



Kinetics of the Reduction of μ -Oxo-Tetrakis(1, 10-Phenanthroline) diiron (III) Complex by Thiourea in Aqueous Phenanthroline Buffer

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ABSTRACT

The homovalent oxo-bridged binuclear iron(III) complex ion $[\text{Fe}_2\text{O}(\text{phen})_4\text{Cl}_2]^{4+}$ (phen = 1, 10-phenanthroline) aquates to $[\text{Fe}_2\text{O}(\text{phen})_4(\text{H}_2\text{O})_2]^{4+}$ in aqueous phenanthroline buffer solution (pH 3.25–4.50). The reaction of $[\text{Fe}_2\text{O}_2(\text{phen})_4(\text{H}_2\text{O})_2]^{4+}$ with thiourea in this buffer solution to give $[\text{Fe}(\text{phen})_3]^{2+}$, sulphite ion and urea was studied spectrophotometrically at 510 nm and found to be first order in $[\text{Fe}_2\text{O}_2(\text{phen})_4(\text{H}_2\text{O})_2]^{4+}$ and of mixed zero and first order in thiourea, i.e. reaction order with respect to thiourea varies from one to zero on increasing the thiourea concentration from $1.0\text{--}7.0 \times 10^{-2}$ mol dm⁻³. The reaction is characterized by adduct formation. Changes in pH from 3.25 to 4.50 and ionic strength from 0.10 mol dm⁻³ to 0.60 mol dm⁻³ of the reaction solution were found to have no effect on the reaction rate. Catalysis and retardation were observed with the addition of Mg^{2+} and CH_3COO^- ions respectively. A plausible mechanism consistent with the results obtained is proposed.

Keywords: kinetics, mechanism, oxo-bridged, phenanthroline buffer, thiourea

INTRODUCTION

Thiourea (NH_2CSNH_2) is an organosulphur compound that is structurally related to urea (Daintith, 2004). Oxidation of sulfur compounds is usually complex (Gao *et al.*, 2008; Sahu *et al.*, 2011) and the study of sulphur and sulphur containing compounds like thiourea is very important because they have numerous applications (Sahu *et al.*, 2011; Sharma *et al.*, 2011; Asghari *et al.*, 2015).

A lot have being done on the kinetics and mechanisms of the reactions of thiourea with different oxidizing agents (Rabai *et al.*, 1993; Simoyi, *et al.*, 1994; Mundoma and Simoyi, 2000; Osunlaja *et al.*, 2012; Mohammed *et al.*, 2014) with interest in these studies been mainly due to the exotic and nonlinear behaviour of thioureas reactions (Mundoma and Simoyi, 2000), which cannot be easily explained based on their chemical structure, therefore necessitating more studies on the kinetics and mechanisms of their reactions. Therefore the studies of the reactions of thioureas with μ -oxo-tetrakis(1, 10-phenanthroline)diiron(III) complex in aqueous phenanthroline buffer medium, pH 3.25–4.50 will help throw more light on the nature of their reactions. Literature survey revealed that the reduction kinetics of μ -oxo-tetrakis(1, 10-phenanthroline)diiron(III) complex with thiourea had not been studied yet.

As a component of several essential enzymes (Loehr, 1983; Arulsamy *et al.*, 1994;

Walczak and Flynn, 1998; Gritsenko *et al.*, 2007; Mandal *et al.*, 2009), iron participates in a number of metabolic processes including oxygen transport, oxygen storage, DNA synthesis and electron transfer (Nelson, 1987). In most of these centres, Fe^{3+} ions are strongly antiferromagnetically coupled, indicating the presence of a μ -oxo bridged between the iron ions (Loehr, 1983; Arulsamy *et al.*, 1994). Therefore diiron centers bridged by an oxo group serves as structural and functional models of the active sites of some of these proteins and their studies are important for understanding the chemistry of such metalloenzymes.

Although a lot of binuclear complexes of iron have been synthesized (Arulsamy *et al.*, 1994; Kaasjager *et al.*, 1998; Wang *et al.*, 2003) and the kinetics of some of their reactions studied (Bhattacharyya *et al.*, 2004; Bhattacharyya and Mukhopadhyay, 2005; Bhattacharyya *et al.*, 2007; Das *et al.*, 2008), understanding the way they reacts, especially their biological roles in enzymes, is not well understood probably due to limited mechanistic studies. Since the elucidation of the role of ions in living systems depends on a thorough knowledge of electron transfer, and redox properties of its common oxidation states and how these properties depend upon the ligand environment around the ion (Basolo and Johnson, 1986), information on the reactivity patterns of binuclear complexes of iron could be beneficial for the studies of the biological role of iron. Complexes of 1, 10-phenanthroline and its

derivatives have attracted a lot of interest from both synthetic and medicinal chemists due to its structural similarity to several natural biologically important products, especially alkaloids (Delfourne *et al.*, 2003; Delfourne *et al.*, 2004) and also because they have been found to be useful in catalysis, solar energy conversion, herbicides, molecular recognition, self-assembly and nucleic acid probes (Arifuzzaman *et al.*, 2013).

MATERIALS AND METHODS

All chemicals and solvents were analytical grade reagents purchased from different sources. Solutions were prepared in deionized distilled water. 1, 10–phenanthroline, sodium carbonate, iron(III) chloride, thiourea (hereafter referred to as TU) and sodium chloride were used as received. Hydrochloric acid was standardized with a standard Na_2CO_3 solution using methyl orange as indicator. All the reported kinetic data are at 30.0 ± 1.0 °C and 0.10 mol dm^{-3} ionic strength maintained by NaCl unless stated otherwise.

The μ -oxo-tetrakis(1, 10–phenanthroline)–diiron(III) chloride, $\text{Fe}_2(\text{phen})_4\text{O}(\text{H}_2\text{O})_2 \cdot 6\text{H}_2\text{O}$, was prepared according to literature procedure (Khedekar, *et al.*, 1967; Mandal *et al.*, 2009). This involved the mixing of stoichiometric amounts, ratio 1:2, of aqueous solution of ferric chloride and a suspension of 1, 10–phenanthroline in water at room temperature. The phenanthroline dissolves, and brown crystals begin to precipitate. After standing overnight in the dark for crystallization to complete, the crystals was filtered under suction, washed with ice–cold water and then dried in air and subsequently in a desiccator over silica gel (Khedekar *et al.*, 1967). The synthesized brown binuclear iron complex, with a yield of 50%, gave an identical UV–Visible spectrum similar to literature (Plowman *et al.*, 1984; Walczak and Flynn, 1998). The aqueous phenanthroline solution of the binuclear complex absorbs insignificantly at 510 nm, the wavelength of the orange–red coloured product of the reaction, $[\text{Fe}(\text{phen})_3]^{2+}$, at which the present study is carried out. Stock aqueous phenanthroline buffer of 0.30 mol dm^{-3} concentration was prepared by mixing phenanthroline and hydrochloric acid solutions in the required ratio. A stock solution of thiourea was prepared by dissolving an accurately weighed quantity of the solid reagent in known volume of distilled water.

Solutions of μ -oxo-tetrakis(1, 10–phenanthroline)diiron(III) ion in aqueous phenanthroline buffer undergoes photoreduction (David, 1973; David and de Mello, 1973) and was therefore stored in dark bottle covered with black clothe. The solutions required for kinetic studies were prepared daily by dissolving a known weight of the complex in a specific volume of 0.30 mol dm^{-3} aqueous phenanthroline buffer at pH 4.50 except for the studies that involved determination

of the effect of pH on the reaction where the pH was varied between 3.25 and 4.50.

Stoichiometry and Products Analysis

The stoichiometry of the μ -oxo-tetrakis(1, 10–phenanthroline)diiron(III) complex oxidation of thiourea in aqueous phenanthroline medium was determined by product analysis under kinetic conditions with $[\text{TU}] \gg [\text{Fe}_2\text{O}(\text{phen})_4(\text{H}_2\text{O})_2]^{4+}$, after the reaction was confirmed to have gone to completion (Bhattacharyya and Mukhopadhyay, 2005). An aliquot of a known concentration of the binuclear complex in excess aqueous phenanthroline buffer solution was mixed with a known excess of TU at $T=30.0 \pm 1.0$ °C and $I=0.10 \text{ mol dm}^{-3}$ (NaCl). The visible spectrum as well the wavelength of maximum absorption (λ_{max}) of 510 nm of the orange–red coloured product, recorded using UNICO UV–2102PC Spectrophotometer in the wavelength range 400–700 nm, confirmed it to be $[\text{Fe}(\text{phen})_3]^{2+}$. The products of the oxidation of thiourea, i.e. urea and SO_3^{2-} , were also qualitatively determined by chemical analysis. Products identifications coupled with the comparison of concentrations of $[\text{Fe}(\text{phen})_3]^{2+}$ and that of the initial $[\text{Fe}_2\text{O}(\text{phen})_4(\text{H}_2\text{O})_2]^{4+}$ originally employed indicated the stoichiometries of the reactions.

Kinetics Studies

All kinetic measurements were carried out with a UNICO UV–2102PC Spectrophotometer at an ionic strength of 0.10 mol dm^{-3} under pseudo-first order conditions with TU in at least 200–fold excess at 30.0 ± 1.0 °C. Excess phenanthroline buffer ($C_{\text{phen}}=[\text{phenH}^+] + [\text{phen}] = 3.0 \times 10^{-2} \text{ mol dm}^{-3}$) at pH 4.50 was also employed. The effects of various parameters, including pH, ionic strength, $[\text{TU}]$ were investigated (Table 1). Reactions were monitored at 510 nm, the absorbance maximum of the product $[\text{Fe}(\text{phen})_3]^{2+}$ and observed rate constants were determined from the slope of the plots of $\log(A_\infty - A_t)$ against time, where A_∞ and A_t , stand respectively, for the absorbances of the final $[\text{Fe}(\text{phen})_3]^{2+}$ and $[\text{Fe}(\text{phen})_3]^{2+}_t$ formed after time t . The order of the reaction with respect to TU was determined by repeating the experiment at several initial concentrations of TU.

The effect of changes in the pH on the reaction rate was investigated by keeping all other reaction condition constant except the pH of the solution. The pH of the reaction was varied from 3.25 to 4.50 by varying the phen–phenH⁺ concentration. The ionic strength of the reaction mixture was varied from 0.10 – 0.60 mol dm^{-3} while keeping $[\text{TU}]$, $[\text{Fe}_2(\text{phen})_4\text{O}(\text{H}_2\text{O})_2]^{4+}$, pH and temperature constant. The effect of added Mg^{2+} and CH_3COO^- ions on the reaction rate was investigated by keeping $[\text{TU}]$, $[\text{Fe}_2\text{O}(\text{phen})_4(\text{H}_2\text{O})_2]^{4+}$, pH, temperature and ionic strength constant, and varying $[\text{Mg}^{2+}] = (5\text{--}30) \times$

10^{-3} mol dm⁻³ and [CH₃COO⁻] = (5–40) × 10⁻³ mol dm⁻³ respectively.

RESULTS AND DISCUSSION

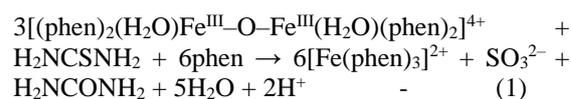
The aqueous solution of the binuclear complex, [Fe₂O(phen)₄Cl₂]Cl₂·6H₂O, is yellow–brown in colour with a negligible absorption at 510 nm (Walczak and Flynn, 1998). There is rapid and complete replacement of the Cl⁻ ligand ions in [Fe₂O₂(phen)₄Cl₂]²⁺ with H₂O to give [Fe₂O(phen)₄(H₂O)₂]⁴⁺ when the solid sample is dissolved in aqueous buffer solutions (Bendix *et al.*, 1974), with the [Fe₂O(phen)₄(H₂O)₂]⁴⁺ further undergoing hydrolysis to produce its conjugate bases, [Fe₂O(phen)₄(H₂O)(OH)]³⁺ and [Fe₂O(phen)₄(OH)₂]²⁺, although the bulk of the diferric species still exists in the protonated form, which is more reactive than the deprotonated conjugate bases (Bhattacharyya and Mukhopadhyay, 2005; Bhattacharyya *et al.*, 2007). [Fe₂O(phen)₄(H₂O)₂]⁴⁺ have also been suggested to be the only kinetically active specie in solution by some authors (Mukherjee *et al.*, 2005), so in this our work it will be assumed that [Fe₂O(phen)₄(H₂O)₂]⁴⁺ represents all the diiron complex present in solution.

The fact that the aqueous solution of the titled complex is slightly acidic with pH of about 4.0, due to the hydrolytic nature of the aquo complex in solution (David, 1973) and also because the aqueous solution of the complex is fairly stable towards self–decomposition in the pH range 3.0 to 7.0 in excess 1,10–phenanthroline (Bhattacharyya *et al.*, 2007), influenced the choice of pH 3.25–4.50. The excess 1,10–phenanthroline employed in the study is not only to buffer the reacting solution against any considerable pH drift but also to ensure quantitative formation of tris(phenanthroline) complexes [Fe(phen)₃]²⁺, from the transient bis(phenanthroline) intermediates (Bhattacharyya and Mukhopadhyay, 2005).

The self decomposition rate in aqueous phenanthroline buffer pH 4.50 which was determined through blank experiment under the same condition as the kinetic study, with 5.0 × 10⁻⁵ mol dm⁻³ [Fe₂O(phen)₄(H₂O)₂]⁴⁺ at I = 0.10 mol dm⁻³ and 30.0 ± 1.0 °C, was found to be (4.21 ± 0.05) × 10⁻⁷ s⁻¹. This showed that the self decomposition rate is slower than the reduction rate and therefore the self decomposition is neglected for the kinetic studies.

μ–oxo–diferric complex is a known two–electron oxidant (Bhattacharyya *et al.*, 2007). It quantitatively oxidizes TU to urea and SO₃²⁻ in the pH interval 3.25–4.50 in which our studies was carried out, with itself being reduced to [Fe(phen)₃]²⁺. The presence of urea in the product solution was confirmed by its reaction with alkaline CuSO₄ (Osunlaja *et al.*, 2012). Similarly SO₃²⁻ was shown to be present by the production of a white precipitate on addition of Pb(CH₃COO)₂ to a reaction mixture in which [Fe₂O(phen)₄(H₂O)₂]⁴⁺

had been completely reduced to [Fe(phen)₃]²⁺ (Svehla, 1997). The solubility of this white precipitate in dilute HNO₃ confirms the formation of SO₃²⁻ as a product of TU oxidation. Also after filtering and washing this white precipitate with distilled water, its solution was found to decolourized acidified KMnO₄ confirming the product as SO₃²⁻ (Svehla, 1997). The net six electron oxidation of the sulphur in thiourea to SO₃²⁻ is provided by two Fe³⁺ of the μ–oxo–diferric complex. These observations confirmed the stoichiometry of the reactions under consideration to be equation (1). Also absorbance measurements of the product, at the λ_{max} established the quantitative conversion of a molecule of the binuclear complex to twice that of [Fe(phen)₃]²⁺, using the relation A = εcl, with ε = 1.11 × 10⁴ dm³ mol⁻¹ cm⁻¹.



The formation of urea and SO₄²⁻, and not SO₃²⁻ as obtained in our studies, is a common feature of the redox reactions of thiourea (Sahu *et al.*, 2011). It should be noted however that the SO₃²⁻ ion can itself be further oxidized to SO₄²⁻ (Busari *et al.*, 2012), but this is a much slower reaction and, especially under pseudo–first–order conditions, where [TU] >> [Fe₂O(phen)₄(H₂O)₂]⁴⁺, [Fe₂O(phen)₄(H₂O)₂]⁴⁺ are rapidly consumed and so the oxidation stopped at SO₃²⁻. The formation of SO₃²⁻ as an intermediate in some reactions of thiourea before it was further oxidized to SO₄²⁻ in the presence of excess oxidant have been proposed by some authors (Gao *et al.*, 2008; Martincigh *et al.*, 2013).

Since the initial points of the experiments are the most accurate with complications arising thereafter, the initial rate method was employed in all the kinetic studies. The complications is expected due to the slow decomposition of the oxidants employed, [Fe₂O(phen)₄(H₂O)₂]⁴⁺, as well as the irreversible decomposition of the orange–red [Fe(phen)₃]²⁺ product obtained. Sigmoidal absorbance–time curve indicating non linear behaviour has earlier been implicated in some thiourea systems (Simoyi *et al.*, 1994; Mundoma and Simoyi, 2000), therefore the best fitting straight lines were drawn to pass through the initial points so as to calculate the observed rate constants, k_{obsd}.

The linearity of these plots is an indication that the initial reaction is first order with respect to [Fe₂O(phen)₄(H₂O)₂]⁴⁺. The observed rate constants, k_{obsd} (Table 1), were found to increase linearly with increasing [TU] from 1.0 × 10⁻²–4.0 × 10⁻² mol dm⁻³ and remain constant afterward (4.0 × 10⁻²–7.0 × 10⁻² mol dm⁻³). Therefore, within the [TU] range 1.0 × 10⁻²–4.0 × 10⁻² mol dm⁻³, the plot of k_{obsd} versus [TU] gave a straight line with r = 0.998

indicating first order dependence with respect to (Figure 1). Plot of $\log k_{\text{obsd}}$ versus $\log[\text{TU}]$ gave a slope of 1.01 ($r = 0.998$) further confirming the first order dependence on $[\text{TU}]$ in this range. Between 4.0×10^{-2} to 7.0×10^{-2} mol dm^{-3} , plot of $\log k_{\text{obsd}}$ versus $\log[\text{TU}]$ gave a linear plot with a slope of zero, indicating that the reaction is independent of $[\text{TU}]$ in these range. This result suggests a Michaelis–Menten-type dependence of the k_{obsd} on $[\text{TU}]$ (Balado *et al.*, 1997; Roat-Malone, 2007) and the variation of k_{obsd} as a function of $[\text{TU}]$ is given by the equation (2):

$$k_{\text{obsd}} = \frac{k_2[\text{TU}]}{a + b[\text{TU}]} \quad (2)$$

Thus, the rate law can be express as Equation (3):

$$\frac{1}{3} \frac{d[\text{Fe}_2\text{O}(\text{phen})_4(\text{H}_2\text{O})_2]^{4+}}{dt} = \frac{k_2[\text{TU}]}{a + b[\text{TU}]} [\text{Fe}_2\text{O}(\text{phen})_4(\text{H}_2\text{O})_2]^{4+} \quad (3)$$

Mixed first and second order with respect to $[\text{TU}]$ have previously reported for the oxidation of thiourea by 12-tungstocobaltate(III) ion, $[\text{Co}(\text{III})\text{W}]^{5-}$ (Mehrotra and Mehrotra, 2003).

Plot of $1/k_{\text{obsd}}$ versus $1/[\text{TU}]$ at $\text{pH} = 4.50$, $I = 0.10$ mol dm^{-3} , $T = 30 \pm 1^\circ\text{C}$ and $[\text{TU}] = 1.0 \times 10^{-2}$ to 4.0×10^{-2} mol dm^{-3} gave a straight line with slope, $a = 168$ s $\text{dm}^3 \text{mol}^{-1}$, intercept, b , of positive value 290 s and $k_2 = (6.18 \pm 0.29) \times 10^{-3}$ $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$.

For $[\text{TU}] = 1.0 \times 10^{-2}$ to 4.0×10^{-2} mol dm^{-3} , where $a \geq b[\text{TU}]$ the rate law gives equation 4, with the rate being first order with respect to both μ -oxo-diferric complex and TU.

$$\frac{d[\text{Fe}_2\text{O}(\text{phen})_4(\text{H}_2\text{O})_2]^{4+}}{dt} = \frac{k_2[\text{TU}]}{a} [\text{Fe}_2\text{O}(\text{phen})_4(\text{H}_2\text{O})_2]^{4+} \quad (4)$$

Whereas for $[\text{TU}] = 4.0 \times 10^{-2}$ to 7.0×10^{-2} mol dm^{-3} , since the reaction is independent of $[\text{TU}]$ and so therefore slope, $a = 0$ and $b[\text{TU}] \geq a$, the rate is then first order with respect to only the μ -oxo-diferric complex and independent of TU (equation 5).

$$\frac{d[\text{Fe}_2\text{O}(\text{phen})_4(\text{H}_2\text{O})_2]^{4+}}{dt} = \frac{k_2}{b} [\text{Fe}_2\text{O}(\text{phen})_4(\text{H}_2\text{O})_2]^{4+} \quad (5)$$

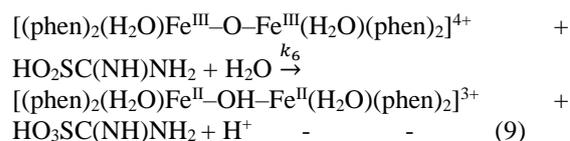
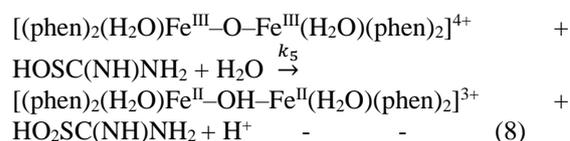
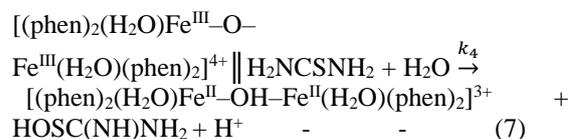
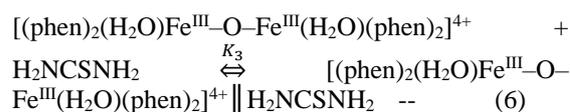
At constant $[\text{Fe}_2\text{O}(\text{phen})_4(\text{H}_2\text{O})_2]^{4+}$, $[\text{TU}]$, temperature, and ionic strength, the reaction rates were found to be independent of change in pH. Also at constant $[\text{Fe}_2\text{O}(\text{phen})_4(\text{H}_2\text{O})_2]^{4+}$, $[\text{TU}]$, temperature and pH, the reactions were observed to be independent of change in ionic strength

suggesting the absence of charged species in the activated complex (Arnaut *et al.*, 2007). The lack of gel formation when acrylamide followed by a large excess of methanol were added to the partially reduced μ -oxo-diferric complex, is an indication that free radical intermediates are not form in the reaction mixtures during the course of the reactions. The absence of intermediate was also confirmed by the non appearance of a new peak apart from the absorption band with peak at 510 nm, characteristic of $[\text{Fe}(\text{phen})_3]^{2+}$, when repetitive spectral scans were taken during the course of the reaction (Busari *et al.*, 2012; Busari *et al.*, 2016).

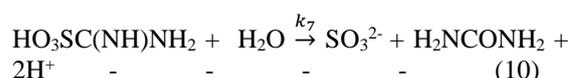
Observed first order dependence of rate of reaction on $[\text{Fe}_2\text{O}(\text{phen})_4(\text{H}_2\text{O})_2]^{4+}$ have been reported by several authors (Chaudhuri and Banerjee, 1998; Bhattacharyya *et al.*, 2004; Bhattacharyya and Mukhopadhyay, 2005; Mukherjee *et al.*, 2005; Bhattacharyya *et al.*, 2007; Das *et al.*, 2008; Mandal *et al.*, 2009).

Proposed Mechanism

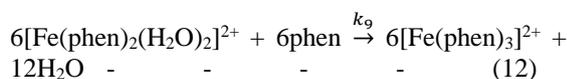
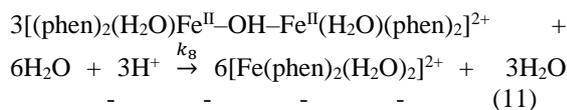
Based on the kinetic data and observations a seven (7) step plausible mechanism initiated by the rapid formation of inner sphere adducts between $[\text{Fe}_2\text{O}(\text{phen})_4(\text{H}_2\text{O})_2]^{4+}$ and H_2NCSNH_2 followed by rate-determining two-electron transfer (one each by Fe^{3+}) to produce $\text{HOSC}(\text{NH})\text{NH}_2$ and $[(\text{phen})_2(\text{H}_2\text{O})\text{Fe}^{\text{II}}\text{OH}-\text{Fe}^{\text{II}}(\text{H}_2\text{O})(\text{phen})_2]^{3+}$ is proposed (Bhattacharyya *et al.*, 2004) for the redox reaction. This mechanism involves the stepwise oxidation of sulphur from the oxidation state of -2 in thioureas to +4 in SO_3^{2-} .



The ureas and sulphite are formed simultaneously from the hydrolysis of the sulphonic acid intermediate, $\text{HO}_3\text{SC}(\text{NH})\text{NH}_2$.



$\text{Fe}^{\text{II}}\text{-O-Fe}^{\text{II}}$ is susceptible to decomposition by aquation (Chaudhuri and Banerjee, 1998; Bhattacharyya and Mukhopadhyay, 2005). It is unstable and rapidly decomposes to $[\text{Fe}(\text{phen})_2(\text{H}_2\text{O})_2]^{2+}$ (Bendix *et al.*, 1974).



Reaction in equation (12) occurs only in the presence of excess 1, 10-phenanthroline (Bhattacharyya and Mukhopadhyay, 2005). All steps following the adduct dissociation are rapid, therefore with equation 7 as the rate determining step, the theoretical rate law for the reaction can be written as equation

$$\frac{d[\text{Fe}_2\text{O}(\text{phen})_4(\text{H}_2\text{O})_2]^{4+}}{dt} = k_4[\text{Fe}_2\text{O}(\text{phen})_4(\text{H}_2\text{O})_2]^{4+} / [\text{H}_2\text{NCSNH}_2]^{4+} \quad (13)$$

From equation 6

$$K_3 = \frac{[\text{Fe}_2\text{O}(\text{phen})_4(\text{H}_2\text{O})_2]^{4+} / [\text{H}_2\text{NCSNH}_2]^{4+}}{[\text{Fe}_2\text{O}(\text{phen})_4(\text{H}_2\text{O})_2]^{4+} [\text{H}_2\text{NCSNH}_2]^{4+}} \quad (14)$$

$$[\text{Fe}_2\text{O}(\text{phen})_4(\text{H}_2\text{O})_2]^{4+} / [\text{H}_2\text{NCSNH}_2]^{4+} = K_3 [\text{Fe}_2\text{O}(\text{phen})_4(\text{H}_2\text{O})_2]^{4+} [\text{H}_2\text{NCSNH}_2]^{4+} \quad (15)$$

$$\frac{d[\text{Fe}_2\text{O}(\text{phen})_4(\text{H}_2\text{O})_2]^{4+}}{dt} = k_4 K_3 [\text{Fe}_2\text{O}(\text{phen})_4(\text{H}_2\text{O})_2]^{4+} [\text{H}_2\text{NCSNH}_2]^{4+} \quad (16)$$

with $k_4 K_3 = k_2/a$ in equations 4, while $k_4 K_3 = k_2/(b[\text{H}_2\text{NCSNH}_2])$ in equation 5.

The intermediate adduct is converted to $[\text{Fe}(\text{phen})_3]^{2+}$ in a series of steps, first through a two electron change to give $\text{Fe}^{\text{II}}\text{-OH-Fe}^{\text{II}}$ dimer that readily dissociate to $[\text{Fe}(\text{phen})_2(\text{H}_2\text{O})_2]^{2+}$. The $[\text{Fe}(\text{phen})_2(\text{H}_2\text{O})_2]^{2+}$ then rapidly forms $[\text{Fe}(\text{phen})_3]^{2+}$ in the presence of excess phenanthroline employed in the study (Bhattacharyya *et al.*, 2004).

Step (7), which involves the acceptance of proton by the μ -oxo bridge thereby allowing electron transfer from the reducing thiourea to the oxo-bridge is a key step in the reaction mechanism of the μ -oxo-diferric complex (Bhattacharyya and Mukhopadhyay, 2005). This is simply referred to as Proton Coupled Electron Transfer (PCET).

The oxidation of thiourea through formamidesulfenic acid ($\text{HOSC}(\text{NH})\text{NH}_2$), formamidesulfonic acid ($\text{HO}_2\text{SC}(\text{NR})\text{NH}_2$), and formamidesulfonic acid ($\text{HO}_3\text{SC}(\text{NH})\text{NH}_2$), with the cleavage of the C-S bond occurring afterwards to give urea (H_2NOCNH_2), under slightly acidic condition has been reported by several authors (Epstein and Simoyi, 1987; Simoyi *et al.*, 1994; Makarov *et al.*, 1999).

The rapid substitution of the Cl^- ions in the solid $[\text{Fe}_2\text{O}(\text{phen})_4\text{Cl}_2]^{2+}$ complex with H_2O , to give $[\text{Fe}_2\text{O}(\text{phen})_4(\text{H}_2\text{O})_2]^{4+}$ in aqueous medium as well as the substitution of H_2O ligands on adding KSCN solution to $[\text{Fe}_2\text{O}(\text{phen})_4(\text{H}_2\text{O})_2]^{4+}$ to yield $[\text{Fe}_2\text{O}(\text{phen})_4(\text{SCN})_2]^{2+}$ are both indication of the labile nature of the monodentate ligands bonded to a d^5 high spin Fe^{3+} centre (Bendix *et al.*, 1974; Bhattacharyya and Mukhopadhyay, 2005). This may explain why CH_3COO^- retards the reaction rate (Table 2), since it will displace H_2O in the complex ion and coordinates stronger making equation 7 slower (Rangappa *et al.*, 1998). The rate retardation may also be due to the competitiveness of CH_3COO^- with TU for the adduct formation (Sriramam *et al.*, 1992). Mg^{2+} ion will likely catalyzed the reaction (Table 2) by interacting with the lone pair of electrons on S atom of TU to form a specie that is more reactive towards the binuclear complex than TU.

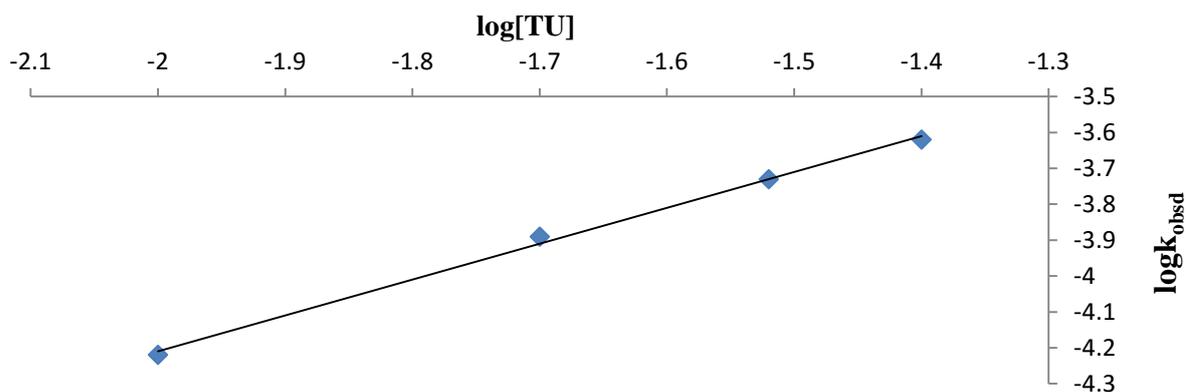


Figure 1: Plot of $\log k_{\text{obsd}}$ versus $\log[\text{TU}]$ for the reduction of $[\text{Fe}_2\text{O}(\text{phen})_4(\text{H}_2\text{O})_2]^{4+}$ by TU at $[\text{TU}]$ range of 1.0×10^{-2} to 4.0×10^{-2} mol dm^{-3}

Table 1: Pseudo first order and second order rate constants for the redox reaction of $[\text{Fe}_2\text{O}(\text{phen})_4(\text{H}_2\text{O})_2]^{4+}$ and TU in aqueous phenanthroline buffer. $[\text{Fe}_2\text{O}(\text{phen})_4(\text{H}_2\text{O})_2]^{4+} = 5.0 \times 10^{-5} \text{ mol dm}^{-3}$, $T = 30 \pm 1.0 \text{ }^\circ\text{C}$, $\lambda_{\text{max}} = 510 \text{ nm}$.

$10^2[\text{TU}]/(\text{mol dm}^{-3})$	pH	$\text{I}(\text{NaCl})/(\text{mol dm}^{-3})$	$10^4 k_{\text{obsd}}/\text{s}^{-1}$	$10^3 k_2/ \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
1.0	4.50	0.10	0.60	6.00
2.0	4.50	0.10	1.30	6.50
3.0	4.50	0.10	1.86	6.20
4.0	4.50	0.10	2.40	6.00
5.0	4.50	0.10	2.44	
6.0	4.50	0.10	2.50	
7.0	4.50	0.10	2.49	
2.0	3.25	0.10	1.44	7.20
2.0	3.50	0.10	1.34	6.70
2.0	3.75	0.10	1.34	6.70
2.0	4.00	0.10	1.41	7.05
2.0	4.25	0.10	1.42	7.10
2.0	4.50	0.10	1.40	7.00
2.0	4.50	0.10	1.30	6.50
2.0	4.50	0.20	1.40	7.00
2.0	4.50	0.30	1.38	6.90
2.0	4.50	0.40	1.44	7.20
2.0	4.50	0.50	1.35	6.75
2.0	4.50	0.60	1.34	6.70

Table 2: Effect of Mg^{2+} and CH_3COO^- on the observed first order and second order rate constants for the redox reaction of $[\text{Fe}_2\text{O}(\text{phen})_4(\text{H}_2\text{O})_2]^{4+}$ and TU in aqueous phenanthroline buffer. $[\text{Fe}_2\text{O}(\text{phen})_4(\text{H}_2\text{O})_2]^{4+} = 5.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{TU}] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$, $\text{pH} = 4.50$, $\text{I} = 0.10 \text{ mol dm}^{-3}$ (NaCl), $T = 30 \pm 1.0 \text{ }^\circ\text{C}$ and $\lambda_{\text{max}} = 510 \text{ nm}$.

X	$10^2[\text{X}]/(\text{mol dm}^{-3})$	$10^4 k_{\text{obsd}}/\text{s}^{-1}$	$10^3 k_2/ \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
Mg^{2+}	0.0	1.30	6.50
	0.5	1.80	9.00
	1.0	2.35	11.75
	2.0	3.18	15.90
	3.0	4.32	21.60
CH_3COO^-	0.5	0.90	4.50
	1.0	0.63	3.15
	2.0	0.41	2.09
	3.0	0.23	1.15
	4.0	0.16	0.80

CONCLUSION

The reaction of μ -oxo-tetrakis(1, 10-phenanthroline)diiron(III) complex with thiourea was found to occur through the proton coupled electron transfer mechanism, which drags the energetically unfavorable reaction to completion in the presence of excess phenanthroline.

Experimental results obtained for the reduction of $[\text{Fe}_2\text{O}(\text{phen})_4(\text{H}_2\text{O})_2]^{4+}$ by TU, at ionic strength of 0.10–0.50 mol dm^{-3} and pH ranges 3.25–4.50 adopted for this work, are in favour of the inner sphere mechanism. First order dependence in $[\text{Fe}_2\text{O}_2(\text{phen})_4(\text{H}_2\text{O})_2]^{4+}$ and Michaelis–Menten-

type dependence on [TU] were observed for the system.

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