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DISCOVERY

Reactions of the 2,5-pyridine dicarboxylic acid (dicarpy)-bridged iron (III) dimer, [Fe((saloph))$_2$-μ-dicarpy], with β-mercaptoacetic acid and β-mercaptoethylamine in aqueous perchloric acid

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ABSTRACT

Kinetics of the reduction of [(Fe(saloph))$_2$-μ-dicarpy] by `β-mercaptoacetic acid and β -mercaptoethylamine was followed spectrophotometrically at 424 nm. The reactions were conducted at pseudo-first order conditions of a large excess (≥ 20-fold) of the reductants over the oxidant at $29^{o}C$ and ionic strength of $0.001\ moldm^{-3}$ ($NaClO_4$). Under these conditions, k_{obs} increased with concentration of reductants and pseudo-first order plots were linear for at least 85% extent of reaction. Second order rate constants were fairly constant at $0.112 \pm 0.007\ dm^3mol^{-1}S^{-1}$ (β-mercaptoacetic acid) and $0.59 \pm 0.016\ dm^3mol^{-1}S^{-1}$ (β-mercaptoethylamine) indicating first order dependence of rate on concentration of the reductant. Plots of log k_{obs} versus Log[reductant] gave slopes close to unity for both reactions, implying first order dependence of rate on concentration of the reductants respectively. Within the acid concentration $1x\ 10^{-4} \leq [H+] \geq 80\ X10^{-4} mol\ dm^{-3}$ rates of the reactions decreased as acid concentration increased. This has been interpreted in terms of possible protonation or deprotonation of the redox partners before the electron transfer step. Both reactions showed positive primary salt effect, indicating involvement of like charges at the rate determining step. There was insignificant retardation of the reactions on addition of catalytic amounts of CH_3COO^-, Cl^- and NO_3^-. This is indicative of likely operation of parallel inner and outer-sphere paths for the reactions. The reactions have been rationalized on the basis of parallel inner-sphere and outer-sphere paths mediated by protonated reductants and oxidant species at low pH for β -mercaptoethylamine reaction and dissociated β-mercaptoacetic acid molecule for the [(Fe(saloph))$_2$-μ-dicarpy)]- mercaptoacetic acid reaction.

Keywords: β-mercaptoacetic acid; β-mercaptoethylamine; aqueous perchloric acid

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1. INTRODUCTION

Binuclear iron (III) complexes had been synthesized. These include the μ-oxo-bridged complexes of the form, $[Fe_2O]^{4+}$ or $[Fe(OH)_2]^{4+}$ (Scheidt et al., 1992; Costes et al., 1995; Stefánsson, 2007). The other types are the dicarboxylic acid-bridged dimers incorporating salen and saloph ligands (Dalla-Cort et al., 2010; Kopel et al., 1998; Ashmawy et al., 1991). These complexes have been studied as models or mimics of superoxide dismutase (Dalla-Cort et al., 2010; Ashmawy et al., 1991). Some of these studies indicated high bioactive properties of most of these iron (III) dimers. The salen and saloph iron (III) dimers resemble the porphyrins and their study has enhanced our understanding of physiological action of related systems (Sheriff et al., 1987; Roseweig et al., 1995).

In furtherance of the search for a deeper insight into the dynamics of these complexes, their redox characteristics are being investigated. The μ-oxo-bridged iron (III) dimer, $[(FeHEDTA)_2O]^{2+}$ was reduced to Fe (II) by ascorbic acid (Ukoha and Iyan, 2002), mercaptoacetic acid (Ukoha and Iyan, 2005), mercaptoethanol and mercaptoethylamine (Ukoha and Iyan, 2001). These reactions occurred by the outer-sphere mechanism with intervening ion-pairs formation. Another oxo-bridged analogue, $[(Fe_2(bipy)O]^{4+}$ was reduced by catechol (Idris et al., 2004), mercaptoacetic acid (Idris et al., 2004), thiosulfate (Idris et al., 2008) and L-cysteine (Idris et al., 2011). The electron transfer reactions occurred by the outer-sphere mechanism.

Recently, the adipato bridged iron (III)-salen dimer, $[(Fe(salen)_2\mu\text{-adi}]^{,}$ was studied for its redox behavior using dithionate (Atiga et al., 2014), trioxosulfate (IV) (Atiga et al., 2015), dithionite (Ukoha et al., 2015), benzyl mercaptan (Ugwuanyi and Ukoha, 2015) and mercaptobenzothiazole (Ugwuanyi and Ukoha, 2017). These reactions followed various pathways. Reactions of the dimer with dithionate and sulfite ions occurred by the outer-sphere path with first order dependence of rate on concentration of the oxidant and zero-order dependence of rate on the reductants (Atiga et al., 2014; Atiga et al., 2015) but the reaction of dithionite followed inner-sphere path with first order dependence of rate on oxidant and reductant concentrations respectively (Atiga et al., 2014).

Reduction of $[(Fe(salen)_2\mu\text{-adi}]$ with benzylmercaptan showed inverse first order dependence of rate on concentration of benzyl mercaptan but first order dependence on the concentration of iron (III) dimer. Reaction of mercaptobenzothiazole with $[Fe(salen)_2adi]$ was first order on both redox partners. Both reactions followed inner-sphere path (Ugwuanyi and Ukoha, 2015; Ugwuanyi and Ukoha, 2017). Also, oxidation of the thiol, mercaptoacetic acid (thioglycolic acid) by $[Fe(salen)_2adi]$ occurred by inner-sphere mechanism with intervening protonated precursor complexes mediating the electron transfer (Ukoha et al., 2018).

The reactions of $[Fe(salen)_2adi]$ in acid medium all showed acid catalysis. This phenomenon was rationalized on the basis of protonation of the oxidant prior to electron transfer. Most of the reactions are enthalpy controlled, endothermic and slow (Atiga et al., 2014; Atiga et al., 2015; Ukoha et al., 2015; Ugwuanyi and Ukoha, 2015; Ugwuanyi and Ukoha, 2017; Ukoha et al., 2018). Kinetic data generated for bridged iron (III) dimers has posed more questions than answers.

Whereas the oxo-bridged dimers tend towards outer-sphere electron transfer route with intervening ion-pair formation for reactions with thiols and ascorbic acid (Sheriff et al., 1987; Roseweig et al., 1995; Ukoha and Iyan, 2002) the adipic acid bridged iron (III) dimer reacted with some thiols following the inner-sphere path but with some oxoanions of sulfur followed the outer-sphere path. It has not been established the reasons for these trends and no general pattern for the dependencies has been arrived. However, one thing very clear about the reactions of these iron (III) dimers is that their electron transfer trajectory is slow and the longer the span of the bridge the more is the tendency to form mixed valence intermediates and products (Atiga et al., 2014; Atiga et al., 2015; Ukoha et al., 2015; Ugwuanyi and Ukoha, 2015; Ugwuanyi and Ukoha, 2017; Ukoha et al., 2018).

In furtherance of the desire to gain more insight into the redox dynamics of iron (III) dimers as mimics of iron enzymes, we are probing a new regime of iron (III) dimers. These are the dicarboxylic and tricarboxylic acid bridged iron (III)-saloph complexes (Anidobu, 2017). Reduction of the pyridine dicarboxylic acid-bridged iron (III)-saloph dimer, $[(Fe(saloph))_2\mu\text{-dicarpy}]$, by ascorbic acid has been reported to follow outer-sphere route and the reaction was retarded by acid and was generally slow (k_2 = 0.11 $dm^3mol^{-1}s^{-1}$) (Ukoha et al., 2018).

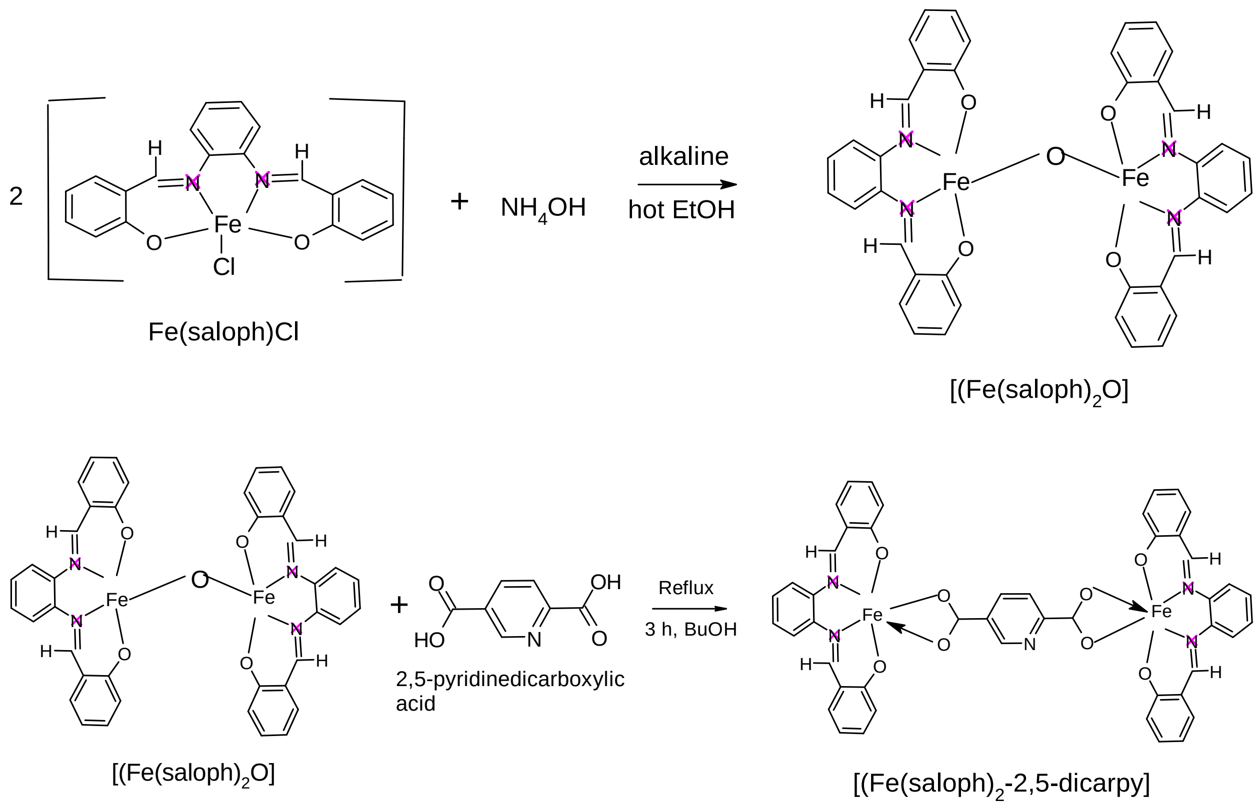
The present effort is a report on the study of the electron transfer reaction of $[(Fe(saloph))_2\mu\text{-dicarpy}]$ with β-mercaptoacetic acid and β-mercaptoethylamine. The choice of these biomolecules at physiological pH is aimed at better comparison with bioinorganic systems based on how the RSH and RSSR redox couple mediates redox potentials at biological sites (Ziegler, 1985). It is hoped that our results will aid in answering some questions raised by the hitherto generated kinetic data from earlier studies of iron (III) dimers and unravel some mysteries surrounding iron electron transfer enzymes physiologically.

2. EXPERIMENTAL

Mercaptoethylamine (Aldrich-sigma, 95%), mercaptoacetic acid (Aldrich-sigma, 99%), sodium acetate (BDH, 99%), K_2SO_4 (May and Baker, 99%), $NaClO_4$ (May and Baker, 99%), $HClO_4$ (BDH, 69.07%) and $MgCl_2.6H_20$ (kermel, 98%) were of analytical grade and were used on supplied except otherwise stated. Solutions of reagents were prepared using doubly distilled, de-ionized water. Uv-Visible spectra were obtained using HEλIOSα Uv-visible spectrophotometer V4.24.FTIR spectra were recorded on Agilent Technology Cary 630 FTIR Spectrophotometer. $NaClO_4$ and dimethylsulfoxide (DMSO) were used in adjusting ionic strength and dielectric constant respectively of the reaction media. Acidity level of the reactions were altered using $HClO_4$ while the salts K_2SO_4, CH_3COONa, $MgCl_2$ and KNO_3 were used to investigate catalysis or otherwise of the reaction.

Preparation of [(Fe(saloph))$_2$O] and [(Fe(saloph))$_2$ -2,5-dicarpy].H_2O

N, N'-bis(salicylidene)-o-phenylenediamine(saloph) was prepared following the method of Liu et al., (2007). Kopel et al., (1998) method was employed in synthesizng the intermediate Fe(saloph)Cl. The method of Kopel and co-workers was also followed to prepare the μ-oxo-bridged and dicarpy-bridged Fe (III)-salophdimmers. Concentrated NH_4OH was added to hot ethanol solution of Fe(saloph)Cl in a beaker with constant stirring until the mixture registered pH 10.02. [(Fe(saloph))$_2$O] precipitated a red solid at this pH. [(Fe(saloph))$_2$O] (0.1 mmol, 0.7644 g) was suspended in 40cm^3 of hot butanol and mixed with 10cm^3 of hot butanol solution of 2,5-pyridine dicarboxylic acid (0.6 mmol, 0.1 g). The mixture was refluxed for 3 h at 60^0C. On cooling, reddish precipitate was formed, which was filtered, washed with butanol and dried under anhydrous Na_2SO_4 for 24 h.



Scheme 1 Synthesis of [(Fe(saloph))$_2$O] and [(Fe(saloph))$_2$-2,5-dicarpy]

Kinetic study

The rate data for the reduction of [(Fe(saloph))$_2$-μ-dicarpy] hereinafter denoted as [Fe$_2$dicarpy] by thiols: β-mercaptoacetic acid (MSH) and β-mercaptoethylamine (ETSH) was generated spectrophotometrically by monitoring the decrease in absorbance of [Fe$_2$dicarpy] at 424 nm. At this wavelength only the iron (III) dimer absorbed maximally, the reductants and products of reaction did not pose any significant interference. All kinetic runs were performed under pseudo-first order conditions with the concentrations of the reductants at least 20 times greater than [Fe$_2$dicarpy]. Pseudo-first order rate constants, k_{obs}, were obtained from slopes of logarithmic plots of change of absorbance against time according to equation (1) (Atiga et al., 2014).

$$\mathrm{In}(A_t - A_\infty) = \mathrm{In}(A_\infty - A_0) - k_{obs}t \qquad (1)$$

Where A_∞ = final absorbance, A_t= absorbance at time t, A_0 = initial absorbance and k_{obs} = pseudo- first order rate constant.

Stoichiometries of the reactions were determined by spectrophotometric titration on the basis of the mole ratio method (Atiga et al., 2014). Final absorbances of separate reaction mixtures composed of [Fe$_2$dicarpy] 1.0×10^{-5} moldm^{-3}, [reductants] = $1.0\times10^{-5} - 8.0\times10^{-4}$ moldm^{-3}, [H$^+$] = 1.0×10^{-4} moldm^{-3}, I = 1.0×10^{-3} moldm^{-3} ($NaClO_4$), T= 29.0^oC and λ = 424 nm. The point of inflexion on the curve of the plots of A_∞ against mole ratio of reactants gave the stoichiometries of the reactants.

Presence of free radical intermediate was monitored by adding acrylamide to partially reacted reaction mixtures in excess methanol as reported elsewhere (Atiga et al., 2014; Atiga et al., 2015; Ukoha et al., 2015). Gel formation indicated presence of free radicals. Test for the presence of stable, detectable intermediates formed during the course of reaction was investigated by reacting 5.0×10^{-5} moldm^{-3} of oxidant with 6.0×10^{-3} moldm^{-3} of reductant while keeping other parameters constant. Electronic spectra of the reaction mixture were recorded at 10 min intervals as the reaction progressed.

3. RESULTS AND DISCUSSION

Stoichiometry

Spectrophotometric titration of various concentrations of the reductants against a fixed concentration of the oxidant at 424 nm indicated the consumption of one mole of the oxidant for two moles each of the reductants oxidized. The result is in accord with equations (2) and (3)

$[\mathrm{Fe_2dicarpy}] + 2\mathrm{HSCH_2COOH} \rightarrow [\mathrm{Fe_2dicarpy}]^{2-} + \mathrm{HOOCCH_2SSCH_2COOH} + 2\mathrm{H^+}$ (2)

$[\mathrm{Fe_2dicarpy}] + 2\mathrm{HSCH_2CH_2NH_2} \rightarrow [\mathrm{Fe_2dicarpy}]^{2-} + \mathrm{H_2NCH_2CH_2SSCH_2CH_2NH_2} + 2\mathrm{H^+}$ (3)

The iron (III) dimer, $[(\mathrm{Fe(saloph)})_2\text{-}\mu\text{-dicarpy}]$ was reduced to the iron (II) dimer, $[(\mathrm{Fe(saloph)})_2\text{-}\mu\text{-dicarpy}]^{2-}$ and the thiols oxidized to the disulfides.

Qualitative tests using fresh solutions of KSCN and $K_3[Fe(CN)_6]$ on the acidified products of the reactions gave pale red coloration and deep blue-green precipitate respectively indicating presence of Fe (II). This assertion had been made for other reactions of Fe^{3+}dimers with thiols. Fe_2O^{4+} was reduced to Fe^{2+} by the thiols, mercaptoacetic acid (Roseweig et al., 1995), mercaptoethanol and mercaptoethylamine (Ukoha and Iyun, 2001) with the concomitant oxidation of the thiols to disulfides. Also, reactions of the adipato bridged Fe (III) dimer, [Fe_2adi], with oxoanions of sulfur (Atiga et al., 2014; Atiga et al., 2015; Ukoha et al., 2015) and with benzyl mercaptan (Ugwuanyi and Ukoha, 2015), thiolbenzothiazole (Ugwuanyi and Ukoha, 2017) and thioglycolic acid (Ukoha et al., 2018) resulted in reduction of the Fe (III) complex to the Fe (II) analogue.

The thiols were oxidized to disulfides. Earlier report Ukoha et al., (2018) has shown that [Fe_2dicarpy] was reduced to [Fe_2dicarpy]$^{2-}$ by ascorbic acid (Ukoha et al., 2018). The organic products of the reactions were extracted with diethylether, washed, dried and their FTIR spectra obtained. Figure 1 and 2 show no V(S-H) bands around 2600-2550cm^{-1}, but have weak V(C-S) band between 730-600 cm^{-1}. There were also no bands for C-S=O of sulfoxides. These results strongly indicate formation of disulfides as product of reaction. Most mild oxidizing agents oxidize thiols bearing –S-H groups to disulfides whereas those bearing R-S-R groups are prone to form sulfoxides.

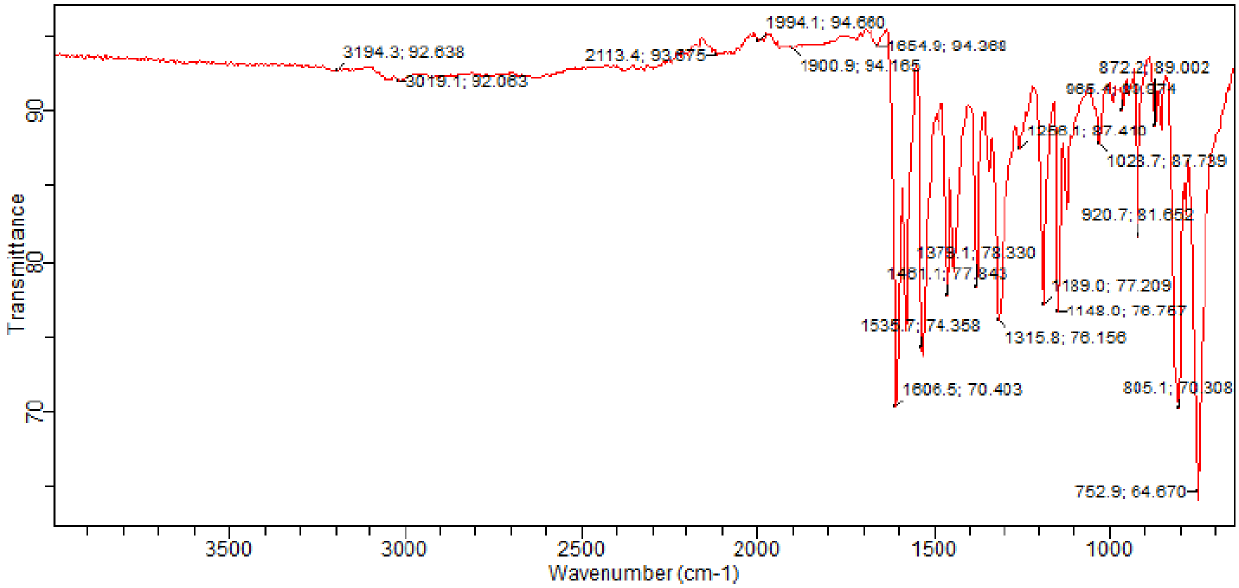


Figure 1 FTIR Spectrum of Product of $[(\mathrm{Fe(saloph)})_2\text{-}\mu\text{-dicarpy}]$ – Mercaptoacetic Acid reaction

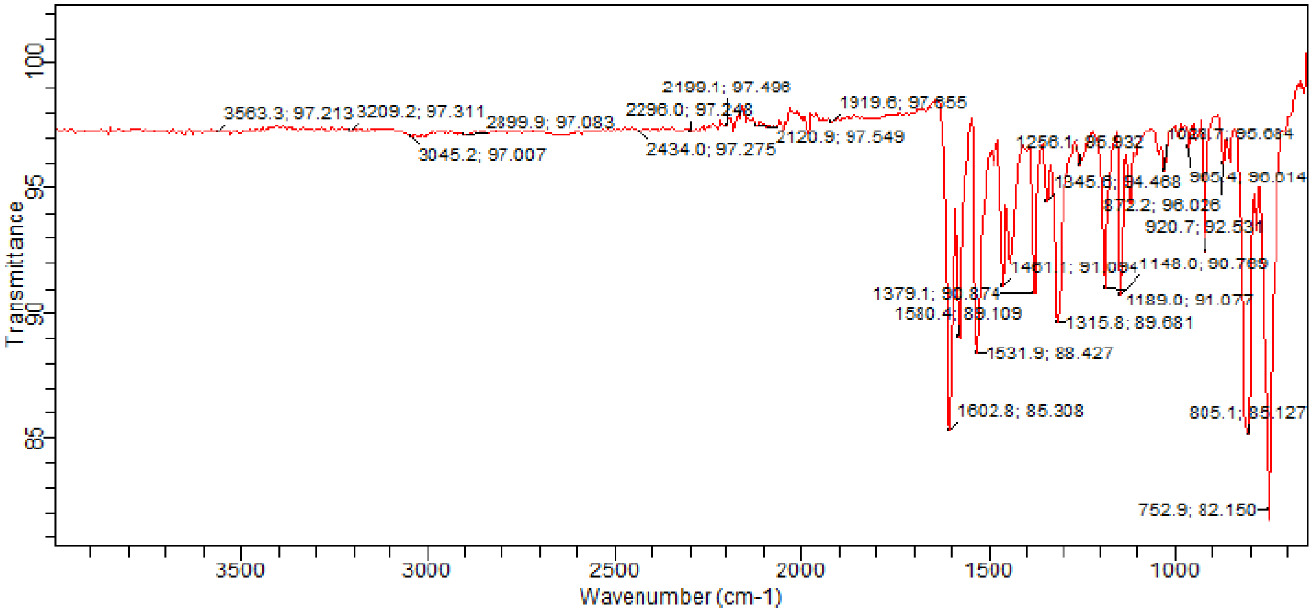


Figure 2 FTIR Spectrum of Product of [(Fe(saloph)$_2$-μ-dicarpy]-Mercaptoethylamine reaction

Kinetic Study

Under pseudo-first order conditions, plots of In(A_t-A_∞) against time were linear to more than 85% extent of reaction, indicating first order dependence of rate with respect to concentration of the oxidant. Pseudo-first order rate constants, k_{obs} are in (Table 1, 2). On increasing the concentration of the reductants from 4.0x10^{-3} to 1.0x10^{-2} moldm^{-3} at [Fe$_2$dicarpy] of 1.0x10^{-5} moldm^{-3}, k_{obs} also increased. From the ratios of k_{obs}: [reductants], second orders rate constants k_2, were derived as in (Table 1, 2). k_2 values were fairly constant at 0.112±0.007 dm^{3}mol^{-1} s^{-1} for [Fe$_2$dicarpy]-mercaptoacetic acid reaction and 0.59±0.02 dm^{3}mol^{-1} s^{-1}for [Fe$_2$dicarpy]-mercaptoethylamine reaction.

Table 1 Pseudo-first order and second order rate constants for the reaction of [(Fe(saloph))$_2$-μ-dicarpy] by $\boldsymbol{\beta}$ −mercaptoacetic acid at [(Fe(saloph))$_2$-μ-dicarpy] = 1.0 x 10^{-5} mole dm^{-3}, T = 29 °C and λ_{max} = 424 nm

10^3 (mercaptoacetic acid) (mole dm^{-3})	10^4[H$^+$] (moldm^{-3})	[I] (moldm^{-3}) (NaClO$_4$)	10^4k_{obs}(s^{-1})	k_2 (dm^{3}mol^{-1}s^{-1})
4.0	1.0	0.001	5.15	0.13
6.0	1.0	0.001	6.67	0.11
7.0	1.0	0.001	7.94	0.11
8.0	1.0	0.001	8.49	0.11
10.0	1.0	0.001	9.89	0.10
10.0	1.0	0.001	9.79	0.098
10.0	5.0	0.001	9.01	0.090
10.0	10.0	0.001	8.33	0.083
10.0	20.0	0.001	7.08	0.071
10.0	50.0	0.001	6.53	0.065
10.0	80.0	0.001	4.77	0.047
10.0	1.0	0.005	9.62	0.096
10.0	1.0	0.01	10.71	0.107
10.0	1.0	0.04	11.86	0.119
10.0	1.0	0.10	19.66	0.197
10.0	1.0	0.15	20.62	0.206

Table 2 Pseudo-first order and second order rate constants for the reaction of [(Fe(saloph))$_2$-μ-dicarpy] by mercaptoethylamine at [(Fe(saloph))$_2$-μ-dicarpy] = 1.0 x 10^{-5} mole dm^{-3}, T = 29 ^{o}C and λ_{max} = 424 nm

10^4 (mercaptoethylamine) (mole dm^{-3})	10^4[H$^+$] (mole dm^{-3}) (HClO$_4$)	10^3[I] (mole dm^{-3}) (NaClO$_4$)	10^4k$_{obs}$/s^{-1}	k$_2$ (dm^{3}mole^{-1}s^{-1})
4.0	1.0	0.001	2.29	0.57
6.0	1.0	0.001	3.50	0.58
8.0	1.0	0.001	4.83	0.60
10.0	1.0	0.001	6.22	0.62
12.0	1.0	0.001	6.93	0.58
6.0	0.25	0.001	4.17	0.70
6.0	0.50	0.001	3.48	0.58
6.0	1.0	0.001	3.02	0.50
6.0	1.5	0.001	2.72	0.45
6.0	2.0	0.001	2.02	0.34
6.0	3.0	0.001	1.65	0.28
6.0	1.0	0.001	3.50	0.58
6.0	1.0	0.002	5.46	0.91
6.0	1.0	0.005	6.13	1.02
6.0	1.0	0.010	7.83	1.30
6.0	1.0	0.040	15.27	2.55

Acid Dependence

Between the acid concentration of $1 \times 10^{-4} \leq [H^+] \geq 8 \times 10^{-3} moldm^{-3}$ which is approximately in the pH range of 4.0 to 2.1, the rate of reaction decreased as the acid concentration increased for the oxidation of β-mercaptoacetic acid by [Fe$_2$dicarpy] (Table 1). Similar trend was observed for the reaction of [Fe$_2$dicarpy] with β-mercaptoethylamine (Table 2). Inverse acid dependence is generally associated with a deprotonation step preceding the electron transfer step (Johannissen et al., 2009). This could suggest the ionization of the thiols to yield thyl anion. However, these thiols have acid dissociation constants for such equilibria at about 9.8 to 10.0 (Sardi et al., 2013). This makes it difficult for such equilibria to subsist at such acid concentration range.

It should be expected at such low pH, protonation of the thiols or dissociation of the carboxylic acid function of the β-mercaptoacetic acid should predominate. In keeping with this neutral thiol molecules, carboxylate ion (carboxylic acid) and protonated amine functions are expected as reductant species in accordance with equations 4 – 6.

$HOOCCH_2SH \rightleftharpoons HSCH_2COO^- + H^+$ (4)

$HSCH_2CH_2NH_2 \overset{H^+}{\rightleftharpoons} HSCH_2CH_2N^+H_3$ (5)

$HOOCCH_2SH \overset{H^+}{\rightleftharpoons} HOOCCH_2SH_2^+$ (6)

Predominance of such reductant species will lead to a less facile electron transfer process since the sulfur atom is the centre of electron transfer. It has been noted that faster electron transfer routes are encouraged by deprotonation of –SH function to yield –S$^-$ prior to electron transfer. It stands to reason then, that any process that does not enhance the formation of S$^-$ will slow down the reaction. This is also the possibility that the new reductant species could form adducts with the oxidant, thereby retarding the reaction by decreasing availability of the oxidant species.

Plots of k$_2$ versus [H$^+$] were not well-correlated (R^2 = 0.501 (mercaptoacetic acid) and 0.8334 (mercaptoethylamine)). The nature of the curve indicates more than one pathway for the reactions there by indicating the complicated nature of the reactions. The linear part of the curves conforms to the equation (7).

$k_H + k_2 = x + y\,[H^+]^{-1}$ (7)

The reactions occur by various acid-dependencies both direct and inverse but the inverse seems to predominate. However, contributions for other paths are significant. The rate of reduction of Fe$_2$dicarpy by β-mercaptoacetic acid was enhanced with increase in ionic strength of the media from 0.005 to 0.15 mole dm^{-3}(NaClO$_4$). Within the ionic strength range of 0.001 to 0.040 mole dm^{-3}(NaClO$_4$), the rate of the Fe$_2$dicarpy- H$_2$N-CH$_2$-CH$_2$SH also increased with ionic strength of medium. For bimolecular elementary reaction and within ionic strengths of ≤ 0.1 primary kinetic salt effect is positive if the redox partners have like charges at the rate determining step in line with equation 8 (Levine, 2009),

$$\log k_r = \log k_r^{\infty} + 1.02 Z_A Z_B \left(\frac{I^{1/2}}{1+I^{1/2}} - 0.30I \right) \qquad (8)$$

The obtained data suggests reaction of protonated Fe$_2$dicarpy and protonated reductant at the rate determining step as could be seen in equation (9).

$[H_2Fe_2dicarpy]^{2+} + [H_2SCH_2CH_2NH_3]^{2+} \rightleftharpoons [H_2Fe_2dicarpy\text{-}SCH_2CH_2NH_3]^{2+} + 2H^+$ (9)

Protonation of the iron (III) dimer has been implicatazzed in some of the earlier reactions (Atiga et al., 2014; Atiga et al., 2015; Ukoha et al., 2015) and the protonated species predicated to be a better oxidant than the native form. Formation of the precursor complexes (equation (9)) will be fast whereas the intramolecular electron transfer step will be slow in keeping with an inner-sphere electron transfer pathway that is kinetically controlled (Levine, 2009; Haim, 1983).

Plots of logk$_r$ versus $\left(\frac{I^{1/2}}{1+I^{1/2}} - 0.30I \right)$ was linear ($R^2 = 0.936$) with a slope of 2.01 for the β-mercaptoacetic acid reaction, thereby suggesting reaction between redox partners of +2 and +1 charges in keeping with equation (8). Similar plot was obtained for the mercaptoethylamine-Fe$_2$dicarpy reaction ($R^2 = 0.958$) with a slope of 4.633 the value suggests redox partners of +2 and +2 charges or +1 and +4 charges at the rate determining step. This is also in keeping with charged reductant and oxidant molecules as redox partners at the rate determining step. This is most likely in agreement with equation (7). However, involvement of other species in a parallel reaction is not ruled out.

Effect of dielectric constant

The rate of the Fe$_2$dicarpy- HS-CH$_2$-COOH reaction showed marginal increase with dielectric constant (Table 3). However, reaction rate of β-mercaptoethylamine with Fe$_2$dicarpy decreased with increase in dielectric constant (Table 4). Increase in rate of β-mercaptoacetic reaction with dielectric constant suggests redox partners of same charge as in equation (8).

For ionic reactions, rate dependence on medium dielectric constant can be analysed using equation (10)

$$\ln k = \ln k_0 - \frac{Z_A Z_B e^2}{DKT r_{\pm}} \qquad (10)$$

Where k = rate constant for the reaction. k$_0$ = rate constant in a medium of infinite dielectric constant, Z$_A$ and Z$_B$ = charges on reactants A and B respectively, D= dielectric constant, r = separation of A and B.

Plot of Ink against 1/D will give a positive slope if the redox partners are of opposite signs (Ukoha et al., 2010). For redox partners having charges of same sign, a negative slope is expected. The positive slope obtained for the β-mercaptoethylamine reaction suggests redox partners of opposite sign. For such reactions ion-paring or complex formation contributes significantly to the course of the reaction. This is also in agreement with the complex nature of this reaction where various equilibria involving dipositive or unipositive reductant molecues are envisaged to be reacting with dissociated oxidant molecules.

Typical reactions occurring in the β-mercaptoethylamine-Fe$_2$dicarpy system could include the following equation (11) – (13):

$SHCH_2CH_2N^+H_3 + Fe_2dicarpy \rightleftharpoons [Fe_2dicarpy - NCH_2CH_2SH]^- + H^+$ (11)

$SHCH_2CH_2N^+H_3 + Fe_2dicarpy \rightleftharpoons [Fe_2dicarpy - SCH_2CH_2NH_2]^{2-} + 2H^+$ (12)

$SHCH_2CH_2N^+H_3 + [H_2Fe_2dicarpy]^{2+} \rightleftharpoons [H_2Fe_2dicarpy - SCH_2CH_2NH_2]^+ + 2H^+$ (13)

Contributions from these reactions will affect the degree of dielectric constant dependence. There is also the likelyhood that the precursor complexes could interact with dimethylsulfoxide used in mediating medium dielectric constant as has been suggested elsewhere (Durovic et al., 2014). The precursor complexes in equation (11-13) depict possible formation of Fe (III)-Fe (III), Fe (III)-Fe (II) and Fe (II)-Fe (II) dimers as has been suggested elsewhere (Esmelindro et al., 2005; Synder et al., 1989).

Table 3 Dependence of rate constant on dielectric constant and on added anions for the reaction of [(Fe(saloph))$_2$-μ-dicarpy] by Mercaptoacetic acid at [(Fe(saloph))$_2$-μ-dicarpy] = 1.0×10^{-5} mole dm^{-3}, [H$^+$] = 1.0×10^{-4} mole dm^{-3}, I =1.0×10^{-3} mole dm^{-3}, T = 29 °C and λ_{max} = 424 nm

10^3 (mercaptoacetic acid) (mole dm^{-3})	X	10^4[X] (mole dm^{-3})	10^3 k$_{obs}$(s^{-1})	k$_2$ (dm^{3}mole^{-1}s^{-1})
6.0	CH_3COO^-	0.5	2.67	0.44
6.0		1.0	2.22	0.37
6.0		2.0	1.98	0.33
6.0		5.0	1.80	0.33
6.0		8.0	1.56	0.26
6.0	Cl^-	0.1	1.83	0.31

6.0		0.3	1.50	0.25
6.0		1.0	1.40	0.23
6.0		2.0	1.27	0.21
	D			
8.0	76.42		7.14	0.89
8.0	77.08		7.69	0.96
8.0	78.74		8.19	1.02
8.0	79.07		8.33	1.04
8.0	79.43		8.62	1.08

Table 4 Dependence of rate constant on dielectric constant and on added anions for the reaction of [(Fe(saloph))$_2$-μ-dicarpy] by Mercaptoethylamine at [(Fe(saloph))$_2$-μ-dicarpy] = 1.0 x 10^{-5} mole dm^{-3}, [H$^+$] = 1.0 x 10^{-4} mole dm^{-3}, I =1.0 x 10^{-3} mole dm^{-3}, T = 29 ^{o}C and λ_{max} = 424 nm

10^4 (mercaptoethylamine) (mole dm^{-3})	X	10^4[X] (mole dm^{-3})	10^3 k_{obs}/s^{-1}	k_2 (dm^{3}mole^{-1}s^{-1})
6.0	CH_3COO^-	0.5	2.86	4.76
6.0		1.0	2.78	4.63
6.0		2.0	2.40	4.00
6.0		5.0	1.36	2.27
6.0	NO_3^-	5.0	3.13	5.21
6.0		6.0	3.04	5.07
6.0		7.0	2.10	3.50
6.0		8.0	1.18	1.96
6.0	SO_4^{2-}	0.1	0.40	0.67
6.0		0.5	0.45	0.74
6.0		0.6	0.46	0.77
6.0		0.8	0.49	0.81
6.0		1.0	0.50	0.83
	D			
8.0	77.08		11.66	14.58
8.0	78.74		6.67	8.33
8.0	79.07		5.54	6.92
8.0	79.43		4.76	5.95

Effect of added ions

Addition of small amounts of CH_3COO^- and Cl^- marginally retarded Fe$_2$dicarpy reactions with HS-CH$_2$-COOH (Table 3) and with H$_2$N-CH$_2$-CH$_2$SH (Table 4) as the rates of the reactions diminished as concentration of added anions increased. Addition of SO_4^{2-} to β-mercaptoethylamine reaction did not alter the rate of reaction and could suggest an inner-sphere electron transfer route (Haim, 1983). Retardation of the reactions in the presence of catalytic amounts of CH_3COO^- and Cl^- suggests involvement of redox partners of cation-anion or neutral-anion species at the rate determining step. It is also indicative of outer-sphere electron transfer pathway.

However, considering the low degree of retardation, it is very likely that the reactions did not follow one pathway. By the suggested pose of the reductants and oxidants in aqueous acid, mixed reaction routes are likely followed involving both inner and outer-sphere paths. Complications in the reactions could result from the possibility that if mixed valence precursor complexes are formed, stability of the complex could be compromised. Bonds between ligands and Fe (II) will be elongated leading to possible decomposition of the complex in solution in the mixed-valence state (Esmelindro et al., 2005; Synder et al., 1989). Formation of species like Fesaloph$^+$, dicarpy$^-$ and [Fe$_2$saloph]$^-$ will not be far-fetched.

Temperature dependence

Dependence of reaction rate on temperature was investigated between 298 to 33 K. Table 5 shows temperature-dependent rate constants. Rate constants increased with increase in temperature.

Activation parameters ($\Delta H^{\neq}\Delta G^{\neq}$and $\Delta S^{\neq}$) were analysed on the basis of Eyring relationship (equation 14).

$$\log\frac{k_2}{T} = \log\frac{k}{h} + \frac{\Delta S^{\neq}}{2.303R} - \frac{\Delta H^{\neq}}{2.303RT} \qquad (14)$$

Where k_2 = 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, T= temperature

From the Arrhenius plot of Ink$_2$ versus 1/T (Figure 3) was linear (R^2 = 0.992 for mercaptoacetic acid) and (R^2 = 0.996 for mercaptoethylamine). Enthalpy of activation (kJmol^{-1}),$\Delta H^{\neq}$ was positive for both reactions at 53.63 (β-mercaptoacetic acid reaction) and 60.18 (β-mercaptoethylamine reaction). Enthropy of activation (Jmol^{-1}K^{-1}),$\Delta S^{\neq}$ was negative for both reaction at -85.21 (β-mercaptoacetic acid reaction) and -47.23 (β-mercaptoethylamine reaction). Free energy of activation ($\Delta G^{\neq}$) as well as activation (Ea) energies were positive. Ea was analysed from Arrhenius plots (Figure 4).

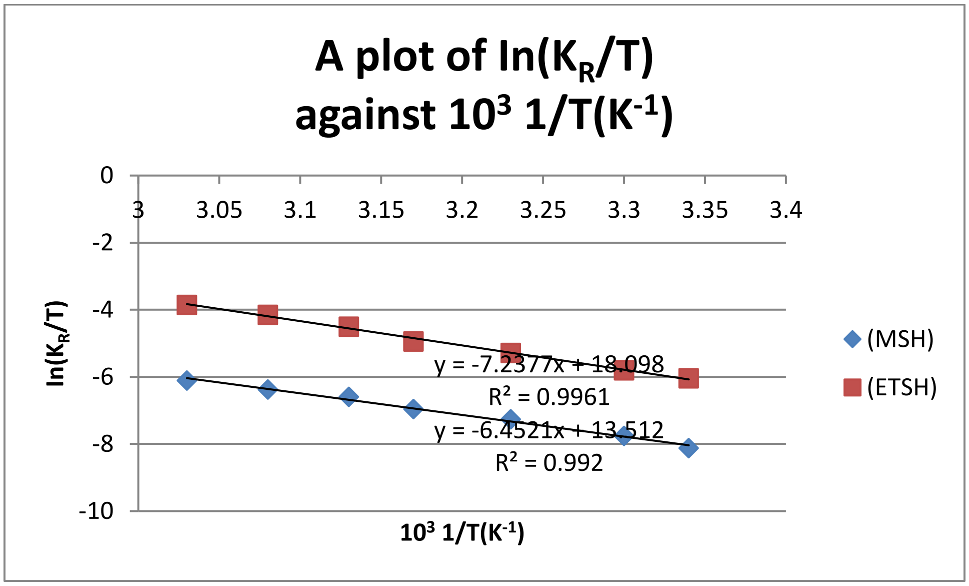


Figure 3 Arrhenius plot of Ink$_2$ versus 1/T for mercaptoethylamine (MSH) and mercaptoacetic acid (ETSH) reaction

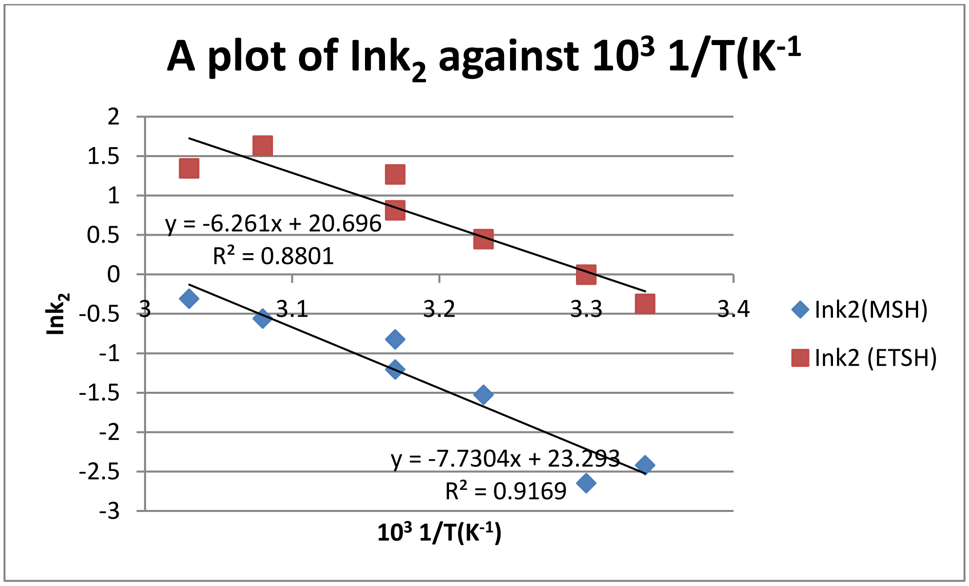


Figure 4 Plots of lnk$_2$ against 10^3 1/T(K^{-1}) for mercaptoethylamine (MSH) and mercaptoacetic acid (ETSH) reaction

The negative entropy of activation for both reactions is indicative of reactions where bond formation is predominating bond dissociation. This could be a consequence of ordered activation complex that is stabilized in solution. Most inner-sphere reactions have negative entropy; fast formation of the activated complex is envisaged in the reaction (Oyetunji et al., 2013). The positive enthalpies of activation can be interpreted in terms of an enthalpy-controlled process. Such reactions require high energy to react the transition state leading to slow reactions. Oxidation of L-ascorbic acid by by $[Mn(salen)(H_2O)]^+$ occurred with $\Delta H^{\neq}$ of 89.2 $kJmol^{-1}$ and this was interpreted to mean fast formation of a precursor complex but rate limiting intramolecular electron transfer.

Positive activation energies for both reactions are indicative of slow reactions requiring high energy to reach transition state (Ukoha et al., 2010). This is corroborated by the positive free energies which support the non-spontaneity and slowness of the reactions. Reaction of a positively charged oxidant species with positively charged reductant species will lead to retardation on the basis of electrostatic factors. Collisions between these species could result to deprotonation before formation of the precursor complex as shown in equations (9). Any of these in steps will slow down the reaction.

Table 5 Temperature dependent of rate constant and activation parameter for the reactions of $[(Fe(saloph))_2$-μ-dicarpy] with mercaptoacetic acid and mercaptoethylamine at $[(Fe(saloph))_2$-μ-dicarpy] = $1.0 \times 10^{-5} moldm^{-3}$, (mercaptoacetic acid) = $4.0 \times 10^{-3} moldm^{-3}$, (mercaptoethylamine) = $6.0 \times 10^{-4} moldm^{-3}$, while other parameters were kept constant at λ_{max} = 424 nm

Reductant	Temperature (K)	$10^4 k_{obs}/s^{-1}$	k_2 ($dm^3mole^{-1}s^{-1}$)	($Jmol^{-1}K^{-1}$)$\Delta S^{\neq}$	10^3 (1/T) (K^{-1})
	298	3.57	0.089		
Mercaptoacetic Acid	310	5.15	-5.7506	-1.9834	3.2258
	315	8.67	-5.7260	-1.9166	3.1948
	320	12.01	-5.6740	-1.7655	3.0959
	330	8.824	-5.5767	-1.5114	3.0030
Mercaptoethylamine	310	0.816	-6.5795	-1.9943	3.2258
	313	2.609	-6.0791	-0.8328	3.1948
	318	4.699	-5.8371	-0.2442	3.1446
	323	4.856	-5.8161	-0.2117	3.0959

4. MECHANISM

On the basis of stoichiometry, acid-dependence, kinetic salt effect, dielectric constant dependence and effect of added ions, the following steps have been suggested for the reactions. Fe_2dicarpy is used to denote either of mercaptoacetic acid or mercaptoethylamine.

$HSCH_2COOH \overset{pH\leq4}{\rightleftharpoons} H_2^+SCH_2COO^- + H^+$ (15)

OR $HSCH_2COOH \overset{pH\leq4}{\rightleftharpoons} HSCH_2COO^- + H^+$ (16)

$HSCH_2CH_2NH_2 \overset{pH\leq4}{\rightleftharpoons} H_2^+SCH_2CH_2N^+H_3 + H^+$ (17)

OR $HSCH_2CH_2NH_2 \overset{pH\leq4}{\rightleftharpoons} HSCH_2CH_2N^+H_3 + H^+$ (18)

$Fe_2dicarpy + 2H^+ \rightleftharpoons H_2Fe_2dicarpy^{2+}$ (19)

Any of the equilibria (equation 15-19) will lead to retardation of reaction as it will lead to redox partners of same electrostatic charge sign, this will encourage repulsion. Due to the complexities arising from likely equilibria envisaged in aqueous acid (pH ≤ 4), the following plausible schemes are proposed for the reactions.

Scheme 1

$[Fe_2dicarpy] + 2H^+ \overset{k_1}{\rightleftharpoons} [H_2Fe_2dicarpy]^{2+}$ (20)

$HSCH_2COOH + 2H^+ \overset{k_2}{\rightleftharpoons} HSCH_2COO^- + H^+$ (21)

$H_2Fe_2dicarpy^{2+} + HSCH_2COO^- \overset{k_1}{\rightleftharpoons} [H_2Fe_2dicarpy\text{-}SCH_2COO^-] + H^+$ (22)

$[H_2Fe_2dicarpy\text{-}SCH_2COO] \overset{k_2}{\rightleftharpoons} HFe_2dicarpy + {}^*SCH_2COOH$ (23)

$HFe_2dicarpy + HSCH_2COOH \overset{k_3}{\rightleftharpoons} Fe_2dicarpy^{2-} + {}^*SCH_2COOH + 2H^+$ (24)

$2\ {}^*SCH_2COOH \overset{k_5}{\rightarrow} HOOCCH_2SSCH_2COOH$ (25)

Formation of the precursor complex (equation 22) will be faster than the electron transfer steps (equation 23 and 24).

Therefore, the rate will be given as

$$\frac{-d[Fe_2dicarpy]}{dt} = k_2[H_2Fe_2dicarpy\text{-}SCH_2COO]^- + k_3[HFe_2dicarpy][HSCH_2COOH] \quad (26)$$

Applying steady state approximation for $[HSCH_2COO^-]$, $[H_2Fe_2dicarpy^{2+}]$ and $[HFe_2dicarpy]$, we obtain that

$$\frac{-d[\mathrm{Fe_2dicarpy}]}{dt} = k_1k_2\,k_1[Fe_2dicarpy]\frac{[HSCH_2COOH]}{k_2} + \frac{[H^+]}{k_3} \qquad (27)$$

Scheme 2

$$H_2Fe_2dicarpy^{2+} + HSCH_2CH_2N^+H_3 \underset{k_3}{\overset{k_3}{\rightleftharpoons}} [H_2Fe_2dicarpy\text{-}SCH_2CH_2NH_2] + 2H^+ \qquad (28)$$

$$[H_2Fe_2dicarpy\text{-}SCH_2CH_2NH_2] \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} [H_2Fe_2dicarpy\text{-}SCH_2CH_2NH_2]^{2-} + 2H^+ \qquad (29)$$

$$[H_2Fe_2dicarpy\text{-}SCH_2CH_2NH_2]^{2-} + HSCH_2CH_2NH_2 \overset{k_5}{\rightleftharpoons} 2^*SCH_2CH_2NH_2 + HFe_2dicarpy^{2-}$$

$$2^*SCH_2CH_2NH_2 \xrightarrow{k_4} H_2NSSCH_2CH_2NH_2 + [Fe_2dicarpy\text{-}SCH_2CH_2NH_2{}^{2-}] \qquad (30)$$

$$\text{Rate} = k_4[H_2Fe_2dicarpy\text{-}SCH_2CH_2NH_2] + k_3[HSCH_2CH_2NH_2] \qquad (31)$$

Apply steady state approximations;

$$[Fe_2dicarpy\text{-}SCH_2CH_2NH_2]^{2-} = \frac{k_1k_2k_3[H^+]]^2[Fe_2dicarpy]}{k_{-3}+k_4[H^+]]^2[Fe_2dicarpy]} \qquad (32)$$

$$\text{Also } [Fe_2dicarpy\text{-}SCH_2CH_2NH_2] = \frac{k_1k_2k_3}{k_4}[H^+]]^2[Fe_2dicarpy] \qquad (33)$$

Substituting equations (32) and (33) into (31) gives that

$$\text{Rate} = \frac{k_3+k_5\{k_+k_2[H^+][Fe_2dicarpy]\mathrm{HSCH_2CH_2NH_2}]\,\}}{k_{-3}+k_4[H^+][Fe_2dicarpy]} \qquad (34)$$

The schemes were arrived at by considering the fact that:

Michaelis-Menten type plots of 1/k_{obs} versus 1/[reductants] for both reaction Figure 5 or 6 were linear (R^2 = 0.998 for mercapthoethylamine reaction), 0.991 for mercaptoacetic acid reaction with intercepts. This implies inner-sphere nature of the reactions and fact that formation of precursor complexes of larger enough equilibrium constants played significant role in the reaction as can be seen in equation (28), (29), (22) and (23).

A closer look at the acid-dependence of the reactions shows that the degree of correlation is very poor implying that various acid dependencies are possible. At pH 3-4, dissociation of β −mercaptoacetic acid will predominate leading to inverse aid dependence. At pH of 1-3, neutral β −mercaptoacetic acid or the protonated form could be reacting. Under this oxidation protonation of the azomethine groups of the saloph complex will be encouraged leading to formation of $H_2(Fe_2saloph)_2$-dicarpy^{2+}.

This form has been encountered in other reaction of the dimer

Stepwise reduction of the dimer to give in the first instance Fe (III)-Fe (II) and finally Fe (II)-Fe (II) is seen in equations (23), (24), (25) and (29). Reaction of Fe (III)-Fe (II) mixed valence dimer in the next electron transfer step is responsible for limiting condition of product retardation of reaction as seen in the rate law equation (34). The two electron transfer steps are rate limiting.

Outer-sphere pathways involving reaction of the unprotonated and undissolved reductant molecule with $HFe_2dicarpy$ will also be rate limiting in the electron transfer step.

The substitution-controlled electron transfer route where rate of formation of precursor complexes of large equilibrium constant is slow and the intramolecular electron transfer process is fast is not ruled out. In such case the following electron transfer steps will occur:

$$H_2Fe_2dicarpy^{2+} + HSCH_2COOH \overset{slow}{\rightleftharpoons} [H_2Fe_2dicarpy\text{-}SCH_2COOH]^+ + H^+ \qquad (35)$$

$$[H_2Fe_2dicarpy\text{-}SCH_2COOH]^+ \overset{fast}{\rightleftharpoons} Fe_2dicarpy_- + 2H^+ + {}^*SCH_2COOH \qquad (36)$$

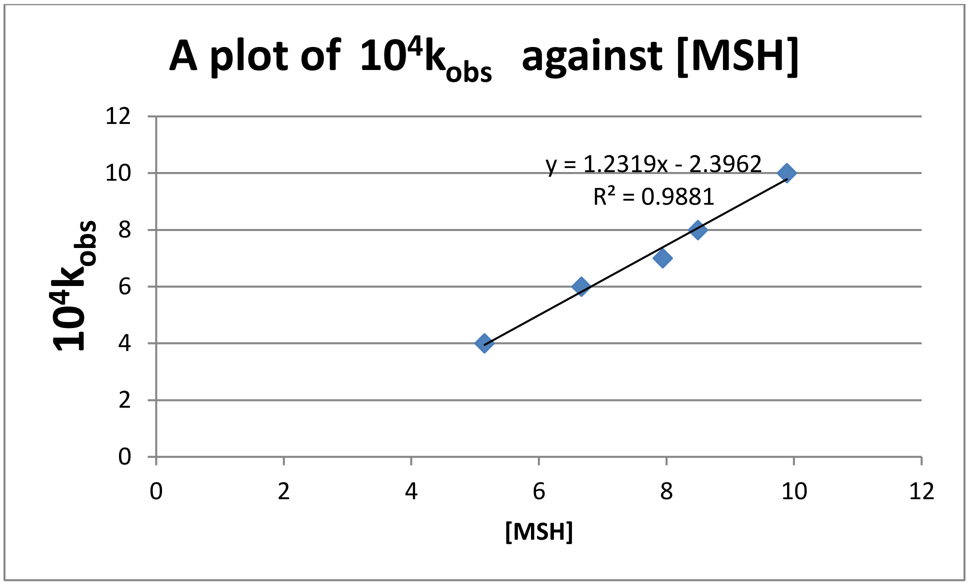


Figure 5 Michaelis-Menten plots for mercaptoethylamine (MSH) reaction

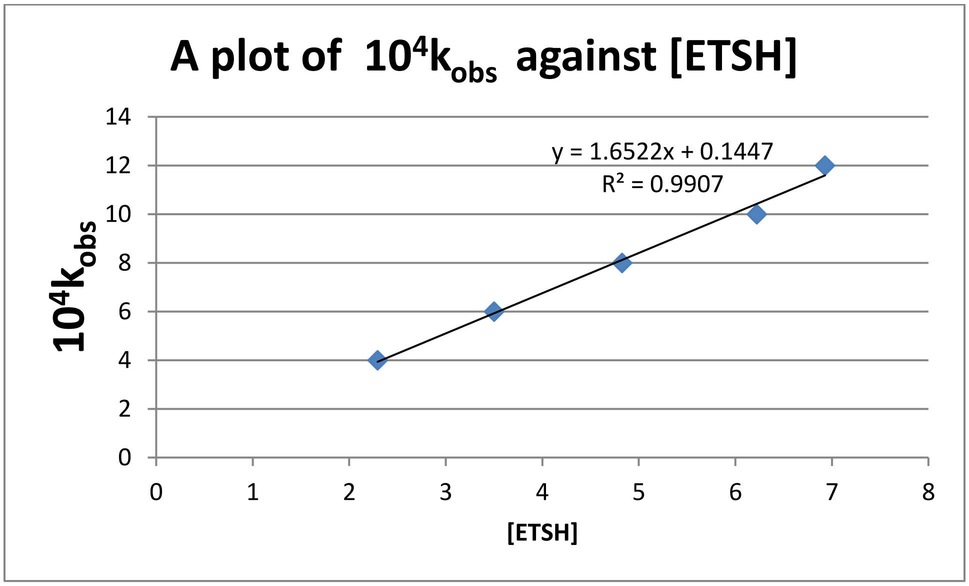


Figure 6 Michaelis-Menten plots for mercaptoacetic acid (ETSH) reaction

5. CONCLUSION

The study of the reduction of the 2,5-pyridinedicarboxylic acid (dicarpy) bridged iron (III) dimer, [(Fe(saloph))$_2$-μ-dicarpy], by the thiolsβ-mercaptoethylamine in aqueous $HClO_4$ has revealed new kinetic traces.

Acid-dependence of the reaction kinetics is complicated and sow sort spasmodic. This has been interpreted in terms of the various equilibria established by the redox partners in acid media (pH≤4). Protonation as well as deprotonation of the redox partners lack place in the acid range.

The complex nature of the reactions has been described in terms of plausible inner-sphere and outer-sphere paths concurrently attending the reactions.

Substitution-controlled and kinetically-controlled inner-sphere electron transfer pathways explain much of the cause of the reactions.

Spectroscopic evidence for likely formation of intermediates of the type, $[H_2Fe_2dicarpy\text{-}SR]^+$, $[H_2Fe_2dicarpy\text{-}SR]$ was obtained by running the UV-spectra of the partially reacted reaction mixtures. Enhanced peaks and change in absorption maxima were evident in the reactions, thereby implying high probability of formation of intermediates.

Stepwise oxidation/reduction of the Fe (III) has been proposed where intermediates of the form Fe (II)-Fe (III) are formed before complete reduction to Fe (II)-Fe (III).

Informed consent

Not applicable.

Ethical approval

Not applicable.

Conflicts of interests

The authors declare that there are no conflicts of interests.

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Data and materials availability

All data associated with this study are present in the paper.

REFERENCES AND NOTES

1. Anidobu CO. MSc Dissertation. University of Nigeria, Nsukka, Nigeria 2017; 154.
2. Ashmawy FM, Ujaimi AR, Mc-Auliffe CA, Parish R, Pritchard RG. A facile synthesis of [(Fe(salphen))$_2$O] (salphenH$_2$◎N,N′-o-phenylenebis(salicylidineimine)) and the X-ray crystal structure of [(Fe(salphen))$_2$O]·DMSO. Inorg Chem Acta 1991; 187:155.
3. Atiga S, Ukoha PO, Ujam TO, Okpareke CO. Kinetics and mechanism of the reduction of μ-adiadi[N,N^1-bis {salicylideneethylenediaminatoiiron (III)}] by dithionate ion. Trans Met Chem 2014; 39:189.
4. Atiga S, Ukoha PO, Ujam TO. Dynamics of electron transfer reaction of trioxosulfate (IV) ion with dinuclear iron (III)-salene complex n perchloric acid medium. Asian J Chem 2015; 27(4): 1274.
5. Costes JP, Tommasino JB, Carre B, Soulet F, Fabre PL. Electrochemical studies of iron (III) Schiff base complexes—II. Dimeric μ-OXO[FeIII(N$_2$O$_2$)]$_2$O complexes. Polyhedron 1995; 14(6):771.
6. Dalla-Cort A, De-Bernardin P, Forte G, Mihan FY. Metal–salophen-based receptors for anions. Chem Soc Rev 2010; 39:3b863.
7. Durovic MD, Puchta R, Bugarcic ZD, Eldik RV. Studies on the reactions of $[AuCl_4]^-$ with different nucleophiles in aqueous solution. Dalton Trans 2014; 43:8620.
8. Esmelindro MC, Oestreicher EG, Marrquez-alverez H, Dariva C, Egues SMS, Fernandez C, Bortoluzzi AJ, Drago V, Antunes OAC. Catalytic Oxidation of Cyclohexanone by a binuclear Fe (III) complex biomimetic to methane monooxygenase. J Inorg Biochem 2005; 99:2054–2061.
9. Gomwalk UD, Mc-Auley A. Metal-ion oxidations in solution. Part V. Cerium (IV) oxidation of thiourea and its N-substituted derivatives. J Chem Soc A 1968; 2948.
10. Haim A. Mechanisms of Electron Transfer Reactions: The Bridged Activated Complex. Prog Inorg Chem 1983; 30:273-355.
11. Idris SO, Iyun JF, Agbaji EB. Kinetic of the reduction of tetrakis(2,2^{1}bipyridine)-μoxodiiron (III)ion by mercaptoacetic acid in aqueous hydtochloric acid medium. Afr J Nat Sci 2004; 10:35.
12. Idris SO, Iyun JF, Agbaji EB. Kinetics and mechanism of the oxidation of thiosulfate by tetrakis(2,2′-bipyridine)-μ-oxodiiron (III) in aqueous acidic medium. Ife J Sci 2008; 10(1): 103.
13. Idris SO, Iyun JF, Agbaji EB. Mechanism of electron transfer reaction between L-Cysteine and tetrakis(2,2′-bipyridine)-μ-oxodiiron (III) ion in aqueous acidic medium. Int J Chem Appl 2011; 3(2):159.
14. Johannissen LO, Irebo T, Sjödin M, Johansson O, Hammarström L. The Kinetic Effect of Internal Hydrogen Bonds on Proton-Coupled Electron Transfer from Phenols: A Theoretical Analysis with Modeling of Experimental Data. J Phys Chem B 2009; 113:16214.
15. Kopel P, Sindelar Z, Klicka R. Complexes of iron (III) salen and saloph Schiff bases with bridging dicarboxylic and tricarboxylic acids. Transit Met Chem 1998; 23:139.
16. Levine IN. Physical Chemistry, 6th Edition. Mc Graw Hill International Publisher 2009; 906–911.
17. Liu J, Zhang B, Wu B, Zhang K, Hu S. The Direct Electrochemical Synthesis of Ti (II), Fe (II), Cd (II), Sn (II) and Pb (II) Complexes with N, N′-Bis(Salicylidene)-o-Phenylene diamine. Turk J Chem 2007; 31:623.
18. Oyetunji AO, Ramokongwa G, Ogunlusi GO, Becker CLA. Ligand substitution and reduction reactions of decakis (isopropylisocyanide)dicobalt(II). Transit Met Chem 2013; 38:235.

19. Roseweig AC, Nordlund P, Takahara PM, Frederick CA, Lippard SJ. Geometry of the soluble methane monoxygenase catalytic diironcenter in 2 oxidation states. Chem Bio 1995; 2:409.
20. Sardi F, Manta B, Portillo S, Knoops B, Comini M, Ferrer-Sueta G. Determination of acidity and nucleophilicity in thiols by reaction with monobromobimane and fluorescence detection. Anal Biochem 2013; 435. doi: 10.1016/j.ab.2012.12.017
21. Scheidt WR, Cheng B, Safo MK, Cukiernik F, Marchon JC, Debrunner PG. New class of bridged diiron (III) complexes with a single hydroxo bridge. The preparation and structure of (.mu.-hydroxo)bis((octaethylporphinato)iron (III)) perchlorate. J Am Chem Soc 1992; 114(11):4420.
22. Sheriff S, Hendrickson WA, Smith JL. Structure of myohemerythrin in the azidomet state at 1.71 A^0 resolution. J Mol Biol 1987; 197:273.
23. Stefánsson A. Iron (III) hydrolysis and solubility at 25 C. Environ Sci Technol 2007; 41:6117.
24. Synder BS, Patterson GS, Abrahamson AA, Holm RH. Binuclear Iron System Ferromagnetic in the three oxidation states: Synthesis, Structures and electronic aspects of molecules with a $Fe_2(OR)_2$ bridge unit containing Fe (III, III), Fe (III, II) and Fe (II, II). J Am Chem Soc 1989; 111:5214–5223.
25. Ugwuanyi KO, Ukoha PO. Kinetics and mechanism of the reduction of $[(Fe(salen))_2adi]$ with benzymercaptan. Proc 38th Ann Int Conf Chem Soc Niger 2015; 401-414.
26. Ugwuanyi KO, Ukoha PO. Kinetics and mechanisms of the reduction of μ-adipato-di (N, N/Bis(Salicylidene) ethylenediaminatoiron (iii) $[(Fe\text{-}Salen))_2adi]$ with 2-mercaptobenzothiazole in aqueous perchloric acid. Niger Res J Chem Sci 2017; 3:41.
27. Ukoha PO, Anidobu CO, Iorungwa PD, Oluigbo IC. Kinetics and mechanism of reduction of $[(Fe(saloph))_2\text{-}\mu\text{-dicarpy}]$ complex by Lascorbic acid in acid medium. FUW Trends Sci Technol J 2018; 3(1):158.
28. Ukoha PO, Asegbeloyin JN, Alioke C, Ujam OT. Kinetics and Mechanism of the oxidation of dithionate ion by N, N′-ethylenebis-[salicylidene] iron (III) complex in aqueous perchloric acid medium. J Chem Soc Niger 2010; 35(1):63.
29. Ukoha PO, Atiga S, Ujam OT, Asegbeloyin JN, Okparaeke CO, Okereke SOE. Kinetics and mechanism of electron transfer reaction of an adipato bridged iron (III) salen complex with dithionite ion in perchloric acid medium. Croat Chem Acta 2015; 88(3):259.
30. Ukoha PO, Iyan JF. Oxidation of L-ascorbic acid by $enH_2[(FeHEDTA)_2O].6H_2O$ in aqueous acid medium. J Chem Soc Niger 2002; 27(2):119.
31. Ukoha PO, Iyun JF. Kinetics of reduction of an iron (III) complex ion by mercaptoethanol and mercaptoethylamine in perchloric acid medium. J Chem Soc Niger 2001; 26(2):163.
32. Ukoha PO, Iyun JF. Mechanism of the oxidation of 2-mercaptoacetic acid by $enH_2[(FeHEDTA)_2O].6H_2O$ in aqueous acid medium. Chemclass J 2005; 2:51.
33. Ukoha PO, Ugwuanyi KO, Obeta RU. Reduction of the adipatobridged binuclear iron (III) complex $[(Fe(salen))_2adi]$, by thioglycolic acid: Kinetic and mechanistic study. Commun Phys Sci 2018; 3(1):49.
34. Ziegler DM. Role of reversible oxidation-reduction of enzyme thiols-disulfides in metabolic regulation. Ann Rev Biochem 1985; 54:305.