Kinetics, Thermodynamics, and Mechanism of Redox Reaction of I-Adipato-di(N,N[1]-bis(salicylidene)ethylenediaminatoiron(II)), [(Fe-salen)$_2$adi], with thiourea and L-cysteine in Aqueous Perchloric acid

Pius O. Ukoha, Ph.D.[1]; Kenneth O. Ugwuanyi, M.Sc.[1]; Uchechukwu S. Oruma, Ph.D.[1*]; Collins U. Ibeji, Ph.D.[1]; and Uchechukwu R. Obeta, M.Sc.[2]

[1]Coordination Chemistry and Inorganic Pharmaceuticals Unit, Department of Pure and Industrial Chemistry, University of Nigeria, Nsukka, Enugu State, Nigeria 410001
[2]Department of Chemistry, Michael Okpara University of Agriculture, Umudike, Abia State, Nigeria 440109

E-mail: susan.oruma@unn.edu.ng*
Telephone: 08061222297

ABSTRACT

Kinetics of the electron transfer reaction of the adipato bridged iron(III)-salen complex [(Fe-salen)$_2$adi], with thiourea and L-cysteine was studied in perchloric acid at I= 0.01 moldm^{-3} (NaClO$_4$), T = 29±1^{0}C and λ_{max} = 495 nm. On the basis of the mole ratio method, one mole of L-cysteine or two moles of thiourea were consumed per mole of [(Fe-salen)$_2$adi] reduced. Under pseudo-first order conditions of [reductant] in at least twenty-fold excess of concentration of the oxidant, pseudo-first order rate constants, k$_{obs}$, varied directly with the concentrations of the reductants. Second order rate constant, k$_2$, were fairly constant at 0.0601±0.002 dm^{3}mol^{-1}s^{-1} (thiourea) and 0.009±0.00022 dm^{3}mol^{-1}s^{-1} (L-cysteine) implying first order dependence of rate on concentration of [(Fe-salen)$_2$adi].

Least square fits of log [reductants] against logk$_{obs}$ were linear with slopes of 1.08 (thiourea) and 1.02 (L-cysteine) indicating first order dependence of rate on concentrations of the reductants. Within the acid concentration range, 1x10^{-3} moldm^{-3}≤ [H]$^+$≤ 2.0 x10^{-2} moldm^{-3}, the rate of reactions increased with increase in [H]$^+$. The rate of [(Fe-salen)$_2$adi]-reductants reactions decrease as ionic strength of the reaction media increased. Added Mg^{2+} slightly retarded both reactions. Also, addition of small quantities of ethanoate ion diminished the rates of the reactions. The pathway of the reactions has been resolved in terms of plausible outer-sphere electron transfer mediated by proton coupling.

(Keywords: iron-sulfur electron transfer, kinetics, thermodynamics, chemical oxidation, first order reaction)

INTRODUCTION

Approximately 4200 mg of iron is present in an adult human of about 70 kg body weight[1]. This makes iron the single most abundant trace metal in a mammalian body. Iron is found in the body in the form of electron transfer systems like Fe-S, proteins and cytochromes, dioxygen storage and transport enzymes like hemoglobin, myoglobin, and haemerythrin and as iron storage systems like ferritin and transferritin[2]. Also, most nitrogenase, hydrogenase, and reductases contain iron. Iron therefore has a rich history and chemistry in physiological processes[3,4].

Proper understanding of the biological roles of iron enzymes has relied greatly on *invitro* studies of the synthetic mimics of these enzymes[5-6]. Dimeric iron(III) species have been studied as models for bio-inorganic systems like haemerythrin[7-10] and ferric porphyrins[11-12]. Their redox characteristics have been reported, which have revealed various mechanisms attending such reactions[8,13-17]. Most of the redox reactions of the oxo-bridged iron(III) dimers occurred by outer-sphere electron transfer mechanism[8,16,17].

For the dioic acid bridged Fe(III) dimer [(Fe-salen)$_2$adi], its reduction by SO$_3^{2-}$ and S$_2$O$_6^{2-}$ also occurred by the outer-sphere path[13,15]. However, slow reduction[14] of [(Fe-salen)$_2$adi] by S$_2$O$_4^{2-}$, benzyl mercaptan[18] and mercaptobenzothiazole[19] followed the inner-sphere route. Reduction of the pyridenedicarboxylic acid bridged iron(III) dimer [(Fe-salen)$_2$-I-dicarpy] by L-ascorbic acid followed outer-sphere mechanism mediated by ion-pair complex formation[20].

Interestingly, the results reported so far have indicated several complexities attending these reactions and there are still many questions unanswered. In order to unravel these complexities and also give more insight into the dynamics of operation of some of the iron non–haeme biological systems, we have continued our quest to study more iron(III) dinuclear bridged systems. The present effort is a report on the kinetics and mechanisms of the reduction of the adipato bridged Fe(III)-salen complex, [(Fe-salen)$_2$adi], by thiourea and L-cysteine.

EXPERIMENTAL

μ-Oxo-di(N,N^1-bis{salicylideneethylene-diaminatoiron(II)}], [(Fe-salen)$_2$O] and μ-adipato-di(N,N^1-bis{salicylideneethylene-diaminatoiron(II)}], [(Fe-salen)$_2$adi] were synthesized and characterized based on its UV-Visible and FTIR data (Figures 1 and 2). The results obtained are in accord with the reported data in literature[7,13,21]. Scheme 1 shows the preparation of the complex. All other chemicals were commercial Analar grade product of Aldrich-Sigma ,Kermel, BDH , Fluka and May and Baker. They were used as supplied except otherwise stated.
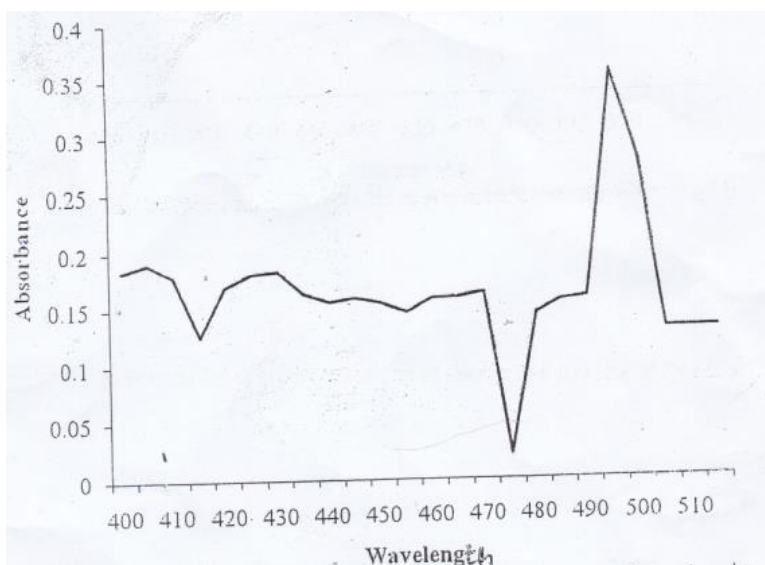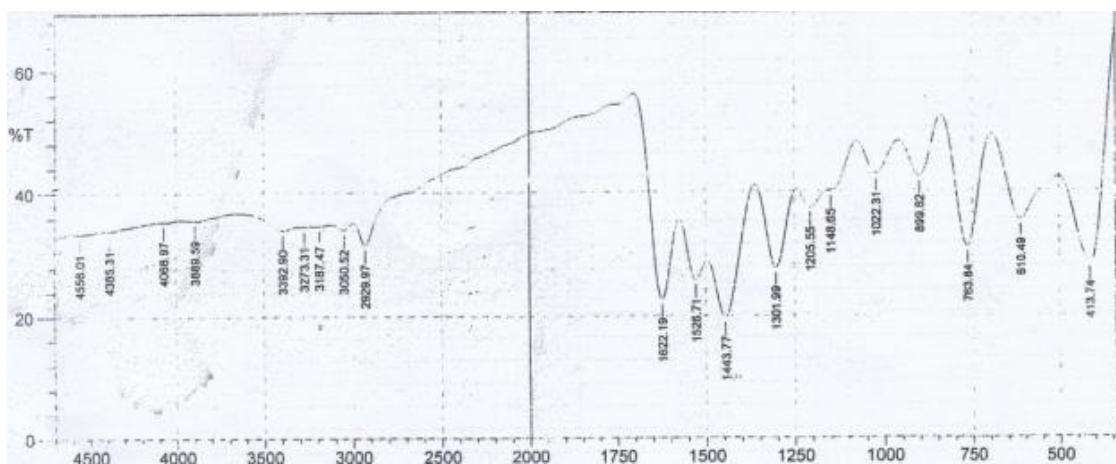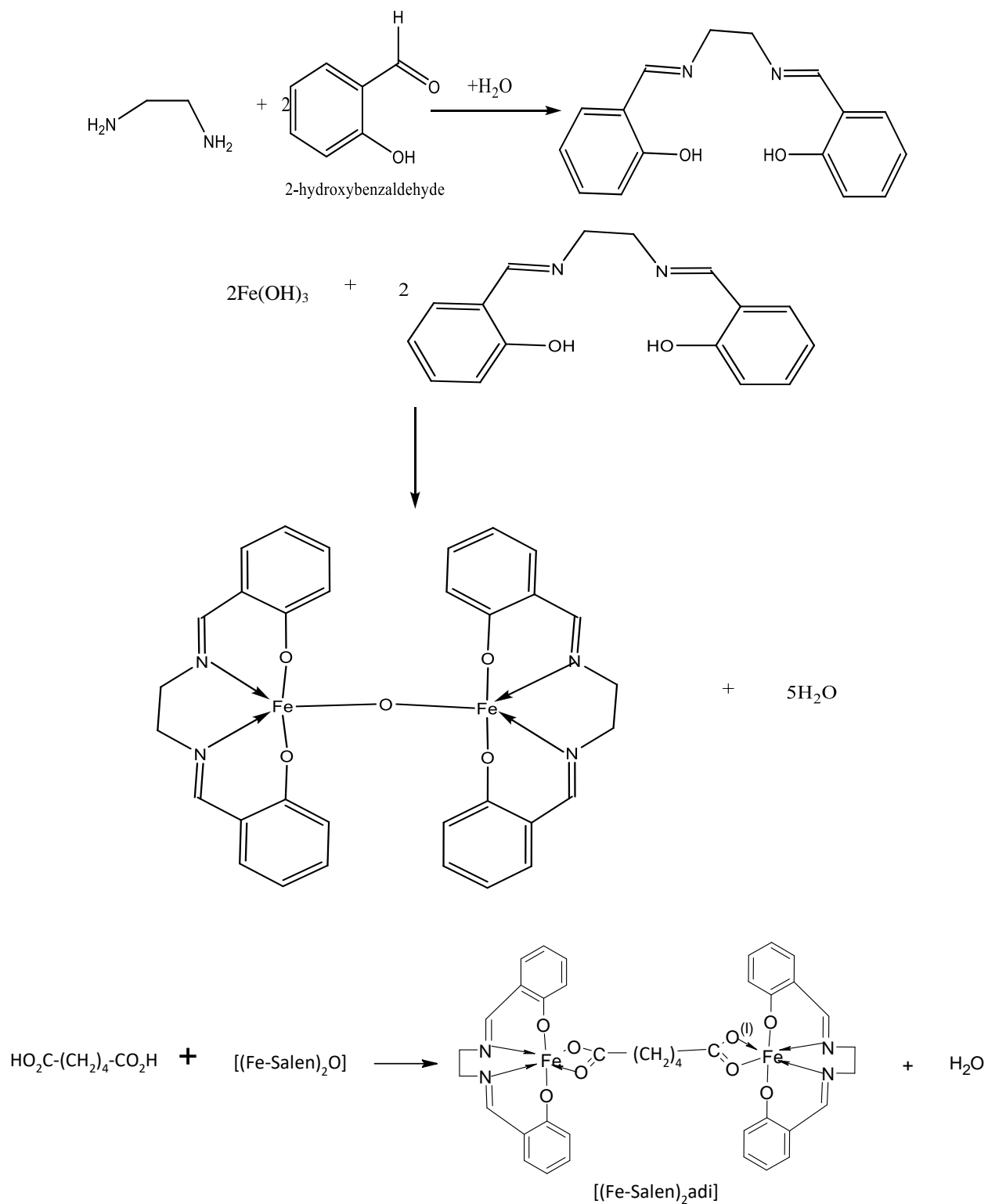

Figure1: Uv-Vis Spectrum of [(Fe-salen)$_2$adi].

Figure 2: FTIR Spectrum of [(Fe-salen)$_2$adi].

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

Standard solutions of reagent grade $HClO_4$ and $NaClO_4$ were used in adjusting the acidity and ionic strength, respectively, of the reaction media. Portions of propan-2-one were added to alter the dielectric constant of the reaction mixtures. Doubly distilled deionized water was employed for all investigations.

UV-Visible spectra of compounds were obtained on Unico 2012 and Jenway 6305 UV-Visible Spectrophotometer. FTIR Spectral data of the compounds on KBr discs were recorded using Shimdazu FTIR-84005 Fourier Transform Infrared Spectrophotometer.

Kinetic Measurements

Rate data for the disappearance of [(Fe-salen)$_2$adi] in the oxidation of thiourea (USH) and L-cysteine (LSH) to the disulfides was recorded as the decrease in absorbance of the reaction mixture at 495 nm. Having ascertained that at this wavelength the products of the reaction and the reductants did not absorb significantly, this wavelength was chosen to denote the rate of loss of the Fe(III) dimer.

Kinetic runs were conducted under pseudo-first order conditions of the concentration of the oxidants in large excess (> 20-fold) over the reductant. Within the boundaries of such conditions, kinetic decays were exponential and pseudo-first order rate constants k_{obs}, were obtained by fitting kinetic data into equation (1) as reported elsewhere[22-25].

$$\ln(A_t - A_\infty) = k_0 t + \ln(A_\infty - A_0) \quad \text{(1)}$$

Where A_∞ = final absorbance, A_t = absorbance at time t, A_0 = initial absorbance and k_0 = pseudo-first order rate constant. Specific rates for replicate runs were consistent and reproducible to within ±6%.

Gel formation by acrylamide in a partially reacted reaction mixture in excess methanol indicated presence of free radicals[7,8,13,14]. Stoichiometries for the reactions were determined following Spectrophotometric titration as reported elsewhere[7,8,13,14]. At a fixed concentration of [(Fe-salen)$_2$adi] (1×10^{-4} moldm^{-3}), concentrations of the reductants varied between 5×10^{-5} to 1×10^{-3} moldm^{-3} were reacted separately with the oxidant at $[H]^+$ = 1×10^{-3} moldm^{-3}, I = 1×10^{-2} moldm^{-3} (NaClO$_4$).

Stoichiometries were obtained as the point of inflexion on a A_∞ (final absorbance) versus mole ratio plot.

Quantum Mechanical Study

[(Fe-salen)$_2$adi] and protonated analogue [(Fe-salen)$_2$adiH$_2$]$^{2+}$ were optimized using the Hybrid Density Functional Theory (DFT) method at B3LYP/6-31G* levels of theory, which is the combination of functional hybrid exchange of Becke's three[26], with functional correlation gradient of Lee and Yang[27].

The heats of formation of [(Fe-salen)$_2$adi] and [(Fe-salen)$_2$adiH$_2$]$^{2+}$ were approximated using Semi-empirical Parameterized Method 3[28]. Geometric properties like bond length, selected dihedral angle between azomethine nitrogen atom and [(Fe-salen)$_2$adi]; electronic properties such as dipole moments and energy gap as well as thermodynamic properties such as entropy (ΔS^0) was calculated using HF-DFT-B3LYP/6-31G** levels of theory. All quantum chemical calculations have been performed using Spartan 14 Program Package.

RESULT AND DISCUSSION

Stoichiometry

Plots of A_∞ against mole ratio of reductant to the iron(III) dimer showed that one mole of [(Fe-salen)$_2$adi] was consumed for two moles of thiourea or one mole of L-cysteine oxidized. The results are consistent with equations (2) and (3). Earlier reports had indicated reduction of the Fe(III) dimer to the Fe(III) analogue[13-15, 18-19]. The evidence for its formation in this case was obtained by reacting the oxidant with excess of the reductant. On completion of reaction, the reaction mixture was acidified with HCl and treated separately with freshly prepared solutions of $K_3[Fe(CN)_6]$ and KCSN. $K_3[Fe(CN)_6]$ gave deep blue precipitate whereas KCSN gave blood-red coloration. These results indicate presence of Fe(II).

The FTIR spectra of the products was also compared with that of [(Fe-salen)$_2$adi] (Figure 3-4). Most of the bands in the complex appeared in the product.
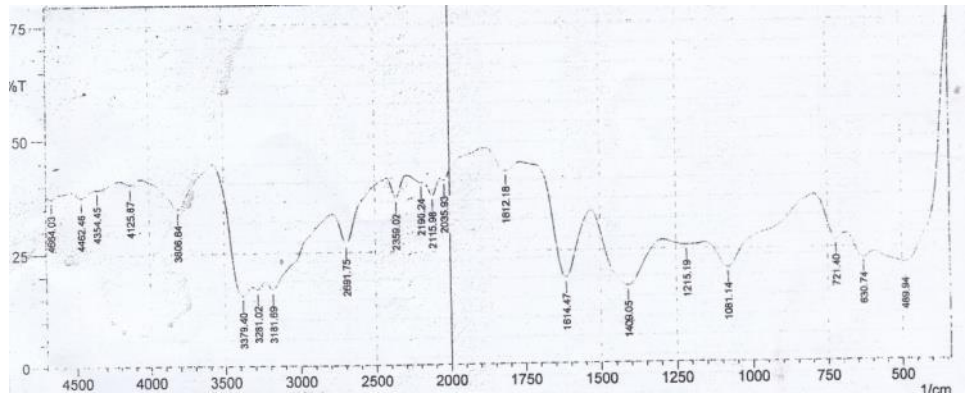
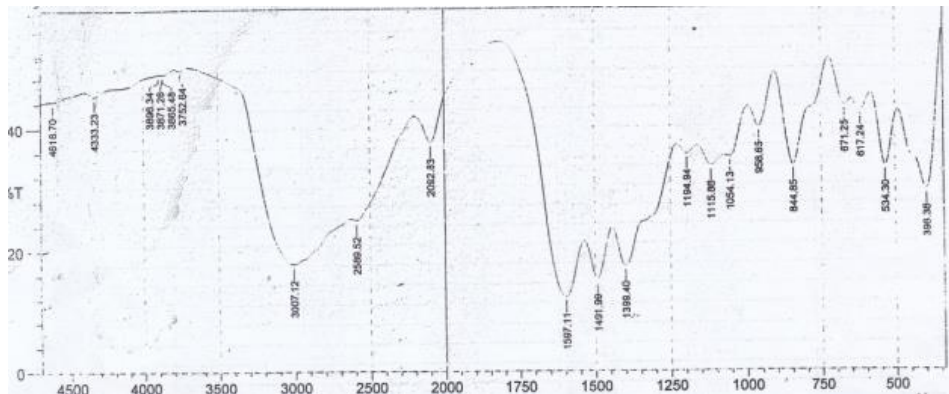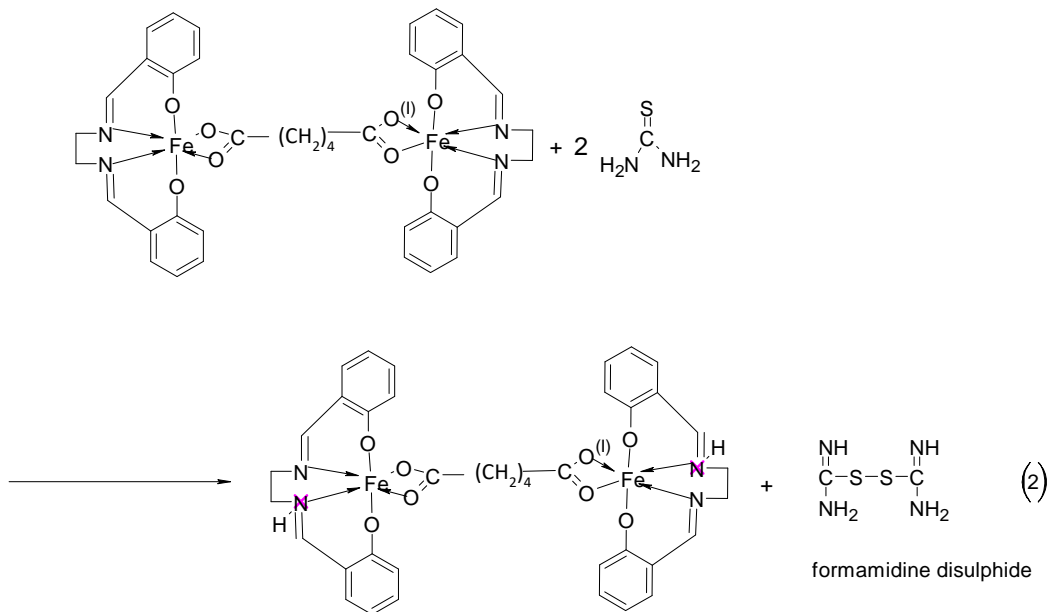**Figure 3:** FTIR Spectrum of Product of [(Fe-salen)$_2$adi] – USH Reaction.

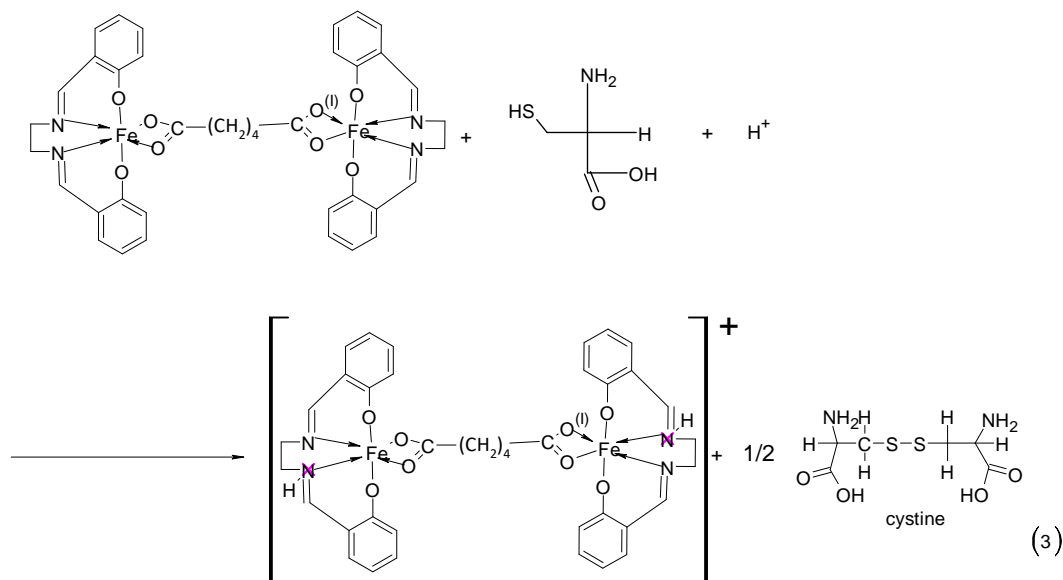**Figure 4:** FTIR Spectrum of Product of [(Fe-salen)$_2$adi] – LSH Reaction.


formamidine disulphide

(2)

The major difference is the broad bands at about 3281cm^{-1} (USH) and 3007cm^{-1} (LSH) which are not found in the spectrum of the complex. These bands are likely, $\acute{V}$(N-H) bands of the protonated iron(II) dimer. These observations were reported for the reduction of [(Fe-salen)$_2$adi] with SO$_3^{2-}$, S$_2$O$_4^{2-}$, S$_2$O$_6^{2-}$, benzyl mercaptan and mercaptobenzothiazole[13-15, 18-19]

Thiourea was oxidized to formamidine disulphide and L-cysteine to L-cystine. Formation of disulfides on oxidation of these reductants by metal ions had been reported earlier[29-33]. There is

general consensus that oxidation of sulfur donors having the thiol (S-H) group leads to disulfide as product especially in the presence of mild oxidizing agents whereas in acidic medium excess strong oxidizing agent like IO$_3^-$ can oxidize the disulfide to yield sulphoxides. Sulfur donors having R-S- group instead of –S-H where R=alkyl or phenyl groups are known to be oxidized to sulphoxides[34]. DL-methionine which consists of the CH$_3$-S- group was oxidized to sulfoxide by Pt(IV)[32], μ-oxoMn (III, IV)[34], K$_3$[Fe(CN)$_6$][35]and OS(VIII)[36] following a general route:

$$\text{(4)}$$
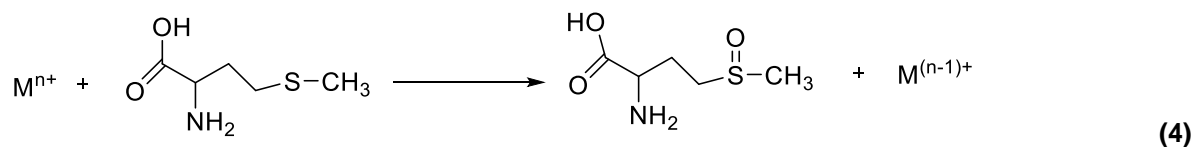
The general pattern of the reaction of those containing the –S-H group like L-cysteine[31-33], glutathione and DL-penicillamine[37] by metal ions is:

M^{n+} + RSH → 1/2RSSR + M$^{(n-x)+}$ **(5)**
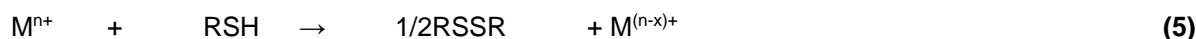
Thiourea is known to react as the enol form containing the sulfhydryl group[29-30,33,38-39] in the equilibrium state:

$$\text{(6)}$$

Its reaction follows the general pathway of R-SH compounds.

The organic product of the reactions was extracted using diethlyether, washed and dried. FTIR spectrum of the product showed significantly $V(C-S)$ weak band at 722 cm^{-1} but no $V(S=O)$ at 1055 cm^{-1} or $V(S-H)$ at 2250-2259 cm^{-1}. This result supports formation of disulfides and not sulfoxides.

Reaction Order

Pseudo-first order decays were linear to greater than 75% extent of reaction for both reactions thereby indicating first order dependence of rate on concentration of [(Fe-salen)$_2$adi]. Pseudo-first order and second order rate constants are displayed in Table 1. Second order rate constants, k_2, were determined as the ratio of k_0 to [reductants] and were constant at $6.0 \times 10^{-2} \pm 2.6 \times 10^{-3}$ dm^{3}mol^{-1}s^{-1} for USH-oxidant system and $9.91 \times 10^{-3} \pm 2.20 \times 10^{-4}$ dm^{3}mol^{-1}s^{-1} for LSH-oxidant system.

Table 1: Pseudo-First Order and Second Order Rate Constants for the Oxidation of Thiourea (USH) by [(Fesalen)$_2$adi] at [(Fesalen)$_2$adi] = 1×10^{-4} mol dm^{-3}, T = 29±1 ^{0}C and λ_{max}= 495 nm.

10^3 [USH] /(mol dm^{-3})	10^3 [H$^+$] /(mol dm^{-3})	10^3I /mol dm^{-3} (NaClO$_4$)	10^4 k_{obs} /s^{-1}	10^{-2} k_2 /(dm^{3}mol^{-1}s^{-1})
5.00	1.00	1.00	2.90	5.80
6.00	1.00	1.00	3.46	5.77
8.00	1.00	1.00	4.79	6.00
10.00	1.00	1.00	6.29	6.29
12.00	1.00	1.00	7.60	6.33
14.00	1.00	1.00	8.45	6.04
10.00	1.00	1.00	6.29	6.29
10.00	5.00	1.00	6.54	6.54
10.00	10.00	1.00	6.79	6.79
10.00	15.00	1.00	7.25	7.25
10.00	20.00	1.00	7.50	7.50
10.00	1.00	1.0	6.29	6.29
10.00	1.00	2.0	5.60	5.60
10.00	1.00	3.0	4.90	4.90
10.00	1.00	5.0	4.30	4.30
10.00	1.00	7.0	3.80	3.80

Table 2: Pseudo-First Order and Second Order Rate Constants for the Oxidation of L-cysteine (LSH) by [(Fesalen)$_2$adi] at [(Fesalen)$_2$adi] = 1×10^{-4} mol dm^{-3}, T = 29±1 ^{0}C and λ_{max}= 495 nm.

10^3 [LSH] /(mol dm^{-3})	10^3 [H$^+$] /(mol dm^{-3})	10^2I /mol dm^{-3} (NaClO$_4$)	10^5 k_{obs} /s^{-1}	10^3 k_2 /(dm^{3}mol^{-1}s^{-1})
3.00	1.00	1.00	3.00	10.00
4.00	1.00	1.00	3.90	9.75
5.00	1.00	1.00	4.80	9.60
6.00	1.00	1.00	5.90	9.83
7.00	1.00	1.00	7.10	10.14
8.00	1.00	1.00	8.10	10.13
5.00	1.00	1.00	4.70	9.40
5.00	5.00	1.00	6.50	13.00
5.00	10.00	1.00	13.70	27.40
5.00	15.00	1.00	14.70	29.40
5.00	20.00	1.00	16.40	32.80
5.00	25.00	1.00	23.00	46.00
5.00	1.00	1.0	4.80	9.6
5.00	1.00	2.0	4.15	8.3
5.00	1.00	3.0	3.70	7.5
5.00	1.00	5.0	3.35	6.7
5.00	1.00	7.0	2.70	5.4

Plot of log k_{obs} against log [USH] (Figure 5) was linear (R^2 = 0.996) with slope of 1.08, also similar plot (Figure 6) for the L-cysteine reaction was linear (R^2 = 0.996) with slope of 1.02. These results point to first order dependence of rate on concentrations of the reductants making each of the reactions second order overall. On the basis of this, the rate of reaction at constant pH can be given by equation (7).
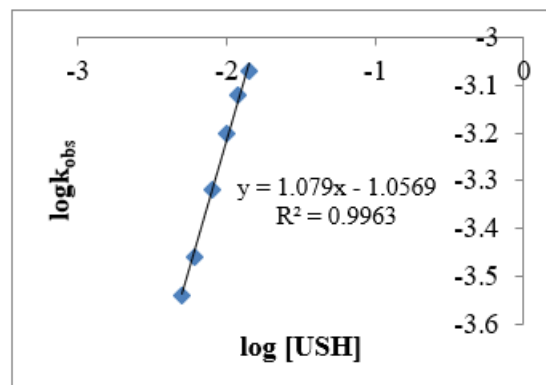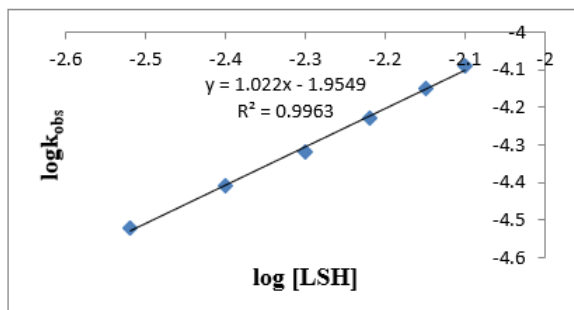

Figure 5: Plot of logk_{obs} versus log [USH]

Figure 6: Plot of $\log k_{obs}$ versus log [LSH]

$$\frac{-d[(Fe\ salen)_2 adi]}{dt} = k_2[(Fe\ salen)_2 adi][RSH] \quad (7)$$

Where RSH = USH or LSH

Earlier reactions of [(Fe-salen)adi] have occurred by first order dependence of rate on [(Fe-salen)$_2$adi][13-15, 18-19]. However, reduction of [(Fe-salen)$_2$adi] by some oxosulfur anions[13-15] were first order dependent on $S_2O_6^{2-}$ but zeroth order dependent on $S_2O_4^{2-}$ and SO_3^{2-} [13-15].

Reduction of [(Fe-salen)$_2$adi] by thiols benzylmercaptan showed inverse first order dependence of rate on concentration of benzyl mercaptan but β-mercaptobenzothiazole reduced it with first order dependence of rate on β-mercaptobenzothiazole. First order dependence of rate on thiourea and L-cysteine is in accord with their status as one-electron reductants implying stepwise reduction of the iron(III) centers leading to likely mixed valence Fe(III)-Fe(II) products stabilized by protonation[14].

Thiourea is reported to be oxidized according to equation (8) with redox potential (E^0) of 0.420V[30].

$$\text{(8)}$$
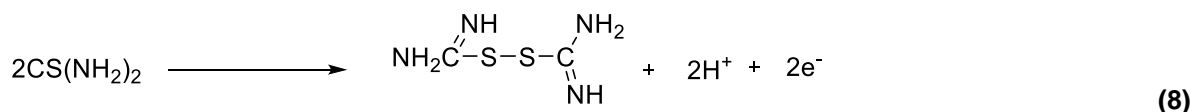
Its oxidation by metal ions is thought to occur as equations (9) and (10)[30,38].

$$\text{(9)}$$

$$\text{(10)}$$
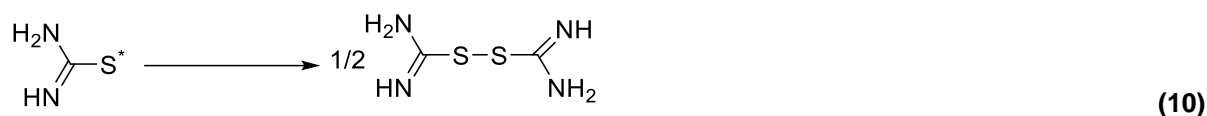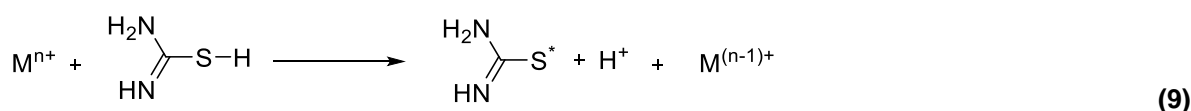
The reactions of L-cysteine follow the same format sometimes with the formation of thioester intermediates proving the one-electron reductant status of these compounds. Reduction of USH or RSH with [(Fe-salen)$_2$adi] could result in species of the form (equation 11).

RSH $+Fe^{(III)}$- adi-$Fe^{(III)} \rightarrow$ RS* + $Fe^{(III)}$- adi-$Fe^{(II)}$ + H^+ **(11)**
(RSH=USH or LSH)
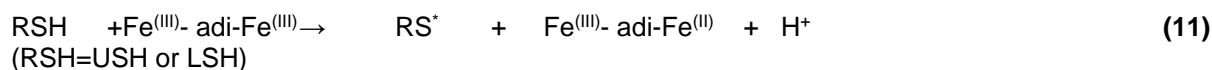
Acid Dependence

The effect of [H$^+$] on the reaction kinetics was investigated by varying the [H$^+$] using HClO$_4$ at 1.0x10^{-3} moldm^{-3} ≤ [H$^+$] ≤ 2.0x10^{-2} moldm^{-3} with other parameters kept constant. Under these conditions, the rate of reaction increased with increase in [H$^+$]. Acid catalysis is an indication of a pre-protonation step before electron transfer. This can be interpreted in terms of the reductants existing as RSH$_2$$^+$ in aqueous acid thereby suppressing the ionization of the thiols to give RS$^-$ as the active reductant species.

Reactions of thiourea with Ce(IV) involved monoprotonated species of thiourea at high acid concentrations (0.6 moldm^{-3})[29,33,38]. Some reactions of L-cysteine at high acid concentrations have also been proposed to occur having the monoprotonated form as the active reductant species[39,40]. However, at the acid concentration (pH = 3.0) of this reaction the thiols will exist mainly as RS$^-$ or RSH. The pKa of L-cycsteine for the formation of RS$^-$ is 8.18, so there is a high probability that at the low acidity of the reaction RS$^-$ will dominate. This has been proved to be the general case of reactions of thiols.

Acid dependence could also be arising from the protonation of the azomethine nitrogens in the oxidant to give the cation [(Fe-salen)$_2$adiH$_2$]$^{2+}$. This scenario has played out in the earlier reactions of [(Fe-salen)$_2$adi][13-15, 18-19]. For any of these protonation steps, the reaction will be acid-catalyzed. However, interaction of two positively charged species at the rate determining step will be very slow from the point of view of electrostatics. Because of repulsion between ions of like charges formation of encounter complexes, the so-called activated complex, will be rate limiting. Such reactions are common in literature and mostly occur by the outer-sphere mechanism. It is very likely that a more facile reaction will involve neutral RSH or RS$^-$ with the protonated oxidant, [Fe-salen)$_2$adiH$_2$]$^{2+}$.

Least square fits of k$_2$ against [H$^+$] (Figure 7) were linear (R^2=0.990) with slope of 0.65 dm^{6}mol^{-2}s^{-1} and intercept of 6.21x10^{-2} dm^{3}mol^{-2}s^{-1} for [(Fe-salen)$_2$adi]-USH, also similar plot (Figure 8) for [(Fe-salen)$_2$adi]-L-cysteine reaction was linear (R^2=0.944) with slope = 6.9842 dm^{6}mol^{-2}s^{-1} and intercept = -12.07x10^{-3} dm^{3}mol$^-$

^{2}s^{-1}. These results imply that dependence of rate of reaction on [H$^+$] can be fitted into equation (12).

Figure 7: Plot of k$_2$ versus [H$^+$] for USH-[(Fe-salen)$_2$adi] Reaction.

Figure 8 : Plot of k$_2$ versus [H$^+$] for LSH[-(Fe-salen)$_2$adi].

$$k_{H^+} = c + m[H^+] \qquad (12)$$

Where c and m are the intercepts and slopes and have the values given earlier. It also infers that the reactions proceed by two parallel routes, an acid-dependent pathway marked by m[H$^+$] and an acid-independent path marked by c. Values of m will incorporate mainly the protonation constants of the redox partners.

Protonation of [(Fe-salen)$_2$adi] to [(Fe-salen)$_2$adiH$_2$]$^{2+}$ as reported elsewhere[13-15] will result in disruption of the electron cloud on two of the azomethine nitrogens giving a more

reactive oxidant as interaction between the positively charged intermediate and neutral RSH or RS^- will be favored over neutral oxidant and neutral reductant[13-15].

Effect of Ionic Strength, Added Ions and Dielectric Constant (D)

The ionic strength of the reaction media was varied from 0.01 to 0.07 $mol dm^{-3}$ using $NaClO_4$ with other parameters kept constant. Under this condition the rate of reaction decreased with increase in ionic strength (Tables 1 and 2). The change in reaction rate with ionic strength indicates primary kinetic salt effect.

Table 3: Dependence of Rate Constants on Dielectric Constant (D) for the Oxidation of Thiourea Fe_2adi (USH) by [(Fesalen)$_2$adi] at [Fe_2adi] = 1×10^{-4} mol dm^{-3}, [USH] = 0.005 mol dm^{-3}, [H^+] = 1×10^{-3} mol dm^{-3}, I = 1×10^{-2} mol dm^{-3}($NaClO_4$), T = 29±1 ^{0}C, λ_{max}= 495 nm.

D	$10^4 k_{obs}$/s^{-1}
68.28	4.61
69.15	3.56
70.15	1.38
71.86	1.06
73.2	0.74

Table 4: Dependence of Rate Constant on Dielectric Constant (D) for the Reaction of [(Fe-salen)$_2$adi] with L-cysteine (LSH) at [(Fe-salen)$_2$adi] = 1×10^{-4} mol dm^{-3}, [LSH] = 0.05 mol dm^{-3}, [H^+] = 0.05 mol dm^{-3}, I = 0.05 mol dm^{-3}($NaClO_4$) and T = 29±1 ^{0}C.

D	$10^4 k_{obs}$ /s^{-1}	$10^3 k_2$/ dm^3 mol^{-1} s^{-1}
68.28	2.08	4.16
69.15	1.67	3.34
70.15	1.39	2.78
71.86	1.00	2.60

Table 5: Dependence of Rate Constant on added Ions, X, for the Oxidation of Thiourea (USH) by [(Fesalen)$_2$adi] at [Fe_2adi = 1×10^{-4} mol dm^{-3}, [USH] = 0.005 mol dm^{-3}, I = 0.01 mol dm^{-3}($NaClO_4$), T = 29±1 ^{0}C, λ_{max}= 495 nm and [$H]^+$ = 0.001 mol dm^{-3}.

X	10^3 [X]/(mol dm^{-3})	$10^4 k_{obs}$ / s^{-1}
Mg^{2+}	1.00	2.85
	2.00	2.72
	3.00	2.63
	4.00	2.42
	6.00	2.05
	8.00	1.72
CH$_3$CHOO$^-$	1.00	2.80
	2.00	2.65
	3.00	1.95
	4.00	1.82
	6.00	1.71
	8.00	1.54

Table 6: Dependence of Rate Constant on added Ions, X, for the Reaction of L-Cystine (LSH) by [(Fesalen)$_2$adi] at [Fe_2adi = 1×10^{-4} mol dm^{-3}, [LSH] = 0.05 mol dm^{-3}, I = 0.05 mol dm^{-3}($NaClO_4$), T = 29±1 ^{0}C, λ_{max}= 495 nm and [$H]^+$ = 0.05 mol dm^{-3}.

X	10^3 [X]/(mol dm^{-3})	$10^4 k_{obs}$ / s^{-1}	$10^3 k_2$/dm^3 $mol^{-1}s^{-1}$
Mg^{2+}	1.0	1.85	3.7
	3.0	1.72	3.44
	5.0	1.52	3.04
	6.0	1.41	2.82
	7.0	1.29	2.58
CH$_3$CHOO$^-$	1.0	2.95	4.00
	3.0	2.42	5.90
	5.0	2.30	4.60
	6.0	2.05	4.50
	7.0	1.52	5.10

For ionic reactions in solution, Debye-HÜckel equation or the modified Davies relation[41] (equation 13) provides that a plot of log k_r versus $I^{1/2}(I + I^{1/2})$ should be linear with slope of 1.02 $Z_B Z_C$ for ionic strength up to 0.1 $mol dm^{-3}$.

$$\log k_r = \log k_r^{\infty} + 1.02\ Z_B Z_C \left(\frac{I^{1/2}}{1 + I^{1/2}} - 0.30 I \right)$$

(13)

Where kr = rate constant for the reaction, k_r^{∞} = rate constant at infinite dilution, $Z_B Z_C$ are the charges on reacting species B and C, and I = ionic strength. For reactions where $++$ charges are involved at the rate determining step, the rate should increase with ionic strength but decrease with ionic strength where $+-$ charges are involved. Reactions involving neutral molecules at the rate determining step will be insensitive to change in ionic strength.

Plot of logk$_2$ versus $I^{1/2}(I + I^{1/2})$ gave slope of -1.87 for USH-[(Fe-salen)$_2$adi] and -1.97 for the LSH-[(Fe-salen)$_2$adi] reactions (Figures 9 and 10). The results indicate that the product of charges $Z_B Z_C$ for USH reaction is approximately -2 meaning operation of $+2-1$ or $+1-2$ charges at the rate determining step for both reactions. The implication of these results is that at the rate determining step, the active reacting species will be US$^-$ and [(Fe-salen)$_2$adiH$_2$]$^{2+}$ or LS$^-$ and [(Fe$_2$adiH]$^{2+}$. Such interaction will likely be the rate deterring step for the acid-catalyzed path.
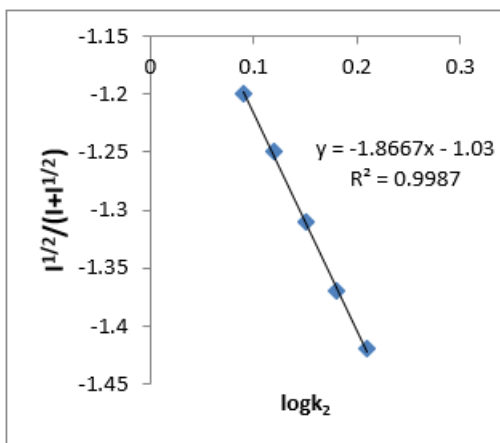

Figure 9: Plot of log k$_2$ versus $I^{1/2}(I + I^{1/2})$ for USH.

Variation of dielectric constant (D) from 71.86 to 68.28 using propan-2-one/H$_2$O water at [USH] = 0.05 moldm^{-3}, [H$^+$] = 0.05 moldm^{-3}, I = 0.2 moldm^{-3}, [(Fe-salen)$_2$adi] = 1x10^{-4} moldm^{-3} and T = 29^{0}C, rate of reaction increased with decrease in D (Table 3). Under the same conditions the rate of [(Fe-salen)$_2$adi]-L-cysteine reaction also increased (Table 4).
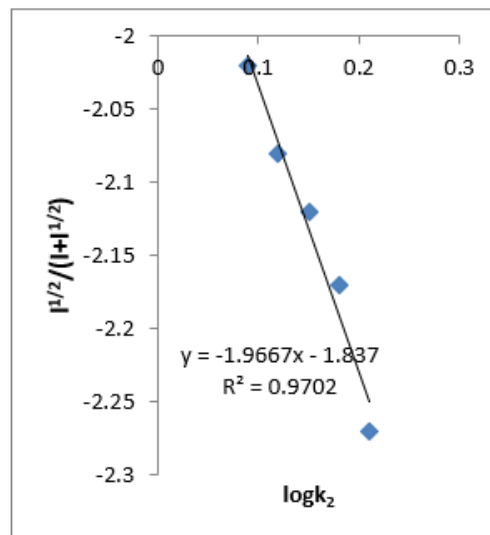

Figure 10: Plot of logk$_2$ versus $I^{1/2}(I + I^{1/2})$ for LSH.

Increase in rate of reaction as D decreases indicates ionic reactions where formation of ion-pairs or complexes is prominent in mediating the course or rate of reaction. This is because as D decreases, the force of attraction of the charges in solution will increase[42,43]. Plot of log k versus 1/ D gave a positive slope in accord with equation (14).

$$\ln k = \ln k_0 - \frac{Z_A Z_B e^2}{D k T r_{\pm}}$$ (14)

(where k = rate constant for the reaction, k_0 = rate constant in a medium of infinite dilution, D = dielectric constant, r$_{\pm}$ is radius of the charges Z_A and Z_B of reacting species.)

These results imply interaction of redox partners of opposite charges at the rate determining step thereby implicating [(Fe-salen)$_2$adiH$_2$]$^{2+}$ reaction with US$^-$ or LS$^-$. Addition of small amounts of Mg^{2+} and CH$_3$COO$^-$ at I = 0.5 moldm^{-3} (NaClO$_4$), [reductant] = 0.05 moldm^{-3}, [(Fe-salen$_2$adi] = 1x10^{-4} moldm^{-3} led to slight reduction in the reaction rate as the amount of added ions increased (Tables 5 and 6). This is a common feature of outer-sphere reactions where the redox partners carry opposite charges[42]. Added ions could retard the rate of reaction since coordination to any of reactants could reduce the degree of attraction between the reactants. This also increases the distance between the redox partners thereby slowing down the rate of

electron transfer[44-45]. This phenomenon strongly indicates lack of operation of inner-sphere electron transfer mechanism. This assertion corroborates earlier assertion that the reaction of [(Fe-salen)$_2$adi] with thiourea and L-cysteine most likely involves [(Fe-salen)$_2$adiH$_2$]$^{2+}$ and US$^-$ or LS$^-$ at the rate determining step and most probably operates through the outer-sphere path.

Michaelis-Menten-type plot of 1/k_{obs} versus 1/[reductant] for both reactions (Figures 11-12) were linear with insignificant intercepts. This is indicative of formation of intermediates with very small equilibrium constant and points to outer-sphere electron transfer path for the reduction of the dimer by these reductants.
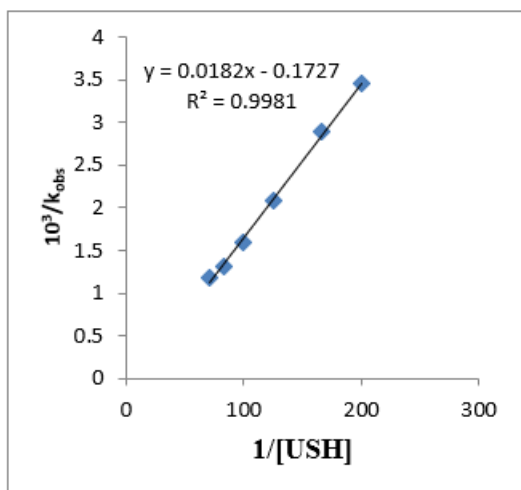

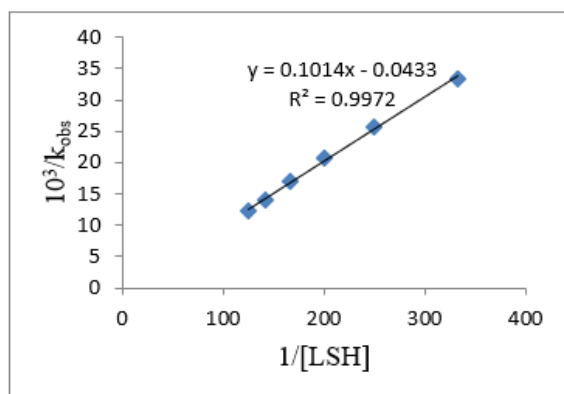**Figure 11:** Michaelis-Menten- Type Plot of 10^3/k_{obs} vs 1/[USH].

Figure 12: Michaelis-Menten- Type Plot of 10^3/k_{obs} vs 1/[LSH].

Temperature Dependence

As the temperatures of the reaction were varied from 283-303 K, with [(Fe-salen)$_2$adi] = 1x10^{-4} moldm^{-3}, [H$^+$] = 0.05 moldm^{-3}, [reductant] = 0.05 moldm^{-3} and I = 0.5 moldm^{-3}, the rate of reaction increased with temperature (Tables 7 and 8).

Fitting the derived data into the Eyring-Polanyi equation (15)[13] and the Arrhenius equation (16)[42] plots of log(k_2/T) against 1/T (Figures 13 and 14) and logk_2 against 1/T (Figures 15 and 16) yielded the activation parameters (Table 9).

Table 7: Temperature Dependent Rate Constants for the Reaction of Fe$_2$adi with USH at [Fe$_2$adi] = 1x10^{-4} mol dm^{-3}, [USH] = 0.005 mol dm^{-3}, [H$^+$] = 1x10^{-3} mol dm^{-3}, I = 1x10^{-2} mol dm^{-3}(NaClO$_4$), T = 29±1 ^{0}C , λ$_{max}$= 495 nm.

X	Temp (K)	10^4 k_{obs} /s^{-1}	Log(k_{obs}/T)	10^3 (1/T)(K^{-1})
USH	283	1.42	-6.30	3.53
	288	1.86	-6.19	3.47
	293	2.15	-6.13	3.41
	298	2.45	-6.09	3.36
	303	2.97	-6.01	3.30

Table 8: Temperature Dependent Rate Constants for the Reaction of Fe$_2$adi with LSH at [(Fe$_2$adi] = 1x 10^{-4} mol dm^{-3}, [LSH] = 0.005 mol dm^{-3}, I = 0.05 mol dm^{-3}(NaClO$_4$), T = 29±1 ^{0}C, λ$_{max}$= 495 nm and [H]$^+$ = 0.05 mol dm^{-3} .

X	Temp (K)	10^4 k_{obs} /s^{-1}	Log(k_{obs}/T)	10^3 (1/T)(K^{-1})
LSH	283	0.85	-6.52	3.53
	288	1.29	-6.35	3.47
	293	1.62	-6.26	3.41
	298	3.18	-5.97	3.36
	303	5.18	-5.77	3.30

$$\log \frac{k_{obs}}{T} = \log \frac{k}{h} + \frac{\Delta S^{\neq}}{2.303R} - \frac{\Delta H^{\neq}}{2.303RT} \qquad (15)$$

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.

$$\ln k_{obs} = \ln(A) - \frac{Ea}{RT} \qquad (16)$$

Where k_{obs} = temperature dependent rate constant,
and T = different temperatures,
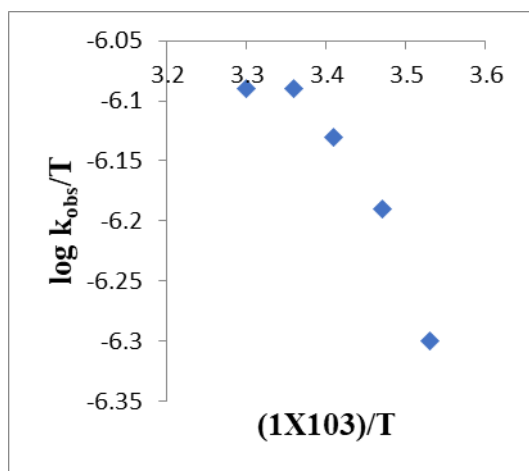E_a = Activation Energy,
R = universal gas constant.

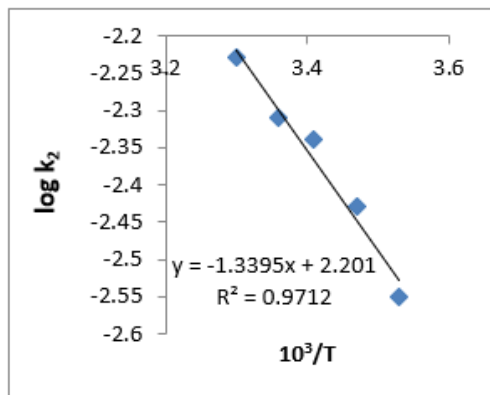**Figure 13:** Plot of log k_{obs}/T against 1/T for USH.

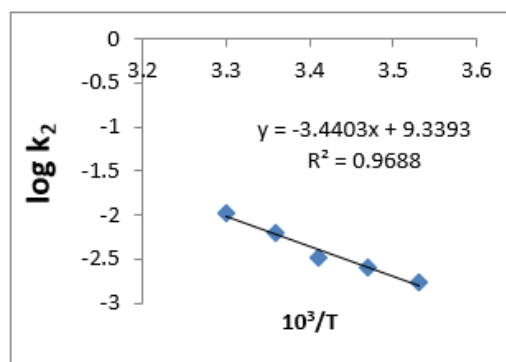**Figure 14:** Plot of log k_{obs}/T against 1/T for LSH.

Figure 15: Plot of log k_2 against 1/T for USH.

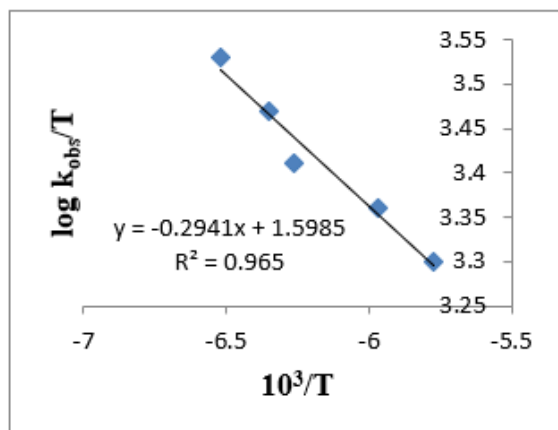**Figure 16:** Plot of log k_2 against 1/T for LSH.

Table 9: Activation Parameters for the Reaction of [(Fe-salen)$_2$adi] with Thiourea (USH) and L-cysteine (LSH).

X	$\Delta G^{\neq}/kJmol^{-1}$	$\Delta Ea^{\neq}/kJmol^{-1}$	$\Delta H^{\neq}/kJmol^{-1}$	$\Delta S^{\neq}/JK^{-1}mol^{-1}$
USH	28.609	25.64	7.62	-69.51
LSH	57.06	65.87	2.44	-108.00

The enthalpy of activation, $\Delta H^{\neq}$ for both reactions are similar: 2.44 kJmol^{-1} (LSH) and 7.62 kJmol^{-1} (USH). These positive values indicate enthalpy controlled (endothermic) system which is a common feature of slow reactions. Reaction of DL-Methionine with HCF had energy of activation of 55.7 kJmol^{-1} and occurred by the outer-sphere mechanism[35]. Similar enthalpies have been reported for slow outer-sphere reactions[13,15].

Negative values of entropy of activation $\Delta S^{\neq}$, -69.513 Jmol^{-1}K^{-1} (USH), -108.00 Jmol^{-1}K^{-1} (LSH), are indicative of associative process, which could be the result of formation of ion-pairs of outer-sphere character[13, 15, 37]. The positive $\Delta G^{\neq}$ of the reactions also point to slow, non-spontaneous reaction.

The high activation energies 25.64 kJmol^{-1} (USH) and 65.87 kJmol^{-1} (LSH) point to slow reactions. The bulkiness of oxidant coupled with its substitution inertness will not only pose a degree of steric hindrance but will decrease the probability of substitution to the inner-sphere. This is a veritable condition for an outer-sphere reaction.

Ab Initio Calculations

For a better understanding of the redox dynamics of [(Fe-salen)$_2$adi] with the various reductants, we investigated the nature of [(Fe-salen)$_2$adi] vis avis the protonated form [(Fe-salen)$_2$adiH$_2$]$^{2+}$.

The molecular structures and numbering [Fe$_2$adi] and [Fe$_2$adiH$_2$]$^{2+}$ are presented in Figures 17a and 17b. The point group of optimized structure (Figure 18) of unprotonated and protonated [Fe$_2$adi] was C1.

The ground state geometric optimization was performed and the result presented in Table 10 together with the available experimental values of Fe complex. The Fe-N bond lengths in [(Fe$_2$adi] designated as 1 and 2 in the molecular structure are similar ($\sim$ 1.86 Å) but $\sim$0.068 Å shorter than its protonated form. This repeating prototype is observed for Fe-O, but in this case a decrease in the bond length was noticed. The bond length for the Fe$_2$O$_2$ in [Fe$_2$adi] is $\sim$0.056 Å longer than [Fe$_2$adi]H$_2$$^{2+}$. The predicted DFT bond length in the [Fe$_2$adi] agrees with the experiment within 0.006 Å.

The calculated dihedral angle for both molecules shows a large deviation from planarity which might be the reason for the C1 point group observed. Atomic charge distribution of Fe significantly changed in [Fe$_2$adi] due to protonation. There is an increase in negative charge at Fe (by about 0.073) followed by a significant charge (positive) increase at the azomethine nitrogen atom by (0.12). This marked increase may be attributed to the destabilization of the [Fe$_2$adi] as a result of the protonation which drives electron transfer process. This increase may also be based upon the fact that there is steric interaction between the Fe atom and the N atom upon protonation.

Electric dipole moment (D$_m$) is an important parameter in structural and spectroscopic chemistry. The Dipole moment of [Fe$_2$adi] was determined using DFT method; this was done by assessing the electron density at each point in the molecule and its coordinates relative to the molecule.
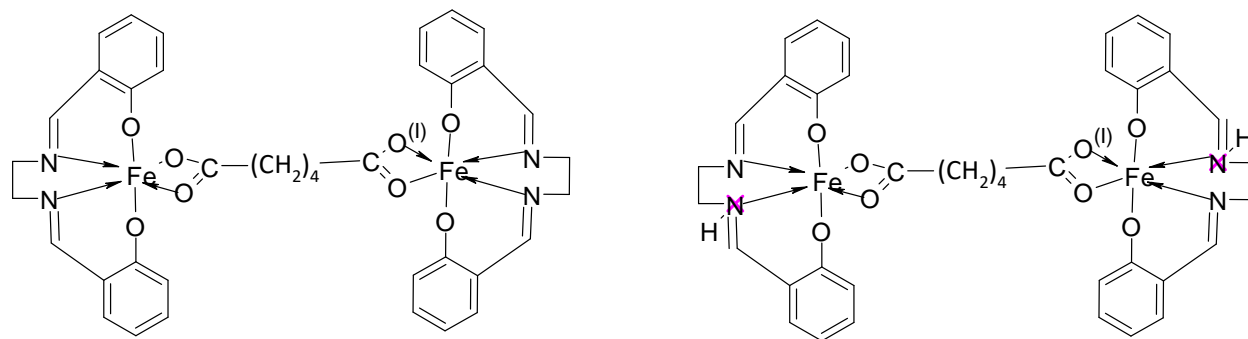
The D$_m$ of [Fe$_2$adi] complex was calculated as 18.69 D, but interestingly upon protonation (2H$^+$) the dipole moment decreased to 15.13 D (Table 10), which may be as a result of the effect of protonation on the azomethine nitrogen atom linked to the complex. This is also in conformity with the account of Hinchiffe and Munn[46, 47], that when a molecule is subjected to an electric field, it may result in the distortion of the molecular charges of the molecule leading to a change in the dipole moment. This change can be expressed by equation (17).

$$D_m = D_{M,0} + \alpha : E + \frac{1}{2}\beta : EE + \cdots \qquad (17)$$

Where α represents the dipole polarizability which is the second rank tensor quantity, D_m is the permanent dipole moment in the absence of a field and β is the hyperpolarizability.

In quantum systems, fluctuations occur in their ground state because they possess allied zero-point energy (ZPE), a corollary of their wave-like character. The uncertainty principle requires every physical system to have zero point energy greater than the minimum of its classical potential well. ZPE evaluates the thermodynamic stability of a system, the more positive the ZPE, the more stable it appears[47].
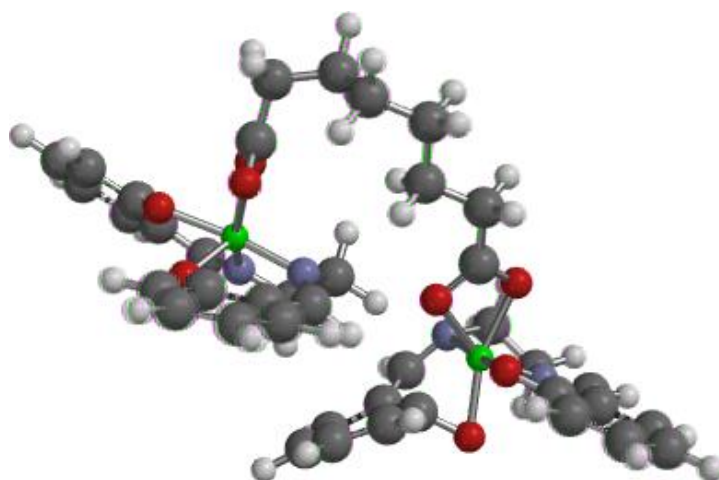
From Table 10, a higher stability is seen in [Fe$_2$adi] due to protonation on the azomethine nitrogen atom which may suggest [Fe$_2$adi]H$_2$$^{2+}$ as a better oxidant than the unprotonated form. ΔG^0 and ΔS^0 were calculated as -1991.7 and 873.91 kJ/mol respectively. The values ΔG^0 and ΔS^0 indicate that the protonation of the azomethine nitrogen atom and electron transfer process is very facile.
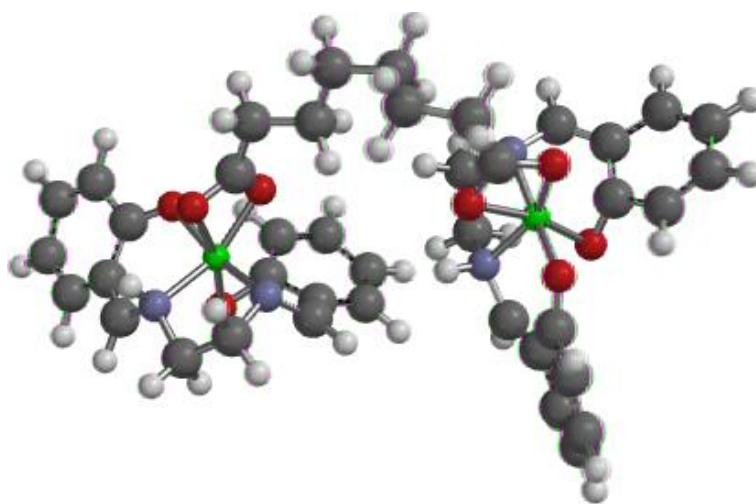
Figure 17: Structure of [(Fe-salen)$_2$adi] (a) and [(Fe-salen)$_2$adiH$_2$]$^{2+}$(b).

(a)

(b)

Figure 18: DFT of the Optimized Structures of (a) [(Fe$_2$adi] and (b)[(Fe$_2$adi]H$_2$ $^{2+}$ Complex.

Table 10: Optimized Geometry and Selected Properties of [Fe₂adi] and [Fe₂adi]H₂²⁺ using DFT-B3LYP/6-31G** Basis Set and Experimental Data are Shown for Comparison.

Parameters	[Fe₂adi]	[Fe₂adi]H₂²⁺	Expt
Selected Bonds (Å)			
Fe1-O1	1.979	1.970	1.985[b]
Fe1-N1	1.856	1.924	1.972[a]
Fe1-O2	2.003	1.947	1.985[b]
Fe1-N2	1.859	1.911	1.972[c]
Selected Dihedral Angles			
N1-Fe1-O1-C1	100.151	175.28	-
N1-Fe2-O2-C2	108.66	80.23	-
Atomic Charges			
Fe1	-0.234	-0.307	-
Fe2	-0.224	-0.308	-
N1	-0.065	-0.037	-
N2	+0.447	+0.563	-
Properties [Method - single point calculations]			
Dipole moment (D)	18.69	15.13	
ZPE(kJ/mol)	1956.00	2022.98	

Mechanisms of Reactions

To arrive at the mechanisms of the reactions, consideration is given to the generated kinetic data: acid-dependence, effect of ionic strength, influence of dielectric constant, catalysis by added ions, Michaelis-Menten-type plot, temperature dependence and stoichiometries of the reactions. The following scheme has been proposed. (RSH = USH or LSH).

$$[Fe(salen)_2adi] + 2H^+ \underset{K_1}{\rightleftharpoons} [Fe(salen)_2adiH_2]^{2+} \tag{18}$$

$$RSH \underset{K_2}{\rightleftharpoons} RS^- + H^+ \tag{19}$$

$$[Fe(salen)_2adiH_2]^{2+} + RS^- \xrightarrow{k_3, \ Slow} [Fe(salen)_2adiH_2,RS] \tag{20}$$

$$[Fe(salen)_2adiH_2,RS] \xrightarrow{k_4, \ fast} [Fe(salen)_2adiH_2]^+ + RS^* \tag{21}$$

$$[Fe(salen)_2adi] + RSH \xrightarrow{k_5, \ Slow} [Fe(salen)_2adi,RS] + H^+ \tag{22}$$

$$[Fe(salen)_2adi,RS] \xrightarrow{k_5, \ fast} [Fe \ salen \ adi]^- + RS^* \tag{23}$$

$$[Fe(salen)_2adi]^- + 2H^+ \rightarrow [Fe(salen)_2adiH_2]^+ \tag{24}$$

$$RS^* + RS^* \rightarrow RSSR \tag{25}$$

Rate of reaction = $\frac{-d[Fe(salen)_2adi]}{dt} = k_3[Fe(salen)_2adiH_2^{2+}] [RS^-] + k_5 [Fe(salen)_2adi][RSH]$ (26)

Applying steady state approximation,

$$[Fe(salen)_2adiH_2^{2+}] = K_1[Fe(salen)_2adi] [H^+]^2 \tag{27}$$
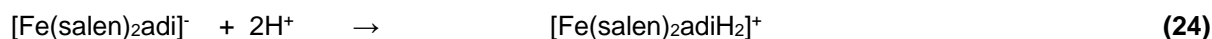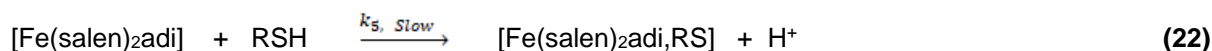
Also $[RS^-]$ = $k_2\dfrac{[RSH]}{[H^+]}$ **(28)**

Substituting equation (27) and (28) into (26) gives:

$\dfrac{-d[Fe(salen)_2adi]}{dt} = k_3k_1\,k_2[Fe(salen)_2adi]\,[H^+][RSH] + k_5[Fe(salen)_2adi]\,[RSH]$ **(29)**

Rate = $k_3k_1\,k_2[H^+] + k_5[Fe(salen)_2adi]\,[RSH]$ **(30)**

Equation (30) is similar to equation (12) where $m = k_3k_1\,k_2$ and $c = k_5$.

The mechanism of oxidation of thiourea and L-cysteine by [Fe(salen)$_2$adi] with regard to kinetic data has been resolved on the basis of the following:

i. Direct acid-dependence of the reaction has been resolved on the basis of protonation of two of the azomethine nitrogens of the oxidation to give the dipositve cation $[Fe(salen)_2adiH_2]^{2+}$ with the protonation constant Kp(K$_1$). Kp is large enough and mediates the rate of the reaction (equation 18)

ii. Negative dependence of rate on ionic strength is because of involvement of redox partners of opposite charge at the rate determining. This is reasoned to involve RS$^-$ and $[Fe(salen)_2adiH_2]^{2+}$ giving charge product of -2 for the acid-dependent path (equation 20).

iii. Retardation of the reactions by added anions and cations is in accord with reactions operating by the outer-sphere pathway where oppositely charged redox partners are involved (equation 20).

iv. Inverse dependence of rate on dielectric constant confirms involvement of redox partners of opposite charges at the rate determining step as force of attraction will be enhanced at low D thereby increasing rate of reaction.

v. Plot of $1/k_{obs}$ vs $1/$ [reductant] was linear with insignificant intercept thereby ruling out intermediates of large equilibrium constant, thereby inferring operation of outer-sphere mechanism.

vi. Interaction of $[Fe(salen)_2adiH_2]^{2+}$ and RS$^-$ will be the rate determining step whereas the intramolecular electron transfer in the ion-pair complex (equation 21) will be fast. This is a substitution-controlled reaction, and such reaction should be very slow. The rate of electron transfer is faster than the rate of precursor complex formation[48-49].

vii. Theoretical quantum chemical studies indicated $[Fe(salen)_2adiH_2]^{2+}$ is a more facile oxidant than [Fe(salen)$_2$adi] corroborating generated kinetic data. These deductions strongly support the view that the reduction of [Fe(salen)$_2$adi] by L-cysteine and thiourea follow the outer-sphere electron transfer route in agreement with proposed reaction scheme.

CONCLUSION

Kinetic data generated as a result of investigation of the reduction of the adipato bridged iron(III) dimer, [Fe(salen)$_2$adi], by thiourea and L-cysteine have led to the proposal of the rate law:

$\dfrac{-d[Fe(salen)_2adi]}{dt} =$ k_3K_1 $K_2[H^+][RSH]$ + $k_5[Fe(salen)_2adi]\,[RSH]$

Where RSH = thiourea or L-cysteine

The proton coupled electron transfer process is rationalized on the basis of protonation of the oxidant to give the postcursor complex, $[Fe(salen)_2adiH_2]^+$ for the L-cysteine reaction likely having mixed valence Fe(III)-Fe(II) centers and $[Fe(salen)_2adiH_2]$ for the thiourea reaction[50].

REFERENCES

1. Housecroft, C.E. and A.G. Sharpe. 2008. *Inorganic Chemistry. 3rd Ed.* Pearson Education Ltd. London, UK. 962-963.

2. Abboud, S. and D.J. Haile. 2008. "A Novel Mammalian Iron-Regulated Protein Involved in Intracellular Iron Metabolism". *J. Biol. Chem.* 275(26): 19906-19912.

3. Leigh, J.G., G.R. Moore, and M.T. Wilson. 1993. *Biological Iron in Chemistry of Iron.* J. Silver (ed,) Blackie: London, UK. 181.

4. Zang, D., M.C. Ghosh, and T.A. Rouault. 2014. "The Physiological Functions of Iron Regulatory Proteins in Iron Hoeostsis: An Update". *Front Pharmocol.* 5: 124.

5. Nair, V.S. and K.S. Hagen. 1992. *Inorg Chem.* 31(20): 4048-4050.

6. Karpishin, T.B, T.M. Dewey, and N.K. Raymon. 1993. *J. Am. Chem Soc.* 115(5): 1842.

7. Smekal, Z., F. Brezina, Z. Sindelar, R. Klicka, and M. Naduornik. 1996. *Trans. Met. Chem.* 21: 49-51.

8. Ukoha. P.O. and J.F. Iyun. 2001. *J. Chem. Soc. Nigeria.* 26: 163-168.

9. Okamura, M.Y., M. Wotzt, C.E. Johnson, M.R.C. Winter, and R.J.P. William. 1996. *Biochem* 8: 1951-1958.

10. York, J.R. and A.J. Bearden. 1970. *Biochem.* 9: 4549-4554.

11. Cohen, I.A. 1969. *J. Am.Chem-Soc.* 91: 1980-1983.

12. Scadasivan, N., H.I. Eberspaecher, W.H. Fuschsman, and W.S. Caughey. 1969. *Biochem.* 8: 534-541.

13. Atiga, S, P.O. Ukoha O.T. Ujam, and O.C. Okpareke. 2014. *Trans Met. Chem.* 39: 189-194.

14. Ukoha, P.O., S. Atiga, O.T. Ujam, J.N. Asegbeloyin, O.C. Okpareke, and S.O.E. Okereke. 2015. *Croat Chem. Acta.* 88(3): 259-266.

15. Atiga, S., P.O. Ukoha, and O.T. Ujam. 2015. *Asian Journal of Chemistry.* 27(4): 1274-1278.

16. Idris, S.O., J.F. Iyun. and E.B. Agbaji. 2009. *Trans Met Chem.* 34: 205-208.

17. Ukoha, P.O. and J.F. Iyun. 2005. *J.Chem Class.* 2: 51-54.

18. Ugwuanyi, K.O. and P.O. Ukoha. 2015. "Kinetics and Mechanism of the Reduction of [(Fe-salen)2adi] with Benzyl Mercaptan". *Proc. 38th International Conf. Chemical Society of Nigeria.* 401-414.

19. Ugwuanyi, K.O. and P.O. Ukoha. 2017. "Kinetics and Mechanism of the Reduction of [(Fe-salen)2adi] with 2-mercaptobenzothiazole in Aqueous Perchloric Acid". *Nigeria Research Journal of Chemical Science.* 3: 41-50.

20. Ukoha, P.O., C.O. Anidobu, P.D. Ioriengwa, and I.C. Oluigbo. 2018. "Kinetics and Mechanism of Reduction of [(Fe-saloph)2 -I-dicarpy] Complex by L-ascorbic acid in Acid Medium". *FUW Trends Science Technology Journal.* 3(1): 158-162.

21. Kopel, P., Z. Sindelar, and R. Klicka. 1998. "Complexes of Iron(III) salen and saloph Schiff Bases with Bridging Dicarboxylic and Tricarboxylic Acids". *Transition Met. Chem.* 23: 139-142.

22. Alioke, C.U., P.O. Ukoha, N.M. Ukwueze, O.T. Ujam, and J.N. Asegbeloyin. 2012. "Kinetics and Mechanism of the Reduction of the N,N1-salicylideneiminatoiron(III) Complex Ion by L-ascorbic acid in Aqueous Acid Medium". *Chemistry and Materials Research.* 2(7): 48-57.

23. Zhang, J., S. Huo, S. Shen, and Y. Shang. 2013. "Kinetic and Mechanistic Studies of the Oxidation of Pyrrolidine by bis(hydrogen-periodato)argentite(III) Complex Ion". *Trans. Met. Chem.* 38: 15-20.

24. Al-Blewi, F.F., H.A. Al-Lohedan, M.Z.A. Rafiguee, and Z.A. Issa. 2012. "Kinetics of Hydrolysis of Procaine inn Aqueous and Micellar Media". *International J. Chemical Kinetics.* Doi 10.1002/kin.20735.

25. Ewais, H.A., S.S. Ahmed, and A.A. Abdel-khalek. 2004. "Kinetics and Mechanism of Oxidation of Chromium(III)-glanosine 5-Monophosphate Complex by Periodate". *J. Chinese Chemical Society.* 51: 713-718.

26. Galinato, M.G.I., C.M. Whaley, D. Roberts, P. Wang, and N. Lehnert. 2011. "Favorable Protonationof the (I-edt)[Fe2(PMe3)4-(CO)2(H-termina)] + Hydrogenade Model Complex over its

bridging I-H counterpart A Spectroscopic and DFT-Study". *Evr. J. Inorg. Chem.* 1147-1154.

27. Grimme, S. 2011. "Density Functional Theory with London Dispersion Corrections". *Computational Chemistry and Molecular Modelling.* 12: 211-228.

28. Becke, A.D. 1993. *J. Chemical Physical.* 5648-5652.

29. McAuley, A. and U.D. Gomwalk. 1969. "Metal-ion Oxidation in Solution. Part VI- Oxidationof Thiourea and its N-Substituted Derivatives by Cobalt(III)". *J. Chem. Soc (A).* 977-980.

30. Durovic, M.D., R. Puchta, Z.D. Bagarcic, and R. Van Eldik. 2014. "Studies on the Reactions of [AuCl4]- with Different Nucleophiles in Aqueous Solution". *Dalton Transactions.* 43: 8120-8632.

31. Iyun, J.F. and K.Y. Musa. 1996. "Kinetics of the Reduction of I-oxobis[aquabis(2,21-bipyridine)-ruthenium(III)] by L-cysteine in Aqueous Solution". *Indian J. Chemistry.* 35A: 210-213.

32. Jonavic, S., B. Petrovic, Z.D. Bugarcic, and R. Van Eldik. 2013. "Reduction of some Pt(IV) Complexes with Biologically Important Sulfur-Donor Ligands". *Dalton Transaction.* 42: 8890-8896.

33. Zneva, T.S., E.V. Protopopov, and I.A. Ivanov. 1986. "Role of Thiols (Cysteine and Thiourea) in the Mechanism of the Periodic Decomposition of Hydrogen Peroxide by Potassium Iodate in an Acid Medium". *Teoretricheskayai Eksperimental'naya Khimiya*, 26: 51-56.

34. Lohdip, Y.N. and J.F. Iyun.1998. "Kinetics of Reduction of Di- I-oxo-tetrakis(1,10-pheanthroline)-dimanganese (III, IV) perchlorate by DL-Methionine in Acid Solution". *Bull. Chem. Soc. Ethiop.* 12(2): 1-7.

35. Sharanabasamma an Tuwar S.M. 2010. "Kinetics and Mechanism of Oxidation of DL-Methionine by hexacyanoferrate(IV) in Aqueous Alkaline Medium". *J,.Sulfur. Chem.* 31(3): 177-182.

36. Jose, P.T., S.T. Nandibewoor, and S.M. Tuwar. 2006. "Osmium(VIII) Catalyzed Oxidation of a Sulfur Containing Amino Acid- A Kinetics and Mechanistic Approach". *J. Sulfur Chem.* 27(1): 25-36.

37. Dixon, D.A., T.P. Dasgupta, and N.P. Sadler. 1995. "Mechanism of the Oxidation of the Oxidation of DL-Penicillamine and Glutathione by Chromium (VI) in Aqueous Solution". *J. Chem. Soc. Dalton Trans.* 2267-2271.

38. Gomwalk, U.D. and A. Mc Auley. 1968. "Metal-ion Oxidations in Solution. Part V. Cerium (IV) Oxidation of Thiourea and its N-Substituted Derivatives". *J. Chem. Soc (A).* 2948-2951

39. Ukoha, P.O., O.T. Ujam, J.F. Iyun, and S.O.E. Okereke. 2015. "Mechanism of Oxidation of L-cysteine by tetraoxo-iodate(VII) in Aqueous Acid Medium". *Asian J. Chem.* 27(10): 3777-3780.

40. Lawal, H.M. and J.F. Iyun. 1998. *Indian J. Chem*, 37A: 155.

41. Levine, I.N. 2009. *Physical Chemistry, 6th Ed.* McGraw-Hill: New York, NY. 908.

42. Ukoha, P.O., J.N. Asegbeloyin, C. Alioke, and O.T. Ujam. 2010. "Kinetics and Mechanism of the Oxidation of Dithionate Ion by N,N'-ethylenebis-[salicylideneimiato] iron(III)". *J. Chem. Soc. Nigeria.* 35(1): 163-170.

43. Levine, I.N. 2009. *Physical Chemistry, 6th Ed.* McGraw-Hill: New York, NY. 433-434.

44. Pennington, D.E. and A. Haim. 1968. "The Effect of Added Chloride Ion on the Rate of Chloro-pentaaminecobalt(III)-Chromium (II) Reaction". *Inorganic Chemistry.* 7: 1659-1663.

45. Ukoha, P.O. 1999. "Kinetics and Mechanisms of some RedOx Reactions of I-oxobridged Iron(III) Complex Ion [(FeHEDTA)2O]2- and of some Oxyanions and Thiols". Ph.D. Thesis. Ahmadu Bello University: Zaria, Nigeria. 254 pp.

46. Lee, C, W. Yang, and R.G. Parr. 1988. *Phys. Rev. B.* 1988, 37: 785-789.

47. Hinchliffe, A. and R.W. Munn. 1985. *Molecular Electromagnetism*, Wiley: Chinchester, UK.

48. Haim, A. 1983. "Mechanism of Electron Transfer Reactions. The Bridged Complex". Prog. Inorg. Chem. 30: 273-355.

49. Meyer, T.J. 1978. *Electron Transfer: Comprehensive Coordination Chemistry.* G.Wilkinson (ed.). vol 1. Pergamon Press: London, UK.

50. Seok, W.K and T.J. Meyer. 2004. *Inorg. Chem.* 43(17): 5205-5215.

ABOUT THE AUTHORS

Prof. Pius Oziri Ukoha, is a Professor of Inorganic Chemistry, University of Nigeria, Nsukka. He has graduated numerous Ph.D. and M.Sc. students. His research interests are in the areas of synthesis and characterization of coordination compounds of transition and inner-

transition metals and their pharmacological applications. He also carries out research in areas of kinetic, thermodynamic and mechanism of inorganic reactions.

Dr. Uchechukwu Susan Oruma, is a Lecturer at the University of Nigeria, Nsukka. She is a member of the Chemical Society of Nigeria (CSN), Women in Chemistry (Enugu State chapter) and Organization of Women in Science of the Developing Countries (OWSD). She holds a Ph.D. degree in Inorganic Chemistry from the University of Nigeria, Nsukka. Her research interests are in synthesis, characterization, and biological studies of O,N,S donor ligands and their lanthanide/transition metal complexes. She is also involved in research on Kinetics, thermodynamics and mechanisms of inorganic reactions.

Dr. Collins Ibeji, is a Lecturer at the University of Nigeria, Nsukka. He is a member of the Chemical Society of Nigeria (CSN). He also did his post-doctoral studies with Catalysis and Peptide Research Unit, School of Health Sciences, University of KwaZulu-Natal, Durban 4041, South Africa.

Kenneth O. Ugwuanyi, obtained his M.Sc. in inorganic Chemistry from the University of Nigeria, Nsukka under the supervision of Prof. P.O. Ukoha.

Uchechukwu R. Obeta, obtained her M.Sc. in Physical Chemistry at Michael Okpara University of Agriculture, Umudike, Abia State, Nigeria 440109. She obtained her B.Sc. in Inorganic Chemistry from the University of Nigeria, Nsukka.

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 Pacific Journal of Science and Technology