



REACTION OF $S_2O_5^{2-}$ ION AND μ -OXO-TETRAKIS(1, 10-PHENANTHROLINE)DIIRON(III) COMPLEX ION IN AQUEOUS PHENANTHROLINIUM BUFFER: A KINETIC STUDY



A. Busari^{1*}, S. O. Idris², A. D. Onu³ and I. Abdulkadir²

¹Department of Chemistry, Sule Lamido University, Kafin Hausa, Jigawa State, Nigeria

²Department of Chemistry, Ahmadu Bello University, Zaria, Nigeria

³Department of Chemistry, Federal College of Education, Zaria, Nigeria

*Correspondence author: abdulakeemkekule@yahoo.com

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Abstract: Redox reaction between $S_2O_5^{2-}$ and $[Fe_2O(phen)_4(H_2O)_2]^{4+}$ in aqueous phenanthroline buffer medium, pH 4.50, has been studied. This was carried out under pseudo first order condition such that $[S_2O_5^{2-}] \gg [Fe_2O(phen)_4(H_2O)_2]^{4+}$ by monitoring the formation of $[Fe(phen)_3]^{2+}$, the reduced product of the binuclear complex, on a UNICO UV-2102PC Spectrophotometer at 510 nm, its wavelength of maximum absorption (λ_{max}). The initial reaction rates were determined with variation in the initial concentrations of $S_2O_5^{2-}$, pH and ionic strength of the solution. First order dependence on both the oxidant and reductant concentrations were observed. The reaction rate was observed to increase with increase in pH in the range 3.50–4.50 but decreases with increase in ionic strength from 0.10 to 0.60 mol dm⁻³. Based on the kinetic data and other experimental observations, a plausible reaction mechanism was suggested utilizing the redox characteristics of the binuclear complex and $S_2O_5^{2-}$. This mechanism involves the oxidation of sulphur from the oxidation state of +4 in SO_3^{2-} to +6 in SO_4^{2-} and the reaction appears to proceed through the formation of an adduct intermediate complex, with HSO_3^- considered to be sulphur bonded to $[Fe_2O(phen)_4(H_2O)_2]^{4+}$. Evidence for the formation of sulphite ion radical ($SO_3^{\cdot -}$) via a one-electron transfer step is presented.

Keywords: Binuclear complex, buffer, kinetics, mechanism, metabisulphite, oxo-bridged, redox reaction

Introduction

Metabisulphite ($S_2O_5^{2-}$), sulphite (SO_3^{2-}) and bisulphate (HSO_3^-) all contain sulphur in the +4 oxidation state and are generally referred to as sulphites (Ruiz-Capillas and Jiménez-Colmenero, 2009). As a product of fermentation, they are found naturally in some foods and beverages and due to the fact that they inhibit microbial activities they have been employed as preservatives in foods, beverages and drugs for centuries (Ruiz-Capillas and Jiménez-Colmenero, 2009; Musagala *et al.*, 2013). Also as antioxidants, sulphites are added to food, in a regulated manner, to maintain their color and to prolong their shelf lives (Malik *et al.*, 2007; El Kadil *et al.*, 2014). Their use as preservatives is not without side effects though; they cause nausea, abdominal pain, vomiting, skin reactions, as well as choking and chemical pneumonitis in consumers or handlers (De Andrade *et al.*, 2015). The ability of sulphites to react with biomolecules such as DNA and their ability to generate free radicals such as superoxide when they react makes them toxic to the human system (Musagala *et al.*, 2013). Sulphites are generated in the human body through the degradation of sulphur containing amino acids such as methionine and cysteine (Mitsuhashi *et al.*, 1998).

$S_2O_5^{2-}$ commonly referred to as metabisulphite has disulphite as its IUPAC recommended name (Bellion, 1992). Sodium metabisulphite is often added to soft drinks as a preservative, along with synthetic colours, and has been thought to participate in dye degradation (Damant *et al.*, 1989).

Metabisulphite exists in equilibrium with HSO_3^- in aqueous solution and it has been observed that at low concentration

and at room temperature, its aqueous solution is completely converted into HSO_3^- (Chandr, 1982; Tarun *et al.*, 1982; Liu and Brooks, 1998).

Coordination compounds containing 1, 10-phenanthroline as ligands are amongst the most studied coordination compounds (Wimmer *et al.*, 1988). This is because 1, 10-phenanthroline or the metal ion in them can be varied in an easily controlled manner to facilitate an individual application (Arounaguirri *et al.*, 2000; Schäfer *et al.*, 2007). Some of these complexes were observed to show antimicrobial (Agwara *et al.*, 2010; Aljahdali *et al.*, 2013) and anticancer (Sammes and Yahioğlu, 1994) activity. They are also useful as drying catalyst for oils, varnishes, paints and alkyl resin coatings and as herbicides, pesticides, fungicides, polymerization agents (Schilt, 1969).

Understanding how the reaction of complexes proceeds at the atomic level is of importance to synthetic and analytical chemists and can be used to rationalize the behaviour of catalysts and metalloenzymes with similar structure or function (Henderson, 1995). Therefore interest in μ -oxo-diiron complex is mainly due to their use as bioinorganic models for active sites of several proteins (Monzyk, 1997). Several structural, magnetic and spectral properties of modeled binuclear iron complexes containing the μ -oxo unit have been studied (Plowman *et al.*, 1984; Wang *et al.*, 2003). However, kinetic and mechanistic studies of such complexes are not too extensive (Chaudhuri and Banerjee, 1998; Ukoha, 1999; Bhattacharyya *et al.*, 2004; Idris *et al.*, 2004; Bhattacharyya and Mukhopadhyay, 2005; Idris, 2005; Bhattacharyya *et al.*, 2007; Anweting, 2016; Busari *et al.*, 2019). In this paper, we report the kinetic investigation of the

reduction of μ -oxo-tetrakis(1, 10-phenanthroline)diiron(III) complex ion by $S_2O_5^{2-}$ in aqueous phenanthroline buffer.

Materials and Methods

The μ -oxo diferric complex, $[Fe_2O(phen)_4Cl_2]Cl_2 \cdot 6H_2O$, was prepared by the dissolution of $FeCl_3$ (JHD) (2.844 g, 17.5 mmol) in a beaker containing deionized distilled water before an aqueous suspension of 1, 10-phenanthroline monohydrate (Kermel) (6.93 g, 35.0 mmol) was added and the mixture was kept in the dark until the next day, when brown crystals had formed. They were filtered and washed with ice-cold water and then dried in air and subsequently in a desiccator over silica gel (Khedekar *et al.*, 1967; Bhattacharyya *et al.*, 2007; Das *et al.*, 2008; Busari *et al.*, 2019). The aqueous phenanthroline buffer solution of the synthesized brown binuclear iron complex gave UV-Visible spectrum (Fig. 1) as reported by several authors (Plowman *et al.*, 1984; Chaudhuri & Banerjee, 1998; Mukherjee *et al.*, 2005) and it absorbs insignificantly at 510 nm, the wavelength of maximum absorption of $[Fe(phen)_3]^{2+}$, at which the present study is carried out.

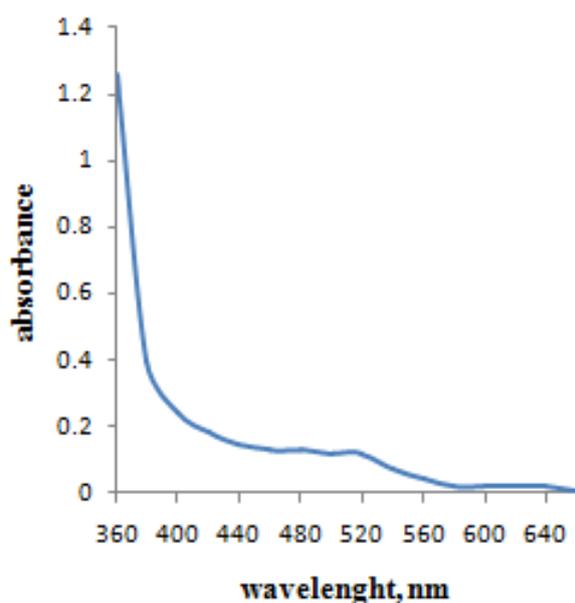


Fig. 1: Spectrum of $5.0 \times 10^{-5} \text{ mol dm}^{-3}$ $[Fe_2O(phen)_4(H_2O)_2]^{4+}$ solution in aqueous phenanthroline buffer, pH 4.5

$0.050 \text{ mol dm}^{-3}$ stock solutions of the binuclear complex at pH 4.50 was prepared daily by dissolving 0.050 g of the solid sample in 0.30 mol dm^{-3} aqueous phenanthroline buffer solution in a 50 cm^3 volumetric flask. The yellow-brown aqueous solution undergoes photoreduction (David and de Mello, 1973) and was therefore kept in an amber coloured bottle covered with black cloth in between use. Working solutions were prepared by appropriate dilution of the stock solution. The pH of the solution was varied by adding required amounts of phenanthroline and/or hydrochloric acid solution. Standard solution of sodium metabisulphite was prepared immediately before use by dissolving known weight of the salt in known volume of deionized distilled water, with working standard solutions obtained by appropriately diluting the stock solution. Sodium chloride was used to maintain ionic strength of the medium.

The stoichiometry of the oxidation reactions of the binuclear complex with $S_2O_5^{2-}$ was investigated at $T = 24.0 \pm 1.0^\circ\text{C}$,

pH = 4.5 (phen/phenH⁺ buffer), and $I = 0.50 \text{ mol dm}^{-3}$ (NaCl) with $[S_2O_5^{2-}] \gg [Fe_2O(phen)_4(H_2O)_2]^{4+}$. Kinetic runs were made under pseudo first order conditions with $[Fe_2O(phen)_4(H_2O)_2]^{4+}$ maintained at $5.0 \times 10^{-5} \text{ mol dm}^{-3}$ while $[S_2O_5^{2-}]$ was kept in excess and ranged from 1.0×10^{-3} to $16.0 \times 10^{-3} \text{ mol dm}^{-3}$ at pH 4.50, $T = 24 \pm 1.0^\circ\text{C}$ and ionic strength 0.50 mol dm^{-3} . The reaction progress was monitored spectrophotometrically using UNICO UV-2102PC Spectrophotometer by following the increase in the absorbance of the product $[Fe(phen)_3]^{2+}$ at 510 nm, its λ_{max} . All other species in solution do not absorb significantly at this wavelength. Observed pseudo first order rate constants (k_{obsd}) were determined from the linear plots of $\log(A_\infty - A_t)$ (where A_∞ = absorbances of the final $[Fe(phen)_3]^{2+}$ and A_t = absorbances of $[Fe(phen)_3]^{2+}$ formed after time t) against time by drawing tangents to the graphs at zero time. Kinetic runs to determine the order of the reaction with respect to $S_2O_5^{2-}$

were carried out by varying the concentration of $S_2O_5^{2-}$ at a constant temperature, fixed $[Fe_2O(phen)_4(H_2O)_2]^{4+}$ and pH, and at a constant ionic strength. The second order rate constants, k_2 , were determined as $k_2 = k_{\text{obsd}}/[S_2O_5^{2-}]$ to obtain the order of the reaction with respect to $[S_2O_5^{2-}]$ (Busari *et al.*, 2019).

The effect of pH on the rate of the reaction was investigated in the pH range 3.50–4.50 (Table 1) at $24.0 \pm 1.0^\circ\text{C}$ and $I = 0.50 \text{ mol dm}^{-3}$ (NaCl), while the concentration of $[Fe_2O(phen)_4(H_2O)_2]^{4+}$ and that of the $S_2O_5^{2-}$ ions were kept constant at $5.0 \times 10^{-5} \text{ mol dm}^{-3}$ and $1.0 \times 10^{-3} \text{ mol dm}^{-3}$, respectively. Keeping the concentrations of all other reactants constants, the effect of ionic strength on the rate of the reaction was investigated in the range 0.10 – 0.60 mol dm^{-3} also at $24.0 \pm 1.0^\circ\text{C}$ and at pH = 4.50.

To understand the type of mechanism operating in the redox process, the effect of added Mg^{2+} (5.0 – $30.0 \times 10^{-3} \text{ mol dm}^{-3}$) and CH_3COO^- (5.0 – $40.0 \times 10^{-3} \text{ mol dm}^{-3}$) on the reaction rate was observed while keeping $[Fe_2O(phen)_4(H_2O)_2]^{4+}$, $[S_2O_5^{2-}]$, ionic strength, pH and temperature constant $5.0 \times 10^{-3} \text{ mol dm}^{-3}$, $1.0 \times 10^{-3} \text{ mol dm}^{-3}$, 0.50 mol dm^{-3} , 4.50, and $24 \pm 1.0^\circ\text{C}$, respectively.

The formation of free radical intermediate during the course of the reaction was confirmed by adding 10 % w/v acrylamide solution to a partially oxidized reaction mixtures followed by addition of a large excess of methanol. Control experiment was carried out by adding the acrylamide to a solution of $[Fe_2O(phen)_4(H_2O)_2]^{4+}$ and $S_2O_5^{2-}$ separately at the stated conditions of pH and ionic strength.

Results and Discussion

The homovalent μ -oxo-bridged diferric complex ion, $[Fe_2O(phen)_4Cl_2]^{2+}$, spontaneously aquates to $[Fe_2O(phen)_4(H_2O)_2]^{4+}$ (Bhattacharyya and Mukhopadhyay, 2005; Bhattacharyya *et al.*, 2007), the most redox active specie (Mukherjee *et al.*, 2005), in aqueous phen-phenH⁺ buffer solution.

The reaction of excess $[S_2O_5^{2-}]$ with $5.0 \times 10^{-5} \text{ mol dm}^{-3}$ $[Fe_2O(phen)_4(H_2O)_2]^{4+}$ at pH = 4.50 and $I = 0.50 \text{ mol dm}^{-3}$

(NaCl) gave $[Fe(phen)_3]^{2+}$ and SO_4^{2-} as products. The visible spectrum, in the wavelength range 400–700 nm, as well as the wavelength of maximum absorption (λ_{max}) of 510 nm of the orange–red coloured product, both recorded using UNICO UV–2102PC Spectrophotometer, confirmed it to be $[Fe(phen)_3]^{2+}$. Using the relation $A = \epsilon cl$, with $\epsilon = 1.11 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, the absorbance measurements at the λ_{max} also established the quantitative conversion of a molecule of $[Fe_2O(phen)_4(H_2O)_2]^{4+}$ to twice that of $[Fe(phen)_3]^{2+}$. The oxidized product of $S_2O_5^{2-}$ was qualitatively confirmed as SO_4^{2-} using the white precipitate it produced with Ba^{2+} (Svehla, 1997). From this result it can be deduced that one mole of $[Fe_2O(phen)_4(H_2O)_2]^{4+}$ reacted with one mole of $S_2O_5^{2-}$ to give two moles each of both $[Fe(phen)_3]^{2+}$ and SO_4^{2-} . On this basis, the overall equation for the reaction can be represented by equation 1.

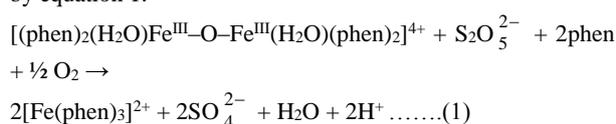


Table 1: Pseudo first order and second order rate constants for the redox reaction of $[Fe_2O(phen)_4(H_2O)_2]^{4+}$ and $S_2O_5^{2-}$ in aqueous phenanthroline buffer. $[Fe_2O(phen)_4(H_2O)_2]^{4+} = 5.0 \times 10^{-5} \text{ mol dm}^{-3}$, $T = 24 \pm 1.0 \text{ }^\circ\text{C}$ and $\lambda_{max} = 510 \text{ nm}$.

$10^3[S_2O_5^{2-}]/(\text{mol dm}^{-3})$	pH	I(NaCl)/ (mol dm^{-3})	$10^2 k_{obsd}/s^{-1}$	$k_2/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
1.0	4.50	0.50	0.217	2.17
2.0	4.50	0.50	0.417	2.09
4.0	4.50	0.50	0.735	1.84
8.0	4.50	0.50	1.53	1.91
12.0	4.50	0.50	2.35	1.96
16.0	4.50	0.50	3.34	2.09
1.0	3.50	0.50	0.087	0.87
1.0	3.75	0.50	0.122	1.22
1.0	4.00	0.50	0.142	1.42
1.0	4.36	0.50	0.146	1.46
1.0	4.50	0.50	0.203	2.03
1.0	4.50	0.10	1.02	10.20
1.0	4.50	0.20	0.444	4.40
1.0	4.50	0.30	0.256	2.56
1.0	4.50	0.40	0.178	1.78
1.0	4.50	0.50	0.164	1.64
1.0	4.50	0.60	0.146	1.46

The linearity of the plots of $\log(A_\infty - A_t)$ against time infers that the order of the reaction with respect to $[Fe_2O(phen)_4(H_2O)_2]^{4+}$ is one. Also the linearity ($r = 0.962$) of

the plot of k_{obsd} against $[S_2O_5^{2-}]$ (Fig. 2) as well as the consistency of the second order rate constants, k_2 (Table 1), indicates that the order of the reaction with respect to $S_2O_5^{2-}$ is also one. This was confirmed by the value of 1.01 obtained as slope of the linear plot of $\log k_{obsd}$ against $\log[S_2O_5^{2-}]$. Therefore, the rate law for the reduction of $[Fe_2O(phen)_4(H_2O)_2]^{4+}$ by $S_2O_5^{2-}$ at pH= 4.50, I = 0.50 mol dm^{-3} (NaCl) and $T = 24 \pm 1.0^\circ\text{C}$ can be express as equation (2), with k_2 obtained as $2.01 \pm 0.17 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$:

$$\frac{d[Fe_2O(phen)_4(H_2O)_2]^{4+}}{dt} = k_2 [Fe_2O(phen)_4(H_2O)_2]^{4+} [S_2O_5^{2-}] \dots (2)$$

This means the $[Fe_2O(phen)_4(H_2O)_2]^{4+}-S_2O_5^{2-}$ system displayed a first order dependence on both $[Fe_2O(phen)_4(H_2O)_2]^{4+}$ and $S_2O_5^{2-}$ in the pH range 3.50–4.50 in which the study was carried out. The observed first order dependence of rate of reaction on $[Fe_2O(phen)_4(H_2O)_2]^{4+}$ have been reported by several authors (Chaudhuri & Banerjee, 1998; Bhattacharyya *et al.*, 2004; Bhattacharyya & Mukhopadhyay, 2005; Mukherjee *et al.*, 2005; Bhattacharyya *et al.*, 2007; Das *et al.*, 2008; Mandal *et al.*, 2009). The rate of reaction of this reaction was found to decrease with increase in the ionic strength. The plot of k_{obsd} versus pH (Fig. 3) indicated that the reaction rate increase with increase in the pH from 3.50 to 4.50 and since pH is inversely related to $[H^+]$, this confirms the formation of H^+ as a product of the reaction as shown by equation 1. Least square analysis of the plots of $1/k_{obsd}$ versus $1/[S_2O_5^{2-}]$ gave a straight line with negligible intercept suggesting the absence of intermediate complex formation in the reaction. Added Mg^{2+} and CH_3COO^- ions were found to have no effect on the reaction rate observed by keeping the concentrations of $[Fe_2O(phen)_4(H_2O)_2]^{4+}$, $S_2O_5^{2-}$, pH, temperature and ionic strength constant at 5.0×10^{-5} , $7.84 \times 10^{-3} \text{ mol dm}^{-3}$, 4.50 and 26°C , respectively.

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 intermediate was form in the reaction mixtures during the course of the reaction.

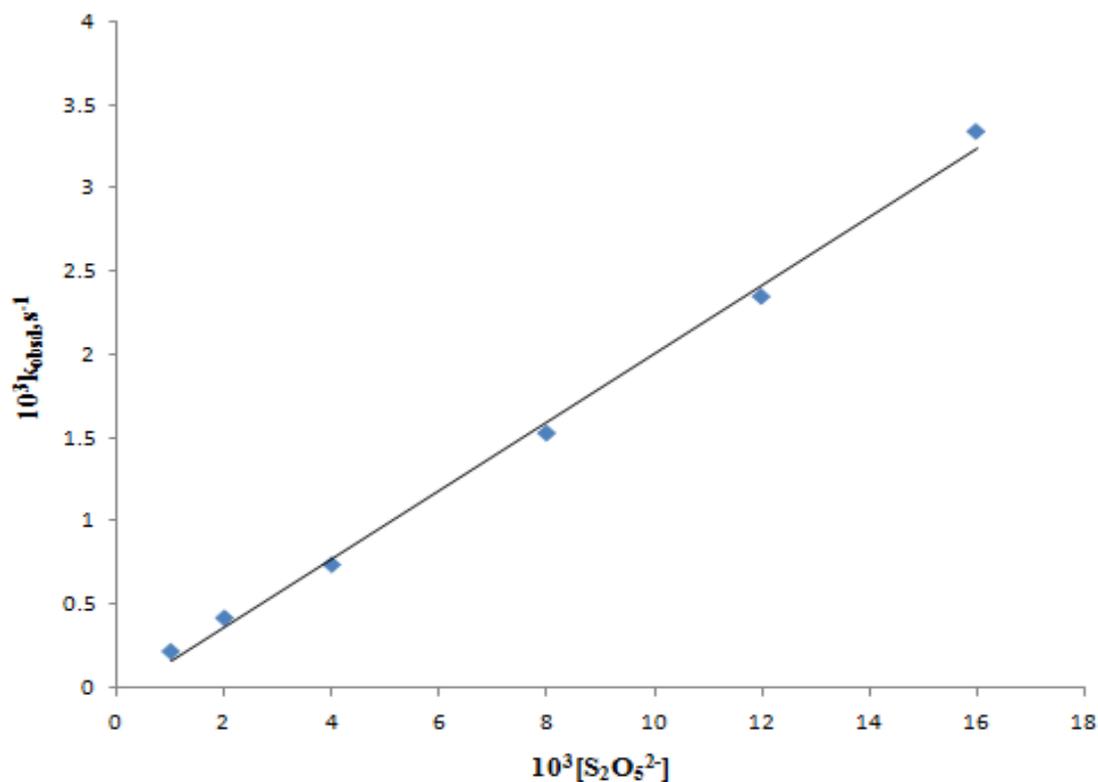


Fig. 2: Plot of k_{obsd} versus $[S_2O_5^{2-}]$ for the reduction of $[Fe_2O(phen)_4(H_2O)_2]^{4+}$ by $S_2O_5^{2-}$

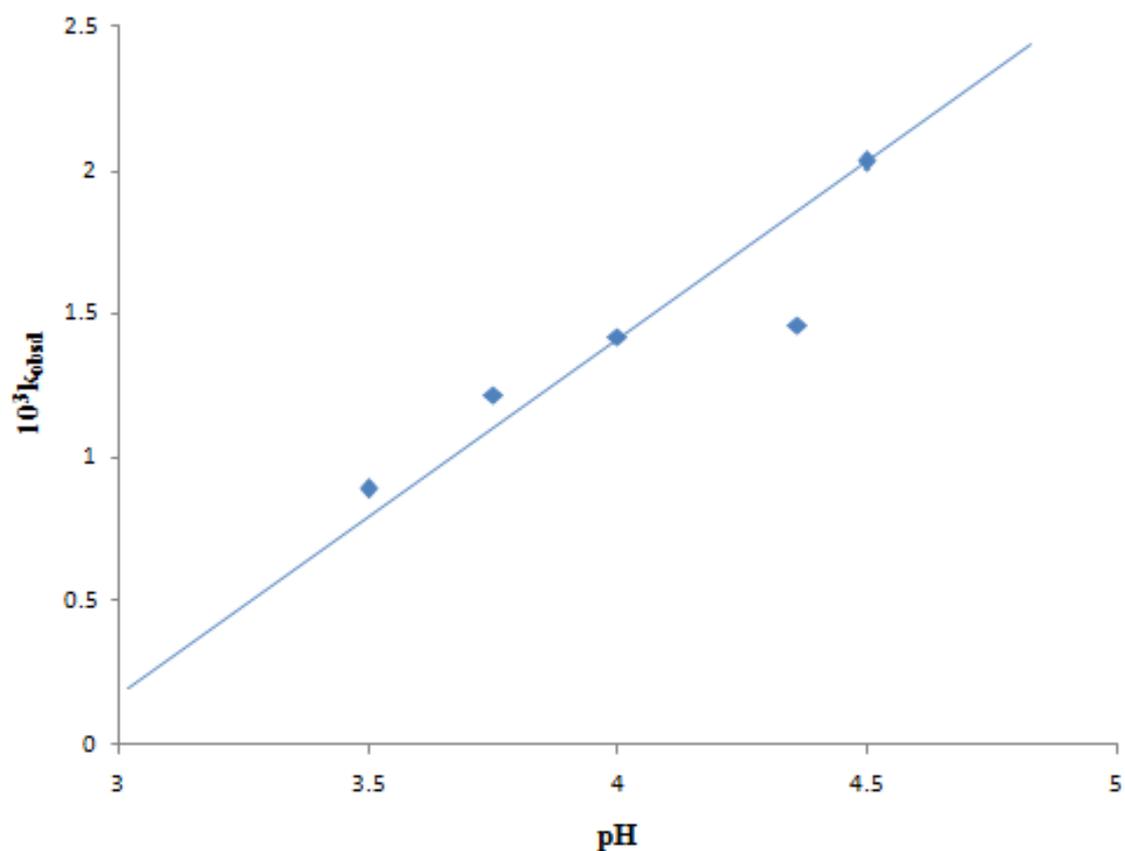
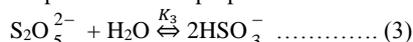


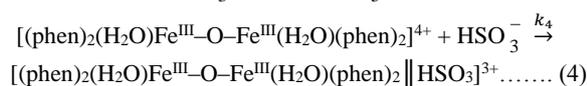
Fig. 3: Plot of k_{obsd} versus pH for the reduction of $[Fe_2O(phen)_4(H_2O)_2]^{4+}$ by $S_2O_5^{2-}$

Proposed mechanism

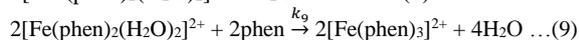
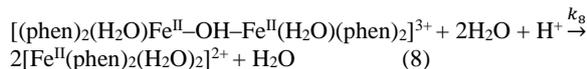
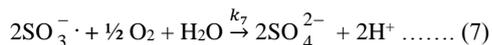
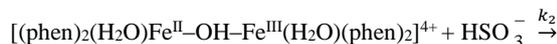
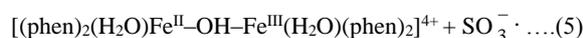
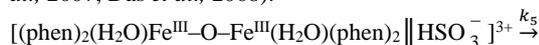
On the basis of the stoichiometry and kinetic data obtained and the reports in the literature relating to the redox reactions involving the use of sodium metabisulphite as reducing agent to give SO_4^{2-} , the following mechanism based on reasonable simple reactions is proposed:



Step (3) is expected as the initiation reaction (Liu and Brooks, 1998), since it is a well known fact that when $Na_2S_2O_5$ is added to water at low concentrations, it is instantaneously converted into bisulphite ion with the equilibrium concentration of $S_2O_5^{2-}$ ions been almost zero in the solution (Golding, 1960; Tarun *et al.*, 1982). Also because the reaction rate increases with the increase of $[S_2O_5^{2-}]$, it confirms that the reactive species responsible for the reactions are the bisulphite ions (HSO_3^-) and not $S_2O_5^{2-}$ ions.



The formation of adduct is well established for reactions of $[Fe_2O(phen)_4(H_2O)_2]^{4+}$ with different reductants (Bhattacharyya and Mukhopadhyay, 2005; Bhattacharyya *et al.*, 2007; Das *et al.*, 2008).



Conclusion

A stoichiometry of 1:1 was obtained for the redox reaction between $[Fe_2O(phen)_4(H_2O)_2]^{4+}$ and $S_2O_5^{2-}$ ion in aqueous phenanthroline buffer medium to yield $[Fe(phen)_3]^{2+}$ and SO_4^{2-} . First order reaction was observed with respect to both reactants, with the rate of the reaction being accelerated with increase in pH of the reaction medium. Added ions were found to have no effect on the reaction rate, supporting inner sphere pre-equilibrium adduct formation suggested in the proposed mechanism.

Conflict of Interest

Authors have declared that there is no conflict of interest in this study.

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