

ELECTRON TRANSFER REACTIONS OF BRIDGED BINUCLEAR IRON(III)- COMPLEXES: A REVIEW

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ABSTRACT

Binuclear iron (III) complexes comprising of the -oxo-bridged form, $[\text{Fe}_2\text{O}]^{4+}$ or $[\text{Fe}(\text{OH})_2]^{4+}$, and the dicarboxylic bridged chains incorporating salen or saloph ligands have been synthesized and characterized. Their close resemblance to some haeme and non-haeme iron-based enzymes has elicited a lot of interest in studying them. Biological studies have shown some of them to be good mimics of superoxide dismutase. The saloph and salen analogues also showed physiological actions very close to the porphyrins. The study of their electron transfer reactions, with a view of understanding their potential as electron transfer enzymes, has generated interesting results and some unusual kinetic behaviours. Reactions of $[(\text{FeHEDTA})_2\text{O}]^{2+}$ with ascorbic acid and some thiols were second order and followed outer-sphere path mediated by ion-pairs formation. However, reaction of $[\text{Fe}_2(\text{bipy})\text{O}]^{4+}$ with some reductants were zero order with respect to the oxidant and also followed outer-sphere path. Reduction of the adipato-bridged dimer, $[\text{Fe}(\text{saloph})_2\mu\text{-adi}]$, by SO_3^{2-} and SO_4^{2-} , $\text{S}_2\text{O}_5^{2-}$, benzyl mercaptan, mercaptobenzothiazole and thioglycolic acid followed inner-sphere paths. However, all the reactions were acid-catalysed and were mediated by intervening protonated oxidant precursor complexes.

Keywords: redox, binuclear, bridged, iron (III)-dimer, electron transfer, thiols, oxidant, reductant

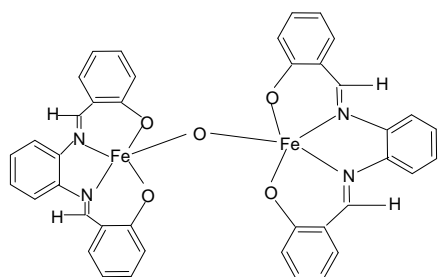
INTRODUCTION

The chemistry of iron has generated a lot of interest particularly the bridged binuclear iron (III) complexes as seen in literature [1-4]. This interest has been presumably prompted by the need to understand its role as a versatile oxidant in the physiological functions of biological systems and its catalytic reactions in metallurgical industries [5].

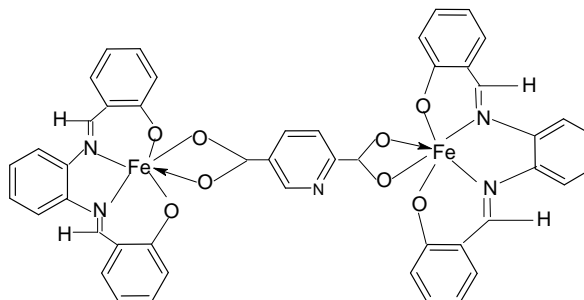
Bridged binuclear iron (III) complexes serve as structural models for metabolic and cellular investigations. In proteins such as hemerythrin and myohemerythrin [6, 7], binuclear iron (III) centres serves as oxygen transport and storage. This can be attributed to the ease of electron exchange between iron (III) and iron (II) states by suitable reductant. Redox processes involving

bridged iron (III) complexes have received special attention mainly due to its potential to serve as bio-models or mimics for biological processes. For example, bridged binuclear ironsalen complex serve as efficient asymmetric catalyst and could improve the hydrolytic cleavage of DNA and RNA [5, 8 – 10]. The

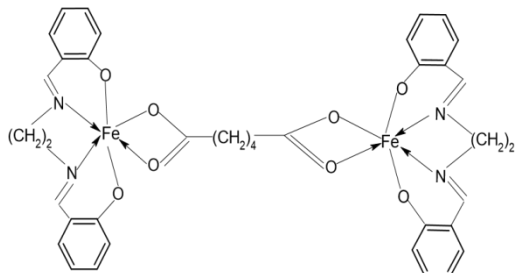
structures of some bridged binuclear iron (III) complexes[5,6] such as $[(\text{Fe}(\text{saloph})_2\text{O})]$, $[(\text{Fe}(\text{saloph})_2\text{-2,5-dicarpy})]$, $[(\text{Fe}(\text{salen})_2\text{O})]$, $[(\text{Fe}(\text{salen})_2\text{adi})]$; Protonated $[(\text{Fe}(\text{salen}))_2\text{adi}]$, $[\text{L}^n\text{Fe}^{\text{III}}(\text{bpy})\text{Fe}^{\text{III}}\text{L}^n]^{2+}$, $[\text{Fe}_2\text{L}_1\text{Cl}_4(\text{H}_2\text{O})_4]\text{H}_2\text{O}$, $[\text{Fe}_2\text{L}_2\text{Cl}_4(\text{H}_2\text{O})_4]\text{H}_2\text{O}$, and $[\text{Fe}_2\text{L}_3\text{Cl}_4(\text{H}_2\text{O})_4]2\text{H}_2\text{O}$ are shown in Figure 1.



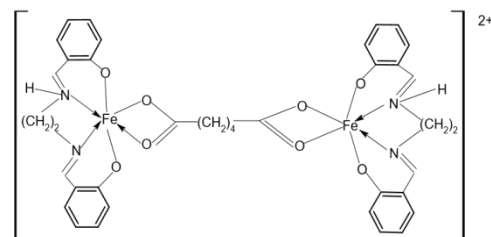
(a.) $[(\text{Fe}(\text{saloph})_2\text{O})]$



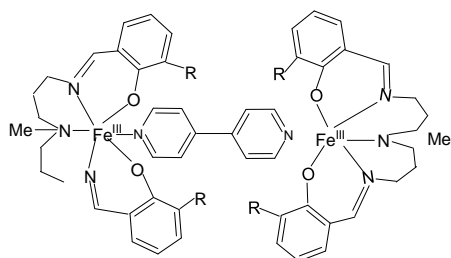
(b.) $[(\text{Fe}(\text{saloph})_2\text{-2,5-dicarpy})]$



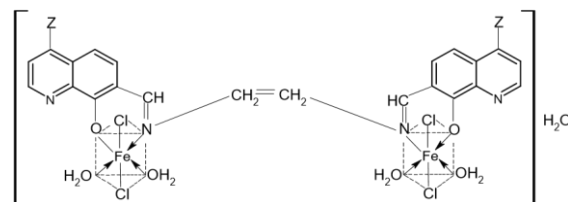
(c.) $[(\text{Fe}(\text{salen}))_2\text{adi}]$



(d.) Protonated $[(\text{Fe}(\text{salen}))_2\text{adi}]$



(e.) $[\text{LnFe}^{\text{III}}(\text{bpy})\text{Fe}^{\text{III}}\text{Ln}]^{2+}$; R = H for L1 and R = OMe for L2 (Z = H) and 4 (Z = Cl)



(f.) $[\text{Fe}_2\text{L}_1\text{Cl}_4(\text{H}_2\text{O})_4]\text{H}_2\text{O}$; complexes 1

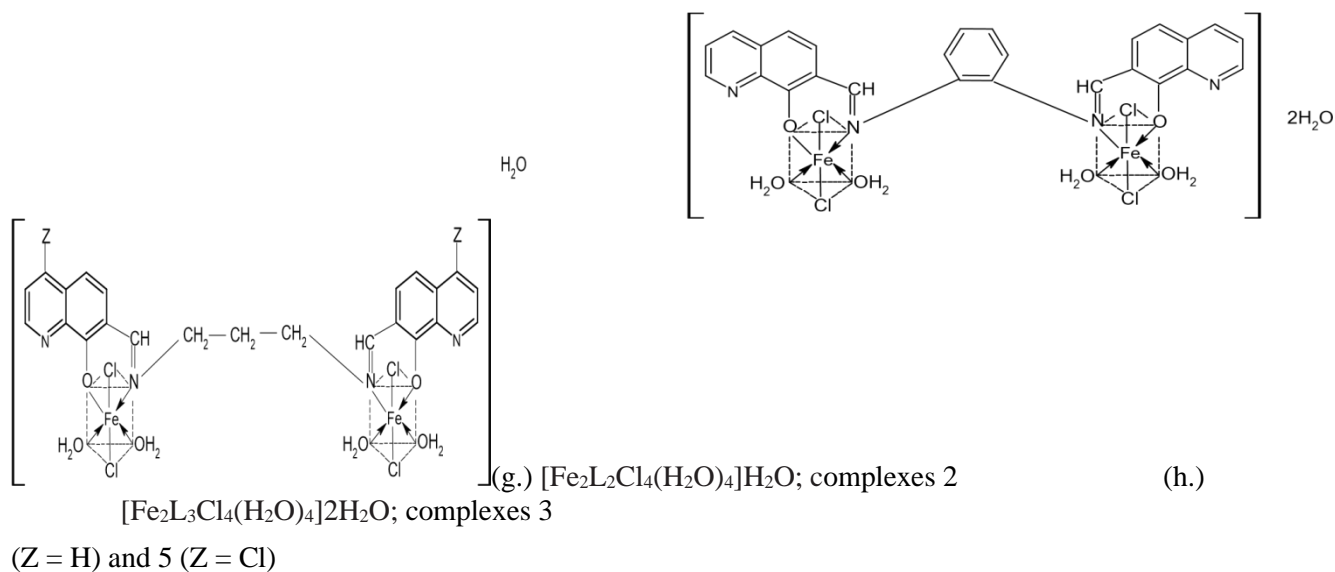


Figure 1: Shows the Structures of (a.) $[(\text{Fe}(\text{saloph}))_2\text{O}]$, (b.) $[(\text{Fe}(\text{saloph}))_2\text{-}2,5\text{-dicarpy}]$, (c.) $[(\text{Fesalen})_2\text{O}]$, (d.) $[(\text{Fe}(\text{salen}))_2\text{adi}]$, (e.) Protonated $[\text{Fe}_2\text{adi}]$, (f.) $[\text{Fe}_2\text{L}_1\text{Cl}_4(\text{H}_2\text{O})_4]\text{H}_2\text{O}$; complexes 1 (Z = H) and 4 (Z = Cl), (g.) $[\text{Fe}_2\text{L}_2\text{Cl}_4(\text{H}_2\text{O})_4]\text{H}_2\text{O}$; complexes 2 (Z = H) and 5 (Z = Cl), and (h.) $[\text{Fe}_2\text{L}_3\text{Cl}_4(\text{H}_2\text{O})_4]2\text{H}_2\text{O}$; complexes 3.

In this article, we present a review of the dynamics of the redox reactions of bridged binuclear iron (III) complexes with different biomolecules and other reductants. The aim of this report is to bring to lime light the key structural and electronic factors surrounding iron electron transfer and give better insight to

Synthesis And Characterization Of Binuclear Iron (III) Complex Containing Redoxactive Bridging Ligands

Some bridged binuclear iron (III) compounds have been synthesized and characterized. These include; μ -oxo-bridged iron (III) complexes of the type, $\text{enH}_2[(\text{FeHEDTA})_2\text{O}]$ [11 – 14], $[(\text{Fe}_2(\text{bipy})\text{O})\text{Cl}_4]$ [15], $[\text{Fe}(\text{salen})_2\text{O}]$ and $[\text{Fe}(\text{saloph})_2\text{O}]$ [16]. Other types of salen-saloph

iron (III) bridging systems having p-quinone bridge [27], terephthalic acids [16], bipyridinedicarboxyaldehyde, pyridine and dicarboxylic acids²⁸ have also been reported.

The Schiff bases (salen and saloph) are synthesized from the condensation of salicylaldehydes or salicylaldehydes derivatives with 1,2-ethylenediamine (salen) or o-phenylenediamine (saloph). These ligands are capable of forming coordinate bonds with different metal ions through azomethine and phenolic groups [17 – 21]. X-ray studies of bridged complexes of salen-saloph iron (III) have been widely reported in literature [22 – 26]. The structures of salen and saloph are shown in Figure 2.

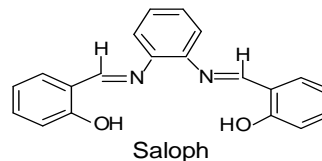
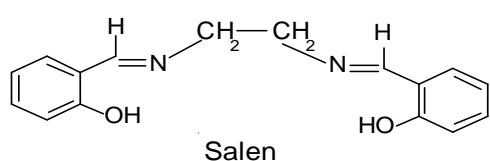


Figure 2: Structure of Salen and Saloph

The complexes $[\text{Fe}(\text{salen})_2\text{L}]$ and $[\text{Fe}(\text{saloph})_2\text{L}]$, where L = terephthalate, fumarate, oxalate or succinate dianion [16] and the saloph analogue, where L = glutarate, adipate, pimelate, suberate or dithiooxamide dianion [29] respectively have also been reported. Kopel, Sindelar and Klicka [22] studied the dicarboxylic and tricarboxylic acids bridged complexes of salen-saloph iron(III). Salen-saloph bridged iron (III) complexes have attracted great interest due to their resemblance to porphyrins and studies on their redox processes has enhanced the understanding of the action mode of closely related biological systems [30 -31].

Other bridged complexes of iron like phthalocyanines and porphyrazines have been synthesized [32] but their redox reactions not fully reported. The structures of μ -oxo diiron (III) porphyrazine complex and the schematic representation of two μ -oxo diiron complexes

with unsubstituted phthalocyanine ligands and their principal properties [32] are shown in Figures 3 and 4 respectively.

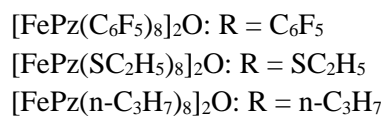
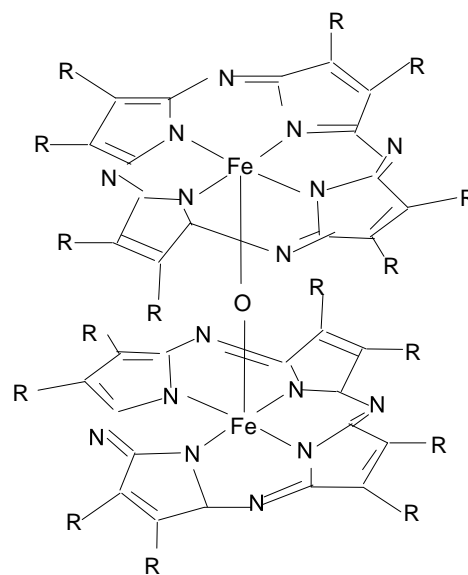


Figure 3: Structures of μ -Oxo Diiron (III) Porphyrazine Complex

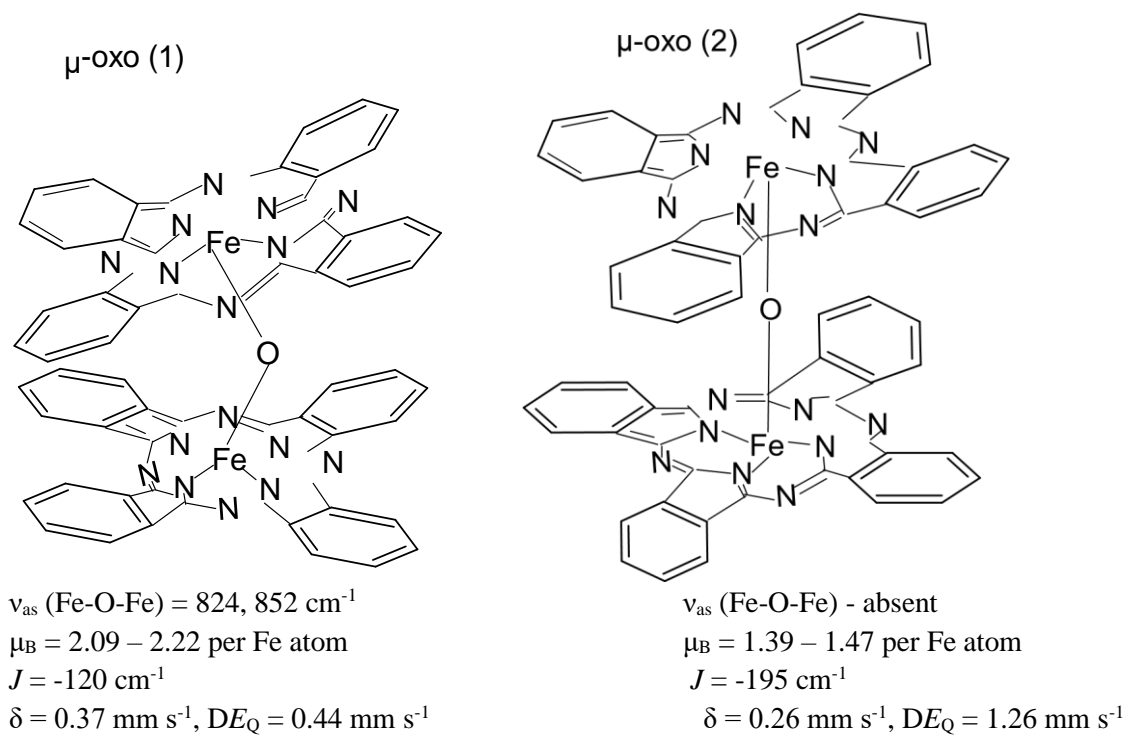


Figure 4: Schematic Representation of two μ -Oxo Diiron Complexes with Unsubstituted Phthalocyanine Ligands and their Principal Properties

Redox Reactions Of Bridged Binuclear Iron (III) Complexes With Some Reductants

Reduction of Bridged Iron (III) Complexes using Thiols

Thiols, also referred to as mercaptans are a class of organic compounds containing sulphhydryl group (-SH) attached to carbon atom. They function as excellent reducing agents due to the presence of the -SH group [33]. Oxidation of thiols has been extensively studied to unravel their reaction mechanism and participation in intercellular reactions of living cells. A number of factors such as pH, concentration ratio, and self exchange rates are vital in the redox reactions of thiols. Depending on the oxidant, they may undergo oxidative dimerization to give

disulphide (RSSR), sulphinic acid (RSO₂H) or sulphonic acid (RSO₃H) as organic product. Stronger oxidants oxidize thiols to sulphonic acid but they are oxidized to disulphide by the weaker oxidants [34, 35].

The study of the redox reactions of μ -oxo-bridged iron (III) complex, [(FeHEDTA)₂O]²⁺ with thiols, mercaptoacetic acid [9], mercaptoethanol and mercaptoethylamine [10] in perchloric acid medium showed that the thiols were oxidized to disulphides while the iron (III) were reduced to iron(II). Under pseudo-first order conditions, kinetic data generated for these systems revealed that the rates of reactions were first order dependent on the concentrations of

both the oxidant (Fe(III) dimer) and the reductants (thiols) to give second order overall as represented in the rate law, equation (1).

$$-\frac{d[FeHEDTA]_2O}{dt} = k_2[FeHEDTA]_2O[RSH] \quad (1)$$

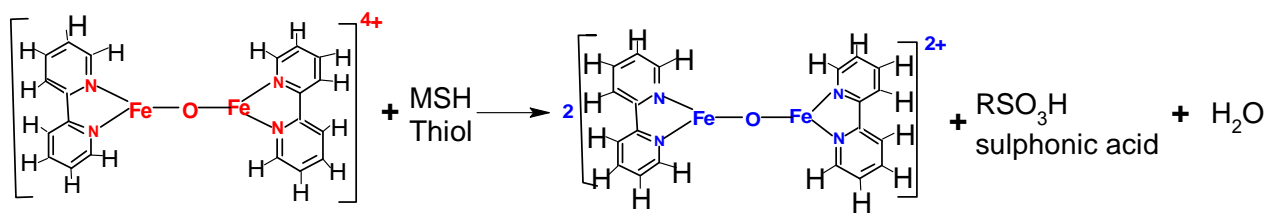
*[RSH] = mercaptoacetic acid, mercaptoethanol or mercaptoethylamine

Spectrophotometric titration was used to determine the stoichiometry; the results obtained showed that two moles of thiol were consumed for every mole of Fe(III) dimer reduced. Decrease in rates of reactions with increase in acid concentrations was observed but reaction rates were invariant to changes in dielectric constant. This observed inverse acid dependence of these systems was interpreted on the basis of deprotonation of the Fe(III) dimer prior to electron transfer [36]. Based on the results presented and other kinetic information generated, outersphere mechanistic pathway with intervening ion-pair formation was established. The electron transfer reaction and mechanism of another analogue of oxo-bridged binuclear Fe(III) complex, tetrakis(2,2'-bipyridine)- μ -oxodiiron (III) ion, $[(Fe_2(bipy)O)]^{4+}$ denoted as $[Fe_2O]^{4+}$ with L-cysteine [37], mercaptoacetic acid [38], glutathione [39] and methionine [40] was studied. The reactions followed outer-sphere electron transfer route and rates of reaction showed first order dependence on the

concentration of Fe(III) complex but zeroth-order dependence with respect to the concentrations of the thiols. The rate law of these reactions is presented in equation (2).

$$\frac{1}{2} \frac{dFe^{2+}}{dt} = k_{obs}[Fe_2O]^{4+} \quad (2)$$

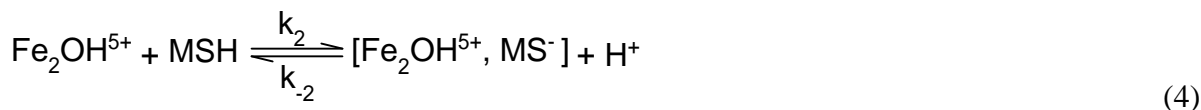
In these reactions, oxo-bridged Fe(III) dimer was reduced to Fe(II) and the thiols were oxidized as follows; glutathione was oxidized to disulphide [39], methionine to sulphoxide [40], while Lcysteine and mercaptoacetic acid [37, 38] were oxidized to sulphonic acid respectively. These observed behaviours were rationalized on the basis that though oxidation of thiols is dependent on the nature of oxidant [34, 35], thiol oxidation can also occur through N, O, or S atom. For Lcysteine and mercaptoacetic acid reaction systems, electron transfer occurred more readily via S atom since S is more nucleophilic than N or O atoms [37]. The stoichiometry of L-cysteine and mercaptoacetic acid reaction systems can be seen in Scheme 1. The authors reported no changes in rate when ionic strength was varied, but varying the dielectric constant led to increase in reaction rates for the systems. Inverse acid catalysis is observed for methionine system but the reactions showed no dependence on hydrogen ion concentration $[H^+]$, for L-cysteine, mercaptoacetic acid and glutathione systems.



Oxo-bridged iron (III) (bipy)₄ dimer Oxo-bridged iron (II) (bipy)₄ dimer

Scheme 1: Stoichiometry of Reaction of Oxo-bridged Iron (III) (bipy)₄ Dimer with Thiols.

Considering stoichiometry, acid-dependence, effect of ionic strength and dielectric constant; the following key mechanistic steps from equations (3) to (8) represents the reactions since they exhibit similar redox properties.



Resolving $[Fe_2OH^{5+}, MS^-]$ further gives;

$$Rate = k_3[Fe_2OH^{5+}, MS^-] \tag{5}$$

$$[Fe_2OH^{5+}, MS^-] = \frac{k_2[Fe_2OH^{5+}][MSH]}{k_3 + k_2[H^+]} \tag{6}$$

Substituting equation (6) into (5) and resolving it further, brings the rate to;

$$Rate = \frac{k_3k_2k_1[Fe_2O^{4+}]}{k_3 + k_2(k_{-1} + k_2)} \tag{7}$$

Equation (7) is similar to (2) where;

$$k_{obs} = \frac{k_3k_2k_1}{k_3 + k_2(k_{-1} + k_2)} \tag{8}$$

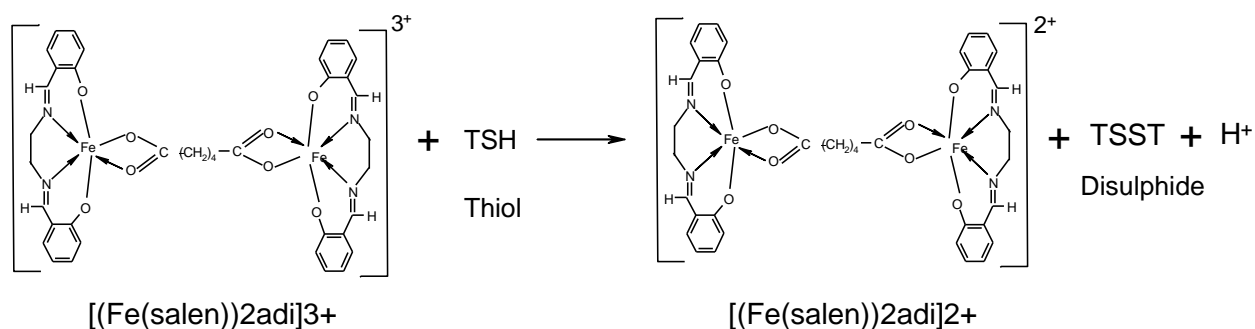
*MSH = L-cysteine, mercaptoacetic acid or glutathione.

Kinetic and mechanism of reduction of μ -adipato bridged Fe(III)-salen complex was studied using

benzylmercaptan [41], 2-mercaptobenzothiazole [42], thioglycolic acid (mercaptoacetic acid) [43],

L-cysteine and thiourea [44]. The reduction of the adipato bridged iron(III)-salen dimer denoted as $[Fe(salen)_2adi]$ with these thiols were studied spectrophotometrically in perchlorate medium. Within the reaction conditions, first order dependence of rate on the concentration of Fe(III)-salen dimer was observed and the dimer reduced to Fe(II). First order dependence of rate on the concentration of reductants, L-cysteine, thiourea, thioglycolic acid and 2-mercaptobenzothiazole was recorded with the rate law given as in equation (9) but negative order on rates was recorded for benzylmercaptan and the rate law represented in equation (10).

$$-\frac{d[Fe(salen)_2adi]}{dt} = k_2[Fe(salen)_2adi][reducants] \quad (9)$$



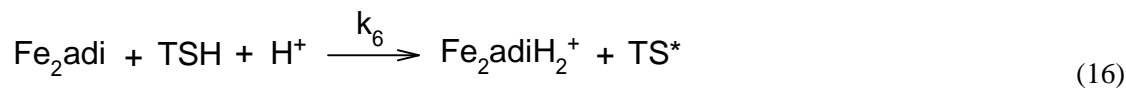
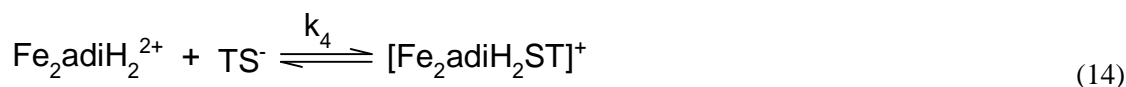
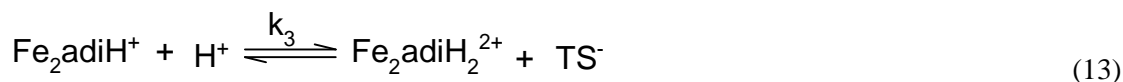
Scheme 2: Stoichiometry of Reaction of Adipato-bridged Iron (III) (salen) Dimer with Thiols.

Considering the stoichiometry, effect of ionic strength, dielectric constant, acid dependence and other results obtained, the following mechanism in equations (11) to (19) have been proposed for

$$-\frac{d[Fe(salen)_2adi]}{dt} = \frac{[Fe(salen)_2adi]}{[BSH]} \quad (10)$$

The stoichiometry of these reactions is represented in Scheme 2; TSH denotes benzylmercaptan, 2-mercaptobenzothiazole, thioglycolic acid, L-cysteine and thiourea. The reactions all showed direct dependence on hydrogen ion, H^+ (acid catalysis) which infers preprotonation of $[Fe(salen)_2adi]$ prior to electron transfer [44]. Also, reactions of the dimer with the thiols occurred via inner-sphere pathway. The rates of reactions was observed to decrease with increase in ionic strength for all the systems but reactions rates were not affected by the decrease in dielectric constant for thioglycolic acid, L-cysteine and 2-mercaptobenzothiazole while increment in rates was observed for thiourea and benzylmercaptan.

the reactions 2-mercaptobenzothiazole, thioglycolic acid, L-cysteine and thiourea with the iron (III) dimer.



$$\text{Rate} = k_5[\text{Fe}_2\text{adiH}_2\text{ST}]^+ k_6[\text{Fe}_2\text{adi}][\text{TSH}][\text{H}^+] \quad (18)$$

Resolving equation (18) further by steady state approximation gives

$$\text{Rate} = k_6 + k_1 k_2 k_3 k_4 [\text{Fe}_2\text{adi}][\text{TSH}] \quad (19)$$

The participation of pyridine dicarboxylic acid bridged iron(III)-saloph complex, $[\text{Fe}(\text{saloph})_2\text{dicarpy}]$, in redox processes was studied [45]. Oxidation of the thiols, L-cysteine, mercaptoacetic acid and mercaptoethylamine by

$[\text{Fe}(\text{saloph})_2\text{dicarpy}]$ showed first order dependence of rate on the concentration of Fe(III)-saloph dimer and the thiols to give second order overall. The rate law is presented in equation (20).

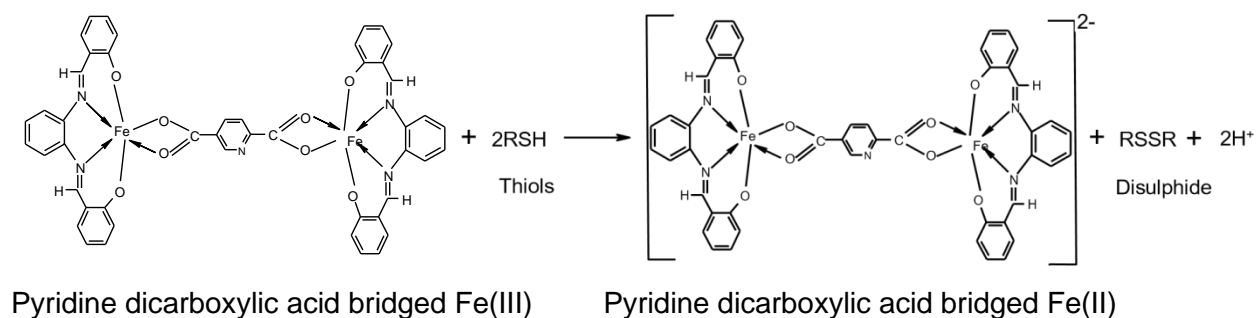
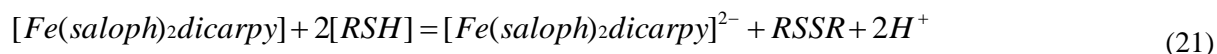
$$\frac{-d[\text{Fe}(\text{saloph})_2\text{dicarpy}]}{dt} = k_2[\text{Fe}(\text{saloph})_2\text{dicarpy}][\text{RSH}] \quad (20)$$

*RSH = L-cysteine, mercaptoacetic acid and mercaptoethylamine

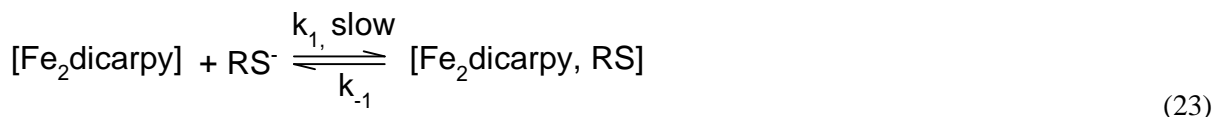
The stoichiometric studies showed that iron (III) is reduced by two mole equivalent each of the thiols to Iron (II) while the thiols were oxidized to disulphide as represented in equation (21), Scheme 3.

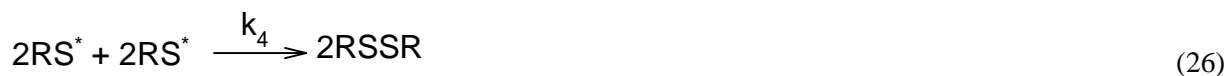
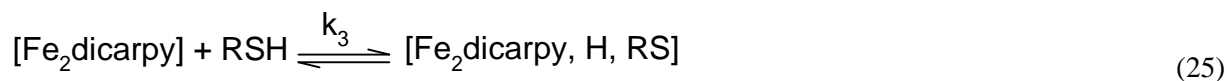
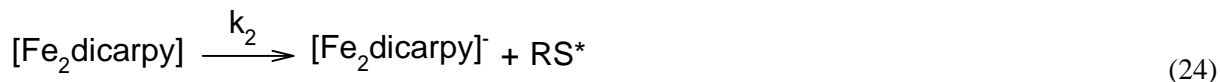
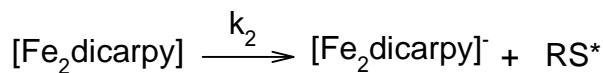
Reaction rates showed inverse dependence on acid concentration for all the systems. This negative acid dependence implies deprotonation step prior to electron transfer. Varying the ionic strength, results showed the rates of reactions increased as concentration of ionic strength increased. However, increasing dielectric constant of the reactions media resulted to decrease in rates of reactions of L-cysteine and mercaptoacetic acid systems but opposite effect

for mercaptoethylamine system was recorded. These phenomenons have been interpreted in terms of medium effect suggesting involvement of cation and neutral species at the rate determining step. The reactions of $[Fe(saloph)_2dicarpy]$ with the thiols studied followed outer-sphere pathway with ion-pair formation. Considering the stoichiometry, ionic strength, acid dependence and dielectric constant results and other kinetic data obtained, the mechanistic routes for the oxidation of the thiols by $[Fe(saloph)_2dicarpy]$ are represented in equations (22) to (28).



Scheme 3: Stoichiometry of Reaction of Pyridine Dicarboxylic Acid Bridged Iron(III)Saloph Dimer with Thiols.





$$\text{Rate} = -\frac{d[\text{Fe}_2\text{dicarpy}]}{dt} = k_1[\text{Fe}_2\text{dicarpy}][\text{RS}^-] + k_3[\text{Fe}_2\text{dicarpy}][\text{RSH}] \quad (27)$$

Applying steady approximation, gives rate as;

$$\text{Rate} = \left\{ \frac{Kk_1}{[\text{H}^+]} + k_3 \right\} [\text{Fe}_2\text{dicarpy}] + [\text{RSH}] \quad (28)$$

*RSH denotes the thiols.

Reduction of Bridged Iron (III) Complexes by L-ascorbic Acid

L-ascorbic acid (L-threo-hex-2-enono-1,4-lactone) also known as vitamin C is found naturally in wide varieties of plants and animals. It is essential to human though it is not produced by human body, thus, its only source is from diet. It serves as a dietary supplement because of its physiological function and it is used in the cure and prevention of scurvy [46] and also in the repair of tissues.

Interest in the reactions of L-ascorbic acid continues to be keen and has caught the attention of researchers. Kinetic studies have been undertaken on L-ascorbic acid so as to understand its oxidation reactions by metal ions, non - metal ions, and metal complexes as oxidants [47 - 51]. Studies involving bridged binuclear iron (III) complexes as oxidant and L-

ascorbic acid as reductant in aqueous acid media is very limited as evident from scanty work documented on the reduction of bridged binuclear Iron (III) complexes by L-ascorbic acid [52 - 54].

The reduction of bridged binuclear iron (III) complexes, $([\text{Fesalen}(\text{H}_2\text{O})_2]^+)$ [52], $([(\text{FeHEDTA})_2\text{O}]^{2+})$ [53] and $[\text{Fe}(\text{saloph})_2\text{dicarpy}]$ [54] by L-ascorbic acid (H_2A) in perchloric acid medium respectively have been investigated. First order dependence of reaction rates on the concentration of both oxidant and reductant was observed for $[\text{Fesalen}(\text{H}_2\text{O})_2]^+$ and $[(\text{FeHEDTA})_2\text{O}]^{2+}$ system respectively. The rate law is represented in equation (29).

$$-\frac{d[\text{Oxidant}]}{dt} = k_2[\text{Oxidant}][H_2A] \quad (29)$$

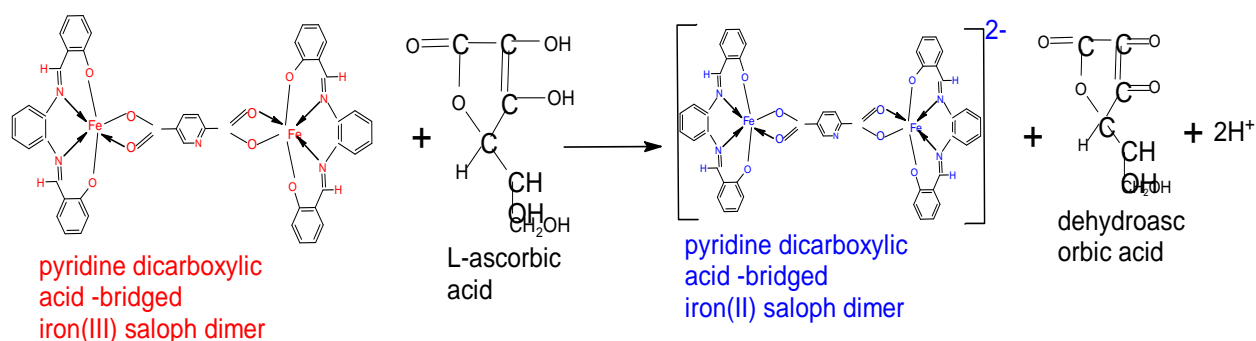
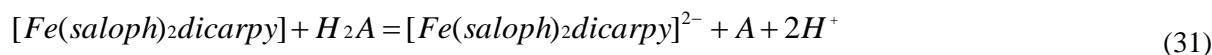
Likewise, $[Fe(\text{saloph})_2\text{dicarpy}]$ -ascorbic acid system showed first order dependence of rate on

$$-\frac{d[Fe(\text{saloph})_2\text{dicarpy}]}{dt} = k[Fe(\text{saloph})_2\text{dicarpy}][H_2A]^{1/2} \quad (30)$$

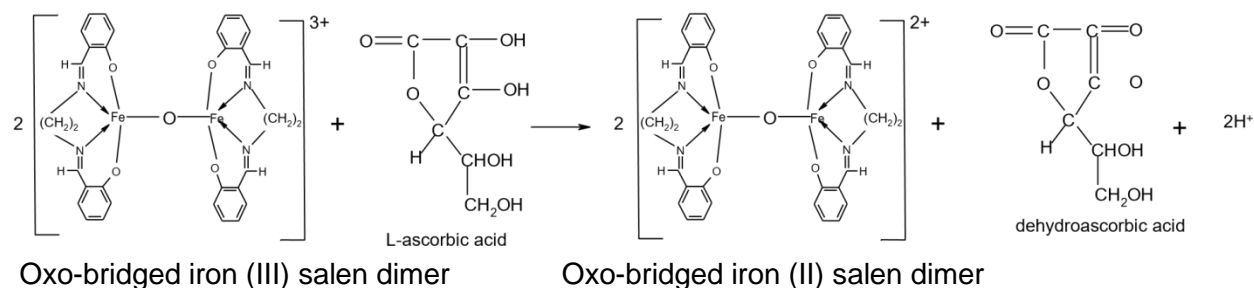
In these redox reactions, the Fe (III) dimers were reduced to Fe(II) and ascorbic acid to dehydroascorbic acid. The results of stoichiometric studies for $[Fe(\text{saloph})_2\text{dicarpy}]$ system showed 1:1 oxidant:reductant ratio

the concentration of the oxidant but half-order dependence on the concentration of L-ascorbic acid and the rate law is given in equation (30). The observed half-order dependence is not so common in reactions of L-ascorbic acid. This could point to a more complex reaction of ascorbic acid.

corresponding to the stoichiometry as represented by equations (31), Scheme 4, while for every mole of ascorbic acid oxidized, two moles equivalent of $[Fe(\text{saloph})_2\text{dicarpy}]^{2-}$ is reduced, equation (32) Scheme 4.



Scheme 4: Stoichiometry of reaction of pyridine dicarboxylic acid bridged iron(III)-saloph dimer with L-ascorbic acid

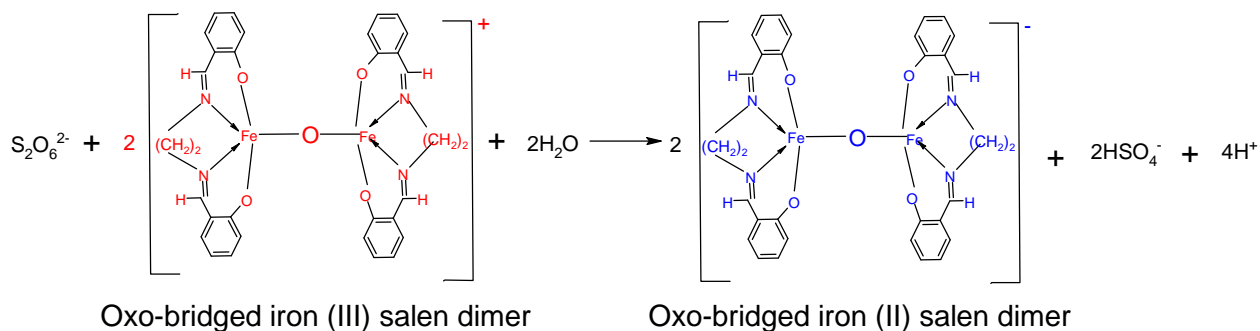


Scheme 5: Stoichiometry of Reaction of Oxo-Bridged Iron(III)-Salen Dimer with LAscorbic Acid

For $[\text{Fe}(\text{saloph})_2\text{dicarpy}]$ system, the reaction followed outer-sphere path with intervening ionpairs formation. Rate of reaction decreased with increase in acid concentration and dielectric constant but increase in rate with ionic strength was recorded. Inner-sphere mechanism was rationalized for $[\text{Fesalen}(\text{H}_2\text{O})_2]^+$ system. Reaction rate was unaffected with changes on the concentration of ionic strength and dielectric constant of the medium but increase in acid concentration increased rate of reaction.

Reduction of Bridged Iron (III) Complexes by Oxyanions of Sulphur

Studies of oxyanions of sulphur with bridged binuclear iron (III) compounds have been undertaken. These include the μ -oxo-bridged and adipato-bridged complexes. Reduction of μ -oxo-bridged iron(III)-salen dimer by dithionate [4] in acidic medium was investigated. At 515 nm, the stoichiometry was monitored spectrophotometrically and showed that for every mole of dithionate ion consumed, two moles equivalent of Fe(III) dimer was reduced corresponding to stoichiometry as represented in Scheme 6.

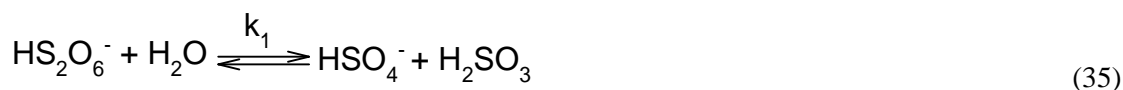


Scheme 6: Stoichiometry of Reaction of Oxo-Bridged Iron(III)-Salen Dimer with Dithionate Ion.

The reaction was zeroth-order with respect to iron(III)-salen dimer but first order with respect to dithionate ion. Rate was observed to increase with increase in acid concentration. This observed acid catalysis was said to have resulted from a pre-equilibrium step before the electron transfer reaction. The negative salt effect and effect of dielectric constant recorded are pointers to interaction between redox partners of opposite sign, $S_2O_6^{2-}$ and H^+ . From the kinetic data

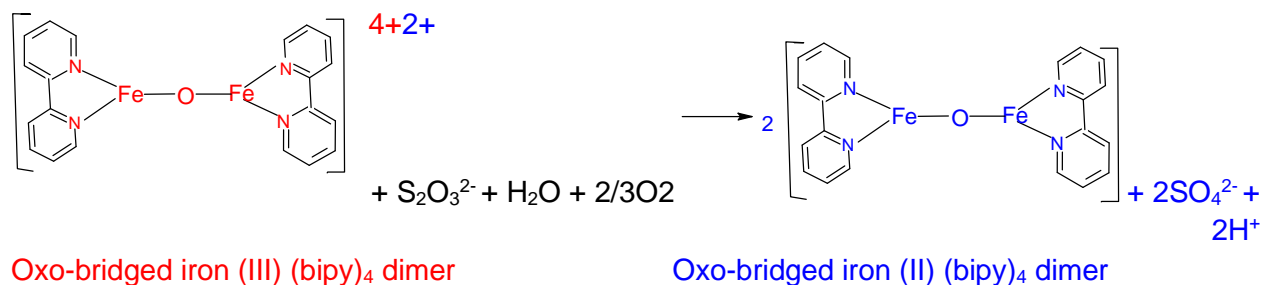
generated for this system, reaction rate is given as equation (33) with the rate constant of $1.92 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

The oxidation of metabisulphite [54] and thiosulphate [55] by oxo-bridged binuclear iron (III) dimer $[Fe_2(bipy)O]^{4+}$ have been documented. The stoichiometry of the reactions is represented as in Scheme 7.



Resolving equation (37) following steady approximation gives;

$$Rate = -\frac{d[S_2O_6^{2-}]}{dt} = K[S_2O_6^{2-}][H^+] \quad (38)$$

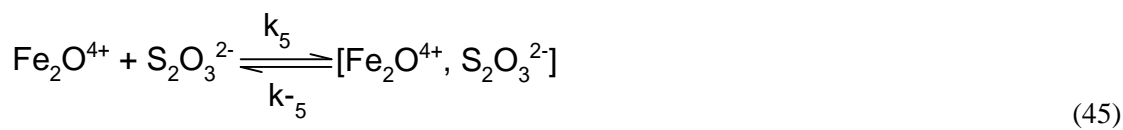
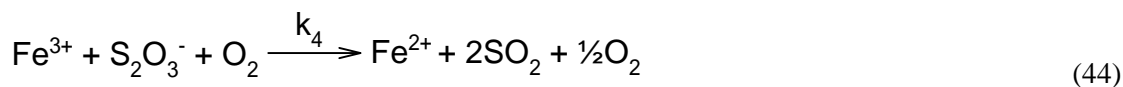
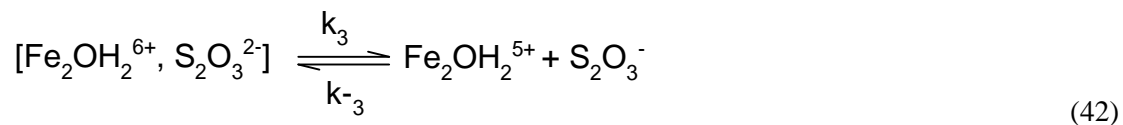
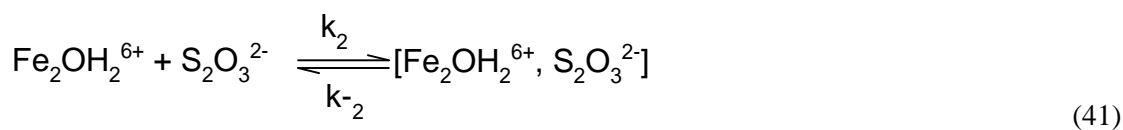


Scheme 7: Stoichiometry of Reaction of Oxo-Bridged Iron(III)-(Bipy)₄ Dimer with Thiosulphate Ion.

The reactions followed outer-sphere electron transfer mechanism and rates of reaction showed first order dependence on the concentration of Fe(III) dimer but zeroth-order dependence with respect to the concentrations of the metabisulphite and thiosulphate respectively. The rate law of these reactions is presented in equation (39).

$$\frac{1}{2} \frac{dFe^{2+}}{dt} = k_{obs}[Fe_2O]^{4+} \quad (39)$$

The reduction of $[Fe_2(bipy)O]^{4+}$ by metabisulphite and thiosulphate respectively



Resolving equation (45) further gives rate as;

showed no dependence of rate on ionic strength and dielectric constant. These observed trends was interpreted to be reactions occurring between an ion and neutral molecule where the product of charges of redox partners at rate determining step is zero. Within the acid range determined, increased rates of reactions with increase in acid concentration was observed.

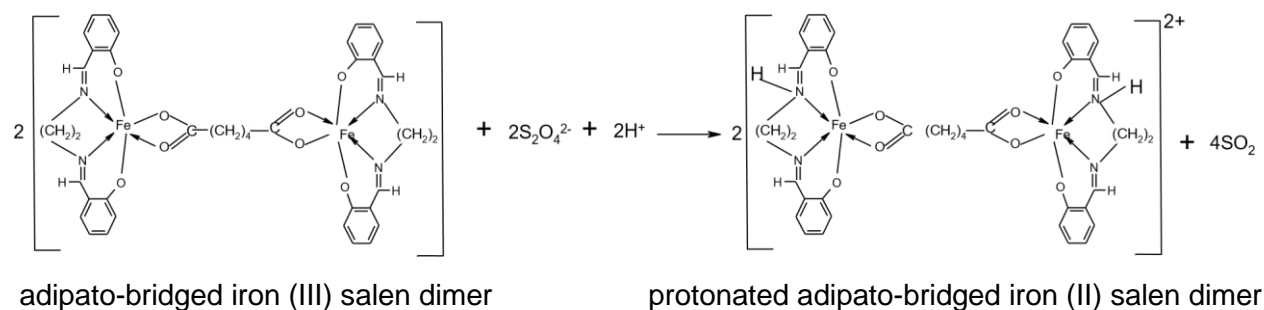
Considering stoichiometry, acid-dependence, effect of ionic strength and dielectric constant, the following key mechanistic steps shown in equations (40) to (47) represent the reactions metabisulphite or thiosulphate, since they exhibit similar redox properties.

$$Rate = k_4[Fe_2OH_2^{5+}] + k_{11}[Fe_2O^{3+}] \quad (46)$$

By applying steady state approximation and further resolving equation (46) brings rate to

$$Rate = \frac{K_8 k_9 k_{10} k_{11}}{k_9 + k_{10}} [Fe_2O^{4+}] \quad (47)$$

Reduction of adipato-bridged binuclear Fe(III)-salen complex by another oxo-sulphur



Scheme 8: Stoichiometry of the Reaction of Adipato-Bridged Iron(III)-Salen Dimer with Dithionite Ion.

First order dependence on the concentration of Fe(III) dimer and zeroth order dependence on the concentration of trioxosulfate(IV) ion and dithionate ion respectively reported and the rate law is represented in equation (48), while first order dependence on the concentration of both Fe(III) dimer and dithionite ion was recorded. The rate law is given in equation (49)

$$-\frac{d[Fe_2adi]}{dt} = k_{obs}[Fe_2adi] \quad (48)$$

compounds, dithionite ion [5], trioxosulfate(IV) ion [6] and dithionate ion [57] was investigated in perchloric acidic medium. Stoichiometry of the reactions was monitored spectrophotometrically at 455 nm. The results obtained showed that for every mole of dithionate and dithionite ions consumed, one mole of Fe(III) dimer was reduced, but two moles of trioxosulfate(IV) ion was oxidized by a mole of Fe(III) dimer. Scheme 8 serves as a representative stoichiometry for the oxyanions of sulphur using dithionite ion as example.

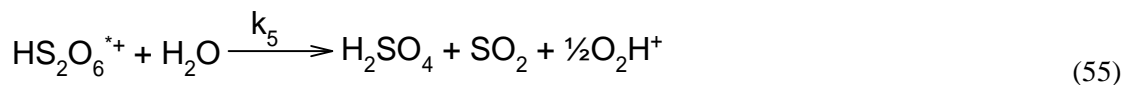
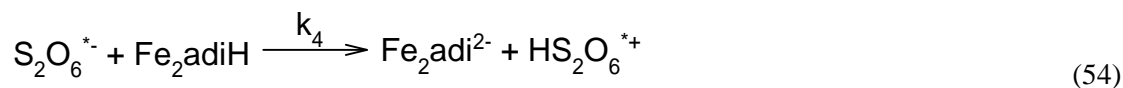
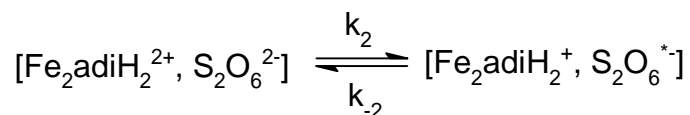
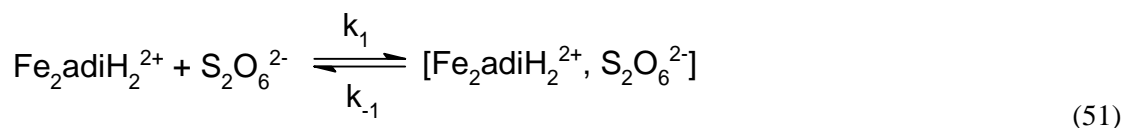
$$-\frac{d[Fe_2adi]}{dt} = k_2[Fe_2adi][S_2O_4^{2-}] \quad (49)$$

In these systems, rates of reactions increased with increase in hydrogen ion concentration (acid catalysis) but were invariant to changes in ionic strength. Varying the dielectric constant of trioxosulfate(IV) ion and dithionate ion systems, rates of reactions showed inverse dependence while dithionite ion system was unaffected by changes in dielectric constant. The observed acid

catalysis was rationalized in terms of preprotonation steps leading to formation of protonated precursor species prior to electron transfer. Lack of primary salt effect is indicative of electron transfer reaction where one of the redox partners is neutral at the transition state. Proton-coupled outer-sphere electron transfer mechanism was proposed for the redox reactions of trioxosulfate(IV) ion and dithionate ion systems but inner-sphere proton mediated

transfer mechanism was reported for dithionite system.

Taking recourse to stoichiometry, acid catalysis, effect of ionic strength, dielectric constant and other kinetic data generated, the following key mechanistic steps in equations (50) to (57) represent the redox reactions of trioxosulfate(IV) ion and dithionate ion systems with adipatobridged Fe(III) dimer.



$$\text{Rate} = k_3[\text{Fe}_2\text{adiH}_2^+] \quad (56)$$

By steady state hypothesis, resolving equation (56) brings rate to;

$$\text{Rate} = \frac{K_a k_1 k_2 k_3 [\text{H}^+]^2 [\text{Fe}_2\text{adi}]}{k_{-1} k_{-2}} \quad (57)$$

Equation (57) is similar to (48) where;

$$k_{obs} = \frac{K_a k_1 k_2 k_3 [\text{H}^+]^2}{k_{-1} k_{-2}}$$

CONCLUSION

In this report, the redox reactions of bridged binuclear iron (III) complexes with some biomolecules (naturally occurring reducing agents) were examined. Redox parameters such as stoichiometry, electron transfer mechanism, effects of ionic strength, hydrogen ion concentration $[H^+]$ and dielectric constant on rates of reactions were evaluated. It was observed from the kinetic data generated for the bridged binuclear Fe(III) complexes studied that the redox reactions of oxo-bridged Fe(III) dimer with L-ascorbic acid and thiols proceeded via outersphere path with intervening ion-pair formation. While, adipato-bridged Fe (III) dimer reacted with thiols following inner-sphere route. The electron transfer reactions of bridged iron (III) dimer with the oxyanions of sulphur followed outer-sphere with proton coupled electron transfer mechanism but inner-sphere mediated by proton transfer was also observed for one of the systems [5].

However, it was noticed that all the redox reactions of pyridine dicarboxylic acid bridged Fe(III) with thiols and L-ascorbic acid occurred via outer-sphere pathway with ion-pair formation. All the redox reactions were performed in aqueous acidic medium. Most of the reactions were slow, enthalpy controlled, and endothermic [4, 45 – 50, 57]. Reasons for these observed patterns of reactions have not been

established and no general trend for the order of dependencies has been arrived at.

Therefore, more research should be devoted to redox reactions of other reductants especially naturally occurring reducing agents with bridged binuclear iron (III) complexes due to the role of iron (III) as structural models or mimics for binuclear site in proteins. This will provide very interesting avenues which would help in understanding the reactions of binuclear iron (III) and other related compounds in biological systems and other fields.

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