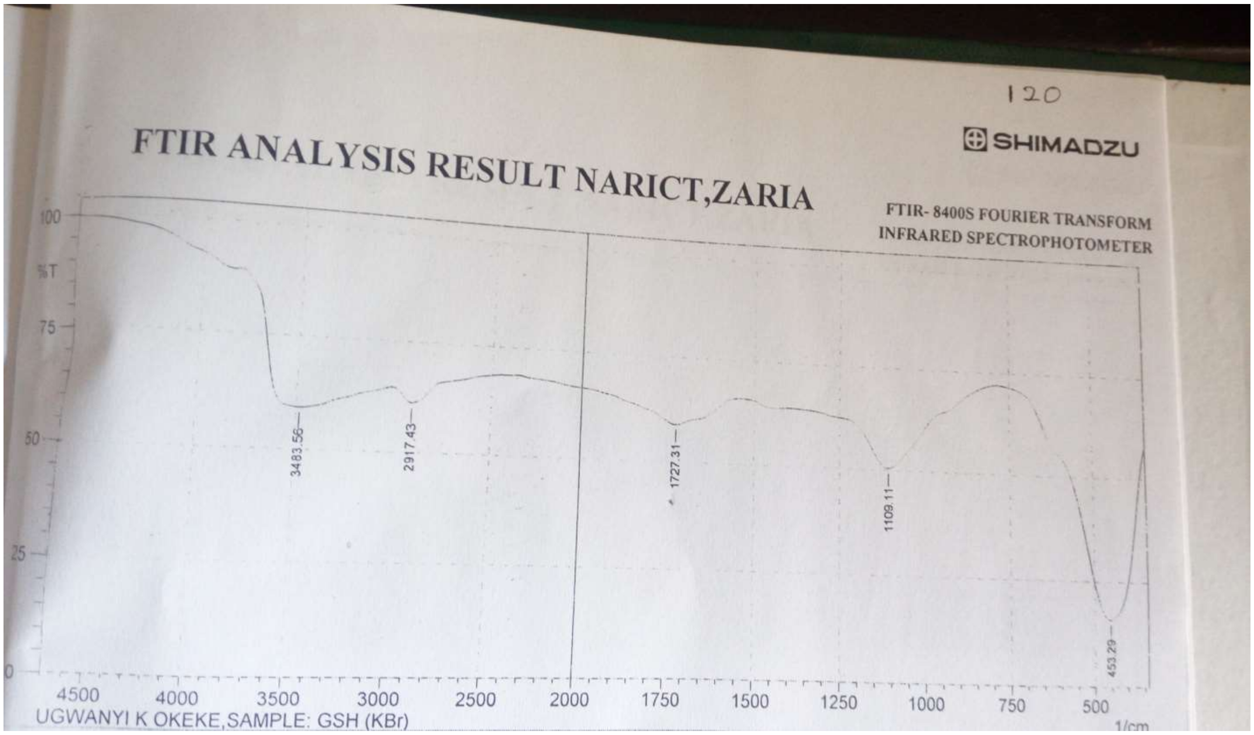


Fig. 2: FTIR Spectrum of Product of reaction of [(Fe-salen)$_2$adi] with thioglycolic acid

3.1 Kinetic Study

Pseudo-first order plots were linear to more than 75% extentof reaction indicating that the reaction is first order in oxidant concentration. Least square fits (Fig 3) of logk$_{obs}$ versus log [RSH] were linear (R^2=0.975) with slope of 1.001 also indicating first order dependence of reaction rate on concentration of reductant. Second order rate constants, k$_2$, were derived as the ratio of k$_{obs}$: [RSH] and were fairly constant at 4.67x10^{-2} ±0.0017dm^{3}mol^{-1}s^{-1}. The reaction was second order overall.

Pseudo -first order and second order rate constants are shown in Table 1. Variation of initial concentration of thioglycolic at4.0x10^{-3}≤ [RSH] ≤ 8.0 moldm^{-3} at fixed concentration of [(Fe-salen)$_2$adi] of 1x10^{-4} moldm^{-3} , [H$^+$]= 1x10^{-3} moldm^{-3} , ionic strength = 1x10^{-2} moldm^{-3}(NaClO$_4$) and T=320 K showed increase in k$_{obs}$with [RSH].

Replicate runs at varying [RSH] were consistent differing by less than 2% standard deviation.Earlier reports of redox kinetics of [Fe$_2$-adi] with oxoanions of sulphur (Atiga *et al.,* 2014; Ukoha *et al.,* 2015; Atiga *et al., 2015*) and with benzyl mercaptan and β-mercaptobenziothiazole revealed first order dependence of rate on concentration of the iron(III) dimer. However, the reactions occurred with varied dependencies of rate on reductants. Dithionite, benzylmercaptan (Atiga *et al*., 2014, Ugwuanyi and Ukoha, 2014), β-mercaptobenzothiozole (Ugwanyi and Ukoha, 2017) showed first order dependence of rate whereas $SO_3^{2-} and S_2O_6^{2-}$ showed zeroth order. Several factors control the order of reactantsthe rate of reaction at fixed pH can be written as:

$$\frac{-d[(Fesalen)_2adi]}{dt} = k_2[(Fesalen)_2adi][RSH]..(3)$$

3.2 Acid Dependence

Variation of acid concentration within the range 1x10^{-3} moldm^{-3} ≤ [H$^+$] ≤ 1.5x10^{-2} moldm^{-3} at constant concentration of oxidant (1x10^{-4} moldm^{-3}), ionic strength = 0.0 1 moldm^{-3} (NaClO$_4$) and T=302 K, the rate of reaction increased as [H$^+$] increased (Table 1). Plot of k_2 against $[H^+]^2$ (Fig 4) was linear (R^2 = 0.990) giving intercept of 4.6x10^{-2} dm^{3}mol^{-1}s^{-1}and slope of 100.00 dm^{9}mol^{-3}s^{-1}. The acid-dependent rate constant can be given as equation (4)

$$k_{H^+} = C + m[H^+] \qquad (4)$$

including the nature of the redox partner, whether single electron or two-electron reductant and also on the reaction medium.

Table 1: Pseudo-first order and second order rate constants for the reduction of [(Fesalen)$_2$adi] by thioglycolic (RSH) acid at [(Fesalen)$_2$adi] = 1x10^{-4} mol dm^{-3}, T = 302 K and λ_{max}= 495 nm.

10^3 [RSH] /(mol dm^{-3})	10^3 [H$^+$] /(mol dm^{-3})	$10^3\mu$ /mol dm^{-3} (NaClO$_4$)	10^4k$_{obs}$/s^{-1}	10^{-2} k$_2$/(dm^{3}mol^{-1}S^{-1})
4.00	1.00	1.00	1.90	4.75
5.00	1.00	1.00	2.25	4.50
6.00	1.00	1.00	2.80	4.67
7.00	1.00	1.00	3.16	4.51
8.00	1.00	1.00	3.92	4.90
5.00	1.00	1.00	2.25	4.50
5.00	3.20	1.00	2.50	5.00
5.00	8.00	1.00	2.75	5.50
5.00	12.00	1.00	3.25	6.50
5.00	16.00	1.00	4.00	8.00
5.00	1.00	5.10	2.20	4.40
5.00	1.00	5.50	2.21	4.42
5.00	1.00	6.00	2.19	4.38
5.00	1.00	6.50	2.18	4.36
5.00	1.00	7.00	2.20	4.40

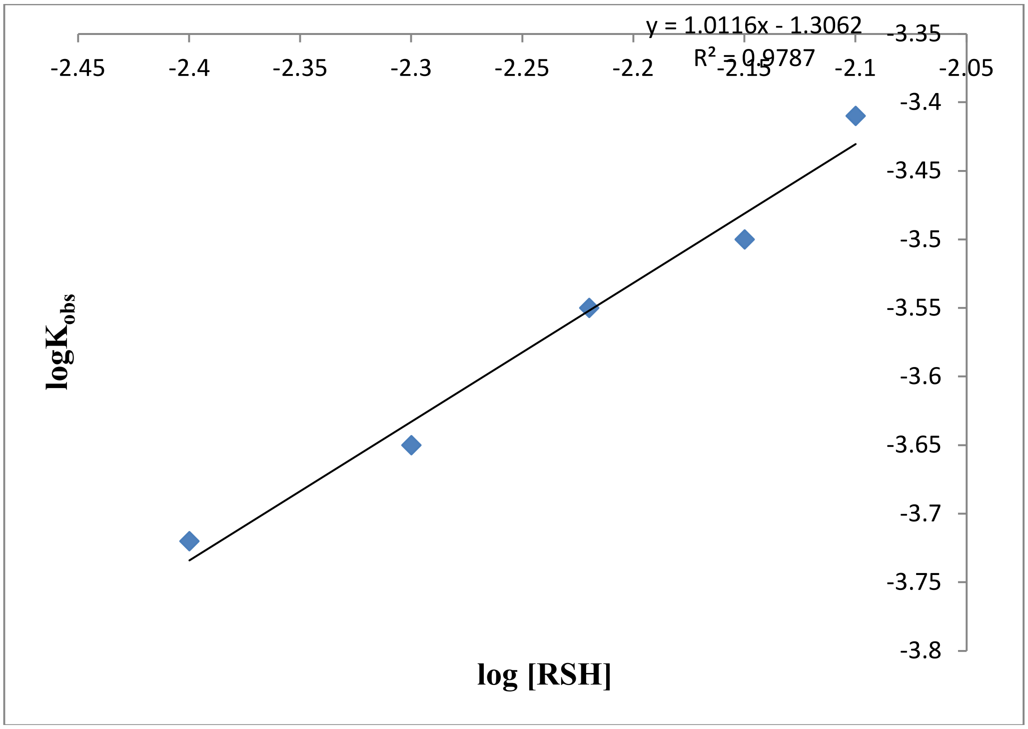


Fig. 3: Plot of logk$_{obs}$ versus log [RSH]

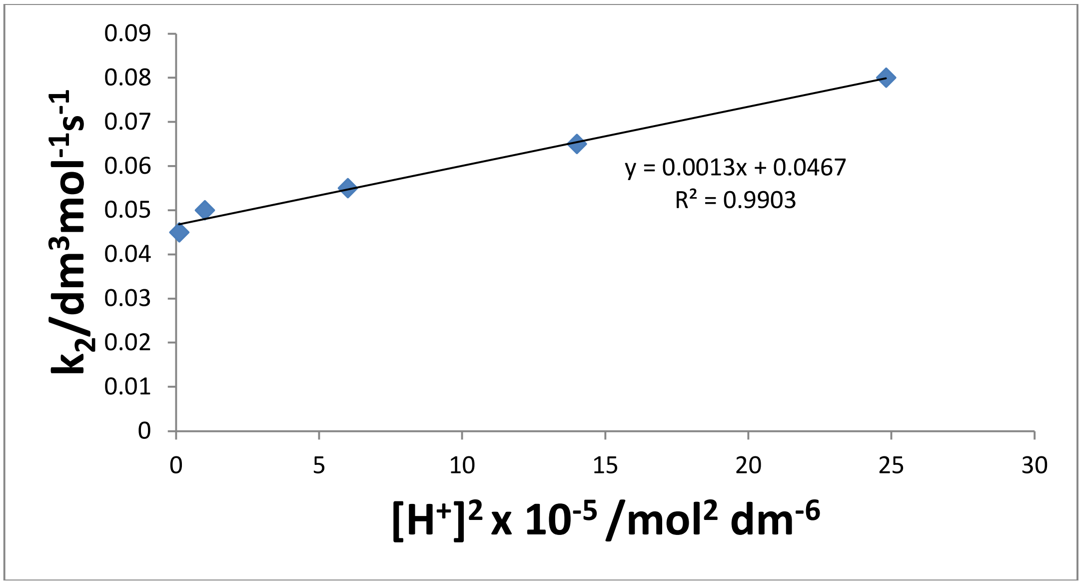
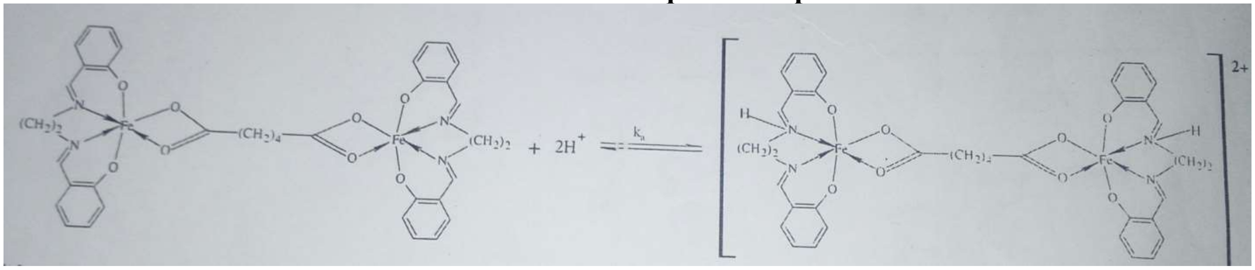


Fig. 4: Plot of k_2 versus[H$^+$]^2

Acid catalysis implies a preprotonation step occurring before electron transfer. Dissociation ofthioglycolic acid will give RS^- and H^+ and will lead to inverse acid dependence. This is common feature of reactiions of thiols. The positive acid dependences are not in accord with this deprotonation step. Moreover, RSH can form RS^- only in alkaline media since the pKa for this process is approximately 10.5 in aqueous solution (Labat, 2014). Practically, thioglycolic will be largely in the form of RSH under the condition of this reaction (pH = 3.0). The formation of the carboxylate ion (pKa = 3.6) which is favoured at lower pH will also be insignificant at pH of 3. Therefore, at the rate determining step RSH will be the main reductant species. However protonation of the azomethine nitrogens of [(Fe-salen)$_2$adi] to [(Fe-salen)$_2$adiH]$^+$ or [(Fe-salen)$_2$adiH$_2$]$^{2+}$(Scheme 1) seem very likely as the step will lead to acid catalysis. The same suggestion has been inferred for the other reactions of the oxidant (Atiga *et al.,* 2014; Ukoha *et al.,* 2015; Atiga *et al.,* 2015; Ugwuanyi and Ukoha, 2015; Ugwuanyi and Ukoha, 2017). The protonated oxidant is thought to be a better oxidant than the native compound as disruption of electron localization on the nitrogen atom will encourage a more facile reaction (Atiga *et al.,* 2014; Ukoha *et al.,* 2015; Atiga *et al.,* 2015).

Equation of protonation



Scheme 2: Protonation of [(Fe-salen)$_2$adi]

3.3 Effects of Ionic Strength (μ), Dielectric Constant (D) and Added Ions

As the ionic strength of the reaction media was varied from 1.0x10^{-2} to 7x10^{-2} moldm^{-3}NaClO$_4$ at [(Fe-salen)$_2$adi] = 1x10^{-4} moldm^{-3}, [H$^+$] = 1x10^{-4} moldm^{-3}, T = 302K and λ=495 nm, the rate of reaction remained unchanged (Table 2). This lack of primary salt effect suggests operation of uncharged species at the rate determining step. The import of this will probably be the reaction of the protonated oxidant, [(Fe-salen)$_2$adiH$_2$]$^{2+}$ and the neutralreductantmolecule, HSCH$_2$COOH, at the rate determining step. Involvement of these species at the rate determining step could result to the formation a precursor complex of the form [(Fe-salen)$_2$adiH$_2$, SCH$_2$COOH] as ion-pair having outer-sphere character or [FesalenH$_2$-SCH$_2$COOH] of inner-sphere character. For any of these cases, it will be the rate determining step.

On the basis of the Debye-Huckel relation (Ukoha *et al.,* 2015; Levine, 2009) (equation 5 and 6), a plot of Log k$_2$versus $\sqrt{\mu}$ was linear with a zero gradient.

$$\log k_2 = \log k_0 + Z_A Z_B \mu^{0.5} \qquad (5)$$

$$\log k_2 = \log k_0 + Z_A Z_B \left[{}^{\sqrt{\mu}}\!/_{(1+\sqrt{\mu})} \right] \qquad (6)$$

Where k$_2$ = rate constant for the reaction. k$_0$ = hypothetical rate constant in a medium of infinite dielectric constant, Z$_A$ and Z$_B$ = charges on reactants A and B respectively, μ = ionic strength.

Varying ratios of propan-2-one and water were used to alter the dielectric constant (Ɗ)of the reaction media while concentrations of other components were kept constant. Results in Table 2 show no significant change in reaction rate.

Table 2: Dependence of rate constant on added ions, X, and dielectric constant D, for the reaction of [(Fesalen)$_2$adi] with thioglycolic acid (RSH) at [(Fesalen)$_2$adi]^2 = 1x 10^{-4} mol dm^{-3} [RSH] = 0.005 mol dm^{-3}, μ = 0.005 mol dm^{-3}(NaClO$_4$), T = 302 K and λ$_{max}$= 495 nm.

X	10^3 [X]/(mol dm^{-3})	10^4 k$_{obs}$ / s^{-1}	10^2k$_2$/dm^3 mol^{-1}s^{-1}
Mg^{2+}	**4.00**	**2.24**	**4.48**
	6.00	**2.26**	**4.52**
	8.00	**2.25**	**4.50**
	10.00	**2.22**	**4.44**
	12.00	**2.24**	**4.48**
CH$_3$CHOO$^-$	**4.00**	**2.30**	**4.60**
	6.00	**2.26**	**4.52**
	8.00	**2.24**	**4.48**
	10.00	**2.25**	**4.50**
	12.00	**2.27**	**4.54**
D	**73.22**	**2.24**	**4.48**
	71.86	**2.25**	**4.50**
	70.51	**2.19**	**4.38**
	69.15	**2.20**	**4.40**
	68.28	**2.23**	**4.46**

For ionic reactants in solution whereintermolecular forces contribute greatly to equilibrium constants and reaction rates (equation 7),

$$F = \frac{1}{4\pi\varepsilon_0\varepsilon_r}\frac{|Q_1Q_2|}{r^2} \qquad (7)$$

$|Q_1Q_2|$ = two charges in a dielectric field

ε_r = dielectric constant

change in dielectric constant could alter the rate or course of the reaction (Levine, 2009). This is because as dielectric constant decreases, degree of ion pairing increases due to increase in magnitude of electrostatic attraction. For reactions operating by the formation of ion-pair precursor complexes, decrease in Ɗ will accelerate the reaction were ions of opposite charges are involved. This effect is not so significant in this reaction and suggests remoteness of formation of ion-pairs within the range of the dielectric constant of the reaction media. The rate determining step will most likely involve the neutral RSH and protonated oxidant in a slow process.

The greater the charges on the reactants the more is the likelyhood to form ion pairs. The formation of such ion-pair did not contribute significantly to the rate of reaction.

Addition of small amounts of Mg^{2+} and CH$_3$COO$^-$in the range 4.0x10^{-3} to 1.2x10^{-2} moldm^{-3} to the reaction mixture and other parameters kept constant did not significantly alter the rate of reaction (Table 2). Lack of anion or cation catalysis is reasoned to indicate formation of a precursor complex prior to electron transfer as a result of inner-sphere electron-transfer pathway (Atiga *et al.,* 2014; Ukoha *et al.,* 2015; Atiga *et al.,* 2015). Likely formation of a precursor complex of the type [(Fe-salen)$_2$adiH$_2$-RS]$^-$ or [(Fe-salen)$_2$adiH-RS] as a precursor complex before electron transfer will make anion or cation catalysis very remote since charged species will not be available for interaction with these ions(Alioke *et al.,* 2012). Modified Michaelis-Menten plot of ${}^1\!/_{k_{obs}}$ versus ${}^1\!/_{[RSH]}$ (Fig 5) was linear (R^2=0.98) with positive intercept (111.0 s) indicating likely formation of intermediate with large equilibrium constant.

3.4 Temperature dependence

Between 283 to 303 K the temperature of the reaction mixtures was varied in a thermostated reacting system and other parameters kept constant. Under these conditions reaction rates increased with increase in temperature. Temperature-dependent rate constants are given in Table 3. Following the Eyring-Polanyi relation (equation 9), plot of log (k$_{obs}$/T) versus ${}^1\!/_T$ (Fig 6) was constructed from which the activation parameters $\Delta S^{\neq}$ and $\Delta H^{\neq}$ were derived.

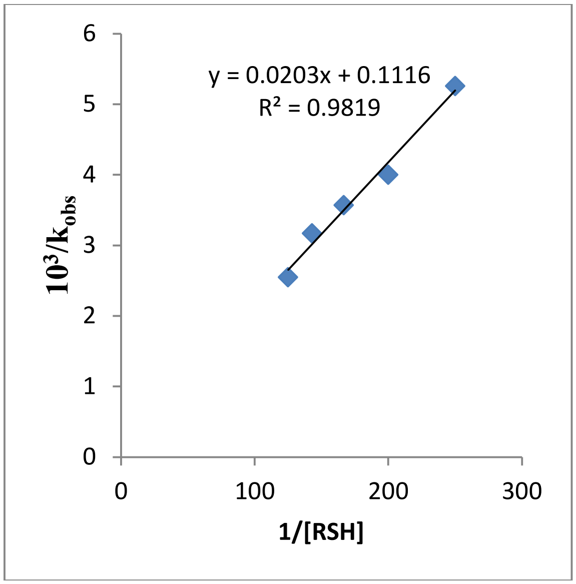


Fig. 5:Michaelis-Menten- Type Plot of $10^3/k_{obs}$ vs 1/[RSH]

$$\log\frac{k_{obs}}{T} = \log\frac{k}{h} + \frac{\Delta S^{\neq}}{2.303R} - \frac{\Delta H^{\neq}}{2.303RT} \qquad (9)$$

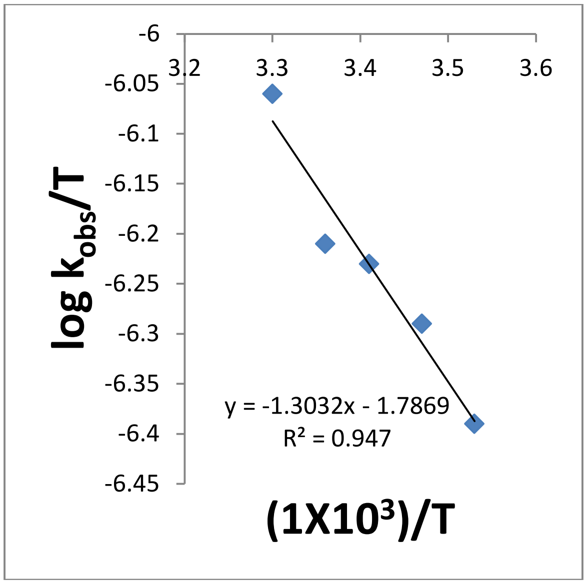
where k_{obs} = temperature dependent rate constant, k = Boltzman constant, h= Planck's constant, R = gas constant, $\Delta S^{\neq}$ = entropy of activations, $\Delta H^{\neq}$ = enthalpy of activation.

$\Delta H^{\neq}$ was determined to be 24.95 kJmol^{-1}and $\Delta S^{\neq}$ was derived as 132.03 JK^{-1}mol^{-1}. Whereas activation parameters are not good enough to indicate the mechanism of a reaction, they can infer the orderliness or otherwise of the transition states., Comparism of activation parameters for similar reactions could also be helpful in ascertaining pathway of a reaction. Marcus and Hush (Housecroft and Sharpe, 2008) had predicted that for outer-sphere reactions kinetic and thermodynamic data for two self-exchange reaction can be related to the cross reaction of the self exchange partners.

Large positive$\Delta S^{\neq}$ as seen for this reaction indicates dis-ordered transition state in agreement with non-involvement of oppositely charged species at the rate determining step. The formation of the activated complex is most likely between RSH and [Fe$_2$adiH$_2$]$^{2+}$. The ΔH^{+}value of 27.38 kJmol^{-1} is similar to what has been reported as inferring enthalpy-controlled reactions which is common with slow reactions. The reactions of [(Fe-salen)$_2$adi] with oxo anions of Sulphur (Atiga *et al.,* 2014; Ukoha *et al.,* 2015; Atiga *et al.,* 2015) showed similar features with $\Delta H^{\neq}$(kJmol^{-1}) of 1.137 (SO_3^{2-}), 10.94 ($S_2O_4^{2-}$) and 13.4 ($S_2O_6^{2-}$). The $\Delta S^{\neq}$ values were in the range -279.20 to -293.50 JK^{-1}mol^{-1} for the same reductants, the common feature of the reaction is the proton coupled electron transfer process. Reaction of benzylmercaptan and β-mercaptobenzothiazole with [(Fe-salen)$_2$adi] followed similar trend with $\Delta H^{\neq}$ of 12.83 and 16.47 kJmol^{-1} respectively (Ugwuanyi and Ukoha 2015; Ugwuanyi and Ukoha 2017).

Table3: Temperature dependence of rate constants for the reaction of Fe$_2$adi with GSH at [Fe$_2$adi] = 1x10^{-4} mol dm^{-3}, [GSH] = 0.05 mol dm^{-3}, [H$^+$] = 0.05 mol dm^{-3}, I = 0.5 mol dm^{-3}(NaClO$_4$), λ_{max}= 495 nm.

X	Temp (K)	10^4 k_{obs} /s^{-1}	Log(k_{obs}/T)	10^3 (1/T)(K^{-1})
GSH	283	1.14	-6.39	3.53
	288	1.47	-6.29	3.47
	293	1.71	-6.23	3.41
	298	1.84	-6.21	3.36
	303	2.66	6.06	3.30



Fig/ 6: Plot of log k$_{obs}$/T against 1/T

Calculation of the free energy of activation,$\Delta G^{\neq}$, for these reactions and similar ones shows that they have large positive $\Delta G^{\neq}$ which is an indication that they are not spontaneous but slow reactions. This may be a consequence of the increased length of the bridging group of up to six carbon atoms. This makes the two Fe (III) groups magnectically dilute since orbital overlap across the bridge will be very difficult. Each atom will likely react separately and possibility of having intermediates with mixed valence of iron is notfarfetched(Ukoha *et al.,* 2015; Robin and Day, 1976).

3.5 Mechanism of reaction

Based on the stiochiometry, acid-dependence, effect of dielectric constant, ionic strength, catalysis, formation of precursor complexes and Michaelis-Menten type plot; the following plausible scheme has been proposed for the reaction: $[(Fe\text{-}salen)_2adi]$ = Fe_2adi and RSH = thioglycolic acid.

$[Fe_2adi] + 2H^+ \overset{Kp}{\rightleftharpoons} [Fe_2adiH_2]^{2+}$ (10)

$[Fe_2adiH_2]^{2+} + RSH \underset{k-1}{\overset{k_1}{\rightleftharpoons}} [Fe_2adiH_2\text{-}RS]^+ + H^+$ (11)

$[Fe_2adiH_2\text{-}RS]^+ \xrightarrow{k_2} [Fe_2adiH_2]^+ + RS^*$ (12)

$Fe_2adi + RSH \overset{k_3}{\rightleftharpoons} [Fe_2adi\text{-}RS]^- + H^+$ (13)

$[Fe_2adi\text{-}RS]^- + 2H^+ \xrightarrow{k_4} [Fe_2adiH_2]^+ + RS^*$ (14)

$RS^* + RS^* \xrightarrow{k_5} RSSR$ (15)

Equations (11) and (13) are the rate determining steps and the rate of reaction could be written as

$$\frac{-d[Fe_2adi]}{dt} = k_2[Fe_2adiH_2^{2+]}[RSH]+k_3[Fe_2adi][RSH[\quad (16)$$

Following steady state approximation,

$[Fe_2adiH_2^{2+}] = K_p\,[Fe_2adi][H^+]^2$ (17)

Substituting equation (17) into (16) gives

Rate = $k_1K_p[Fe_2adi][H^+][RSH] + k_3[Fe_2adi][RSH]$(20)

Equation (20) on rearrangement gives

Rate = $\{k_1K_p[H^+]^2 + k_3\}[Fe_2adi][RSH]$ (21)

Equation (21) is same as equation (4) where m= k_1K_p and c = k_3.

The plausible mechanism for the reduction of Fe_2adi by thioglycolic was arrived by considering the following points:

i. Lack of anion or cation catalysis on adding Mg^{2+} and ACO^- is most likely due to operation of an inner-sphere route. The formation of a precursor complex of $[Fe_2adiH_2\text{-}RS]^+$ before election transfer is very likely. The formation of this complex will be rate limiting. Considering the fact that the complex is coordinatively saturated, coordination to the inner-sphere will be remote. Formation of such a complex will require configurational change and substitution of one of the salen units. This will drastically slow down the reaction. This is likely the reason for the very slow rates of the reaction (k_{obs}= 2.25x $10^{-4}s^{-1}$and k_2= 4.6x $10^{-2}dm^3mol^{-1}s^{-1}$).

RS^- being a one-electron reductant will transfer electron to any of the proximal Fe (III) units leading to a mixed valent Fe (III) – Fe (II) dimer, $[Fe_2adiH_2]^+$, stabilized by protonation of some of the azomethine groups. In the reaction of Fe_2adi with $S_2O_4^{2-}$, protonated Fe (II) dimmers of the form $[Fe_2(salen)_2adiH]^-$ were reported as products (Ukoha *et al.,* 2015). Interaction of RSH and not $RS^-$with the oxidant is not a common feature of reactions of thiols as RS^- had been reported to be the active reductant species (Ayoko *et al.,* 1983) However, thioglycolic has pK_a of 10.5 in H_2O (Labat, 2014)and 9.30 in $NaClO_4$ solution (Rippel, 2014)for the formation of the mercapto ion, RS^-. At the pH of 3.0 that the reaction took place, the reductant will remain as RSH and undeprotonated. Remotely, only the carboxylate ion, $SHCH_2COO^-$, (pK_a = 3.82) may be formed. Its formation will be unimportant since electron transfer is through the sulphur atom and not oxygen. It stands to reason then that RSH will interact with $[Fe_2adiH_2]^{2+}$ at the rate determining. This is cation-neutral molecule interaction.

ii. Lack of primary kinetic salt effect is in support of a rate determining step where cation and neutral molecule interaction is involved. Variation of ionic strength of media will not alter the rate of reaction. This lays credence to equations (11) and (13) as rate determining steps.

iii. Michaelis-Menten-Type plot of $1/k_{obs}$ versus $1/[RSH]$ was linear with intercept. This is a common feature of reactions involving formation of precursor complexes of large enough equilibrium constant. The formation of the precursor complex, $[Fe_2adiH_2\text{-}RS]^+$, is the rate determining step and its intermolecular electron transfer and decomposition to yield postcursor complexes will be faster.

iv. Lack of dependence of the reaction of dielectric constant (Ɗ) also supports the neutral molecule- cation interaction at the rate determining step. Reactions in aqueous solution with cation-anion interaction of high charges (≥2) will result in formationof ion-pairs of outer-sphere character. This will be enhanced at lower values of Ɗ (even for charge product of -1) leading to enhancement of rate of reaction with decrease in Ɗ.

> The lack of dependence on Ɗ rules out cation-cation, or anion-cation, interaction and makes formation of ion-pairs of outer-sphere character very remote.

The assessed data strongly supports an inner-sphere electron transfer route mediated by proton coupling. This is also one of those rare reactions where the rate of electron transfer, k_{et}, is faster than the rate of precursor complex formation, kdpc($k_{et}>k_d^{pc}$ and rate = k_f^{pc} [oxidant][red.]). This is a substitution-controlled reaction (Haim, 1983; Meyer, 1978).

Comparism of rates of reduction of [(Fe salen)$_2$adi] by other reductants(Atiga *et al.,* 2014; Ukoha *et al.,* 2015; Atiga *et al.,* 2015; Ugwuanyi and Ukoha, 2015; Ugwuanyi and Ukoha, 2017) with the titled reaction shows that the inner-sphere reactions with the thiolsbenzylmercaptan and mercaptobenzothiozole had rates of 5.2x 10^{-3} and 0.01$dm^3mol^{-1}s^{-1}$ respectively which indicate slow electron transfer processes and are comparable with 0.0467$dm^3mol^{-1}s^{-1}$ obtained for the reaction of Fe$_2$adi with thioglycolic acid. The outer-sphere reaction with $S_2O_6^{2-}$ and SO_3^{2-} are however faster with rates of 0.24 and 0.42 $dm^3mol^{-1}s^{-1}$ respectively (Atiga *et al.,* 2014; Ukoha *et al.,* 2015).

4.0 Conclusion

This study on the kinetics and mechanism of reduction of [(Fe salen)$_2$adi] by thioglycolic acid (RSH) led to the proposal of the rate law:

$$\frac{-d[\mathrm{Fe_2adi}]}{dt} = \{k_1K_p[H^+]^2 + k_3\}[Fe_2adi][RSH].$$

Plausible inner-sphere electron transfer mechanism mediated by proton coupling has been proposed in accord with acid catalysis of the reaction.

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