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Kinetics of Redox Reactions between Tetrakis (2, 2'- bipyridine)-µ-oxodiiron (III) Complex and Two Derivatives of Thiourea in Aqueous Acidic Medium

Idongesit Bassey Anweting*, Ahmed Adetoro, Bako Myek, and Asiwe Thomas Ndidi

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Abstract: *The kinetics and mechanism of the redox reactions of tetrakis(2,2'-bipyridine)-µ-oxodiiron(III) chloride, [Fe2(bpy)4O]Cl4 (Fe2O4+), with N-methylthiourea (MTU) and N-allylthiourea (ATU) have been investigated spectrophotometrically in aqueous acidic medium. Stoichiometric studies revealed a 1:1 oxidant-to-reductant ratio for both systems, corresponding to the oxidation of the thiourea derivatives to their respective urea analogues with concomitant reduction of the iron(III) complex to Fe2+. The reactions were first order with respect to both Fe2O4+ and the reductants, giving an overall second-order rate law. The second-order rate constants at [H+] = 1.0 × 10−3 mol dm−3, I = 0.30 mol dm−3 (NaCl), T = 27.0 ± 1.0 °C and λmax = 520 nm were (27.99 ± 0.03) × 10−2 dm3 mol−1 s−1 and (6.25 ± 0.02) × 10−2 dm3 mol−1 s−1 for the MTU and ATU systems, respectively, indicating that MTU is approximately 4.5 times more reactive than ATU. The reaction rates were independent of hydrogen ion concentration within the range (4.0 × 10−4–1.4 × 10−3 mol dm−3) and ionic strength within the range 0.10–0.60 mol dm−3. Addition of sulfate and acetate ions significantly retarded the reaction rates, whereas Mg2+ and K+ ions exhibited negligible effects. Acrylamide polymerization tests provided no evidence for free-radical intermediates, while spectroscopic monitoring and Michaelis–Menten analyses showed no detectable intermediate complex formation. The combined kinetic, spectroscopic, and product studies support an outer-sphere electron-transfer mechanism for the oxidation of MTU and ATU by Fe2O4+ in aqueous acidic medium.*

Keywords: *Redox kinetics; µ-oxodiiron(III) complex; N-methylthiourea; N-allylthiourea; outer-sphere mechanism; electron transfer.*

Idongesit Bassey Anweting*
Department of Chemistry, Faculty of Physical Sciences, University of Uyo, Uyo, Nigeria
Email: idongesitanweting@uniuyo.edu.ng
https://orcid.org/0000-0002-9251-3991

Ahmed Adetoro
Department of Chemistry, Nigerian Army University, P.M.B. 1500, Biu, Borno State, Nigeria
Email: lamedaplc@yahoo.com
https://orcid.org/0000-0001-9224-2530

Bako Myek
Department of Pure and Applied Chemistry, Kaduna State University, Nigeria
Email: bakomyek@kasu.edu.ng
https://orcid.org/0000-0001-8241-3236

Asiwe Thomas Ndidi
Department of Chemistry, Delta State University, Abraka, Delta State, Nigeria
Email: michealasiwe@gmail.com
https://orcid.org/0009-0008-7020-817X

1.0 Introduction

Thiourea, which is a well-known sulphur analogue of urea is known to have multifarious biological and chemical applications. The presence of sulfur and nitrogen donor atoms in thiourea derivatives confers unique redox and coordination properties, making them valuable substrates in mechanistic and electron-transfer studies. Their ability to undergo oxidation through different pathways has stimulated considerable interest in understanding their reaction kinetics and mechanisms. Its derivatives are widely used as additives in various electrochemical processes, such as electroplating, electrolysis, refining and the enhancement at the electrodeposition of metals such as Fe and Cu from acidic media. They are commercially used in photographic films, plastics and textiles. Thiourea derivatives are potentially very versatile ligands, able to coordinate to a range of metal centres as neutral ligands, mono anions or dianions.

The oxygen, nitrogen and sulphur donor atoms of thiourea derivatives provide a multitude of bonding possibilities in the complexation processes (Zhang *et al.,* 1998; Subhasis *et al.*, 2012). Both the free thioureas, and their metal complexes have been found to display a wide range of biological activity, including antibacterial, antifungal, antitubercular, antithyroid, antihelmintic, rodenticidal, insectidal, herbicidal, hypnotic antipyretic activities and plant-growth regulator properties (Ren *et al.,* 2000; Yuan *et al.,*2001; Zhang, *et al.,* 2004; Zhou, *et al.*, 2004; Eweis *et al.*, 2006). Some of the thioureas have been screened for anticancer activity (Zaware, 2009).

Moreover, thiourea derivatives are important compounds as building blocks in the synthesis of heterocyclic compounds (Kodomari, 2005). In the past decade, thiourea derivatives have been intensively investigated as organo catalysts in asymmetric reactions because of their strong hydrogen bonding activity (Momiyama and Yamamoto, 2005). However, a study of the metabolism of these compounds has shown that while substituted thioureas, for example, naphylthiourea are toxic, the oxidation product, the corresponding urea, is non-toxic. Hence the conversion of thiourea derivatives into ureas has attracted the interest of chemists as a potential detoxification process. Furthermore, the presence of multiple functional groups in thiourea derivatives makes them attractive substrates for investigating selective oxidation reactions and electron-transfer processes (Prangya *et al.*, 2010).Because the oxidation products of thiourea derivatives often possess industrial, pharmaceutical, and environmental significance, considerable efforts have been devoted to elucidating their oxidation mechanisms using a variety of oxidizing agents.

Redox reactions of thiourea and its derivatives have received global attention due to the applications of the products obtained from such reactions. Michael & John (1997) studied the redox reactions of thiourea and two dialkylthioureas and hydrogen peroxide in acidic medium kinetically, formamidine disulphide cations were formed as the products of the reactions. The reaction proceeded by nucleophilic displacement by sulphur on oxygen. The oxidation of thiourea has been carried out by Fe(V) in aqueous solution (Sharma & O'Connor, 2000). The rate of oxidation was first order with respect to the reactants and the hydrogen ion concentration. The reaction of Fe(V) with thiourea proceeded by a concerted two-electron oxidation mechanism, which converts Fe(V) to Fe(III). Sahoo *et al.* (2010) proposed a five steps mechanism for the desulphurisation reaction of thiourea by cetyltrimethylammonium dichromate (CTADC) wherein the initiation of the reaction was due to protonation of CTADC. Osunlaja (2014) studied the kiinetics of the redox reactions of methylene blue and μ-superoxo binuclear cobalt(III) complex with thiourea and its derivatives (1-methyl-2-thiourea, 1,3-dimethyl-2-thiourea, 1,1,3,3-tetramethyl-2-thiourea and 1-allyl-2-thiourea) spectrophotometrically in acid media. The reactions of methylene blue - thioureas and μ-superoxo binuclear cobalt(III) complex - thioureas were carried out in HCl and $HClO_4$ medium, respectively. All methylene blue-reductant systems studied yielded reduced methylene blue molecules (that has no conjugation in the phenothiazine ring), sulphate ions, urea/urea derivatives. On the other hand, reactions of μ-superoxo binuclear cobalt(III) complex with the reductants gave Co^{2+} as the final inorganic product. Onu *et al.* (2018) studied redox reactions of tris(1,10-phenanthroline)cobalt(III) complex and *N*-methylthiourea in aqueous acidic medium. "Binuclear iron(III) complexes constitute an important class of coordination compounds due to their structural resemblance to active sites found in several biological systems and their ability to participate in electron-transfer reactions. The presence of the μ-oxo bridge facilitates electronic communication between the metal centres and often influences the kinetics and mechanism of redox processes. Consequently, kinetic investigations involving μ-oxodiiron(III) complexes can provide valuable information on electron-transfer pathways and reaction mechanisms in multinuclear metal systems."

Stoichiometric determination depicted that for one mole of the reductant, one mole of the oxidant was consumed.

Despite the extensive applications of thiourea derivatives and the numerous mechanistic studies reported in the literature, information regarding their redox reactions with binuclear iron(III) complexes remains scarce. In particular, there is limited information on the kinetics, mechanistic pathways, and electron-transfer characteristics of reactions involving tetrakis(2,2′-bipyridine)-μ-oxodiiron (III) complexes and substituted thioureas.

Therefore, the present study investigates the kinetics and mechanism of the redox reactions between tetrakis(2,2′-bipyridine)-μ-oxodiiron (III) complex and two thiourea derivatives, namely N-methylthiourea and N-allylthiourea, in aqueous acidic medium. The study is expected to contribute to the understanding of electron-transfer processes involving multinuclear iron complexes and sulfur-containing organic substrates. The findings will provide mechanistic insights into the reactivity of μ-oxodiiron(III) systems and expand the existing knowledge of redox behaviour of biologically and industrially relevant thiourea derivatives.

2.0 Materials and Methods

All chemicals and solvents used were of analytical grade and obtained from BDH, Kermel, and Sigma-Aldrich. The reagents were used without further purification. Distilled water was used throughout for the preparation of all solutions. Stock solutions, 0.05 mol dm^{-3} of *N*'-methylthiourea ($CH_3HNCSNH_2$) and 0.5 mol dm^{-3} of *N*-allylthiourea ($CH_2{=}CHCH_2HNSNH_2$) were prepared by dissolving 0.450 g and 5.81 g of $CH_3HNCSNH_2$ and $CH_2{=}CHCH_2HNSNH_2$ respectively in a 100 cm^3 volumetric flask containing distilled water and made up to the mark with distilled water. Separate 1.00 mol dm−3 stock solutions of MgCl2, KCl, Na2SO4, NaCl, and CH3COONa were prepared by dissolving the appropriate masses (2.375 g, 1.863 g, 3.55 g, 1.46 g, and 2.05 g, respectively) in distilled water and making up to the mark in 25 cm3 volumetric flasks. Synthesised tetrakis(2,2'- bipyridine)-μ-oxo-diiron(III) chloride ($[Fe_2(bpy)_4O]Cl_4$), hereafter referred to as Fe_2O^{4+} and a stock solution of hydrochloric acid were prepared as reported elsewhere (Anweting *et al.,* 2021).

2.1 Methods

2.1.1 Stoichiometric study

The stoichiometries of the reactions were determined spectrophotometrically using the mole-ratio method (Jones *et al.,* 2023a; Adetoro *et al.,* 2024). Each measurement was performed in triplicate and the average values were reported.

The concentration of the oxo-bridged iron complex was kept constant while that of MTU and ATU were varied between the mole ratio 1: 0.2 to 1:3 ([reductant]/ [oxidant]) as follows: for MTU- Fe_2O^{4+} system ; $[Fe_2O^{4+}] = 1.0 \times 10^{-4}$ mol dm^{-3}, $[MTU] = (2.0 - 24.0) \times 10^{-5}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 0.3 mol dm $^{-3}$(NaCl) and T = 27 ±1.0 ºC. For ATU-Fe_2O^{4+} system; $[Fe_2O^{4+}] = 1.0 \times 10^{-5}$ mol dm $^{-3}$, [ATU] = $(3.0 - 30.0) \times 10^{-5}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 0.3 mol dm^{-3}(NaCl) and T = 27 ±1.0 ºC. The reactions were allowed to go to completion, and the absorbances of the completely reacted mixtures (A_∞) were monitored at 520 nm using a Corning Colorimeter 253. The absorbances obtained were plotted against the mole ratios of the reactants. Points of sharp breaks in these plots gave the stoichiometries of the reactions. The wavelength accuracy of the instrument was ±2 nm, and all absorbance measurements were performed using matched 1 cm quartz cuvettes.

2.1.2 Products analysis

At the completion of the reaction, the reaction mixtures were analysed for organic and inorganic products formed in the course of the reaction. The formation of Fe2+, sulfate ions, and the corresponding oxidation products of the reductants was examined using standard analytical procedures.

2.1.3 Kinetic measurements

The rates of reactions of the Fe_2O^{4+} with the reductants were studied by monitoring the increase in absorbance of the reaction mixture at its λ_{max} (520 nm) using a Corning Colorimeter 253. All kinetic measurements were carried out under pseudo-first order conditions with respective reductant concentrations in excess of the oxidant concentration at the stated temperature. Ionic strength as well as hydrogen ion concentration were maintained constant for each system unless otherwise stated (Iyun and Shehu, 2004: Johnson *et al.,* 2023; Myek *et al.,* 2024). Pseudo-first-order plots of $\log(A\infty - At)$ versus time were constructed, where At and A∞ are the absorbances at time t and at completion of the reaction, respectively. The second-order rate constants (k_2) were obtained from the relationship, $k2=k_{obs}[Reductant]$ under pseudo-first-order conditions. (Anweting *et al.,* 2012a, b: Jones 2023a, b).

2.1.4 Effect of change in hydrogen ion concentration and ionic strength on rate of reaction

The effect of hydrogen ion concentration on the reaction rate was investigated by maintaining constant concentrations of the oxidant and reductant while varying the concentration of hydrochloric acid. The ionic strength was maintained at 0.30 mol dm^{-3} using sodium chloride as the supporting electrolyte. Ionic strength, I was maintained constant at the stated temperature at 0.30 mol dm^{-3} (NaCl). The ionic strength of the reaction mixture was varied (0.1- 0.6) mol dm^{-3} (NaCl) while maintaining the concentrations of the oxidant, reductants and hydrogen ions constant at the stated reaction temperature. The concentrations of the oxidant and reductant employed in these experiments corresponded to those used in the standard kinetic runs.

2.1.5 Effect of the addition of ions to the reaction medium on the rate of reaction

The concentrations of added ions were varied within the range (0–0.13) mol dm^{-3}. The effect of added ions on the reaction rate was observed by the addition of various amounts of ions (Mg^{2+}, K^+, SO_4^{2-}, and CH_3COO^-) while maintaining the oxidant, reductant, hydrogen ion concentrations and ionic strength constant at the stated temperature (Ukoha and Ibrahim, 2004).

2.1.6 Test for the participation of free radicals in the course of the reaction

Test for free radicals was carried out by adding 2 g of acrylamide to a partially oxidised reaction mixture containing various concentrations of oxidant, reductant and hydrogen ions for each system. A large excess of methanol was added to the reaction mixture. A control experiment was carried out by adding acrylamide to solutions of oxidant and reductant separately at the same conditions of $[H^+]$, I and temperature. Formation of a gel or precipitated polyacrylamide was taken as evidence for the presence of free radical intermediates during the reaction. (Anweting *et al.,* 2017, 2021; Myek *et al.,* 2024).

2.1.7 Test for formation of intermediate complex prior to electron transfer

A test for the presence of stable, detectable intermediate complexes formed in the course of the reaction was carried out by recording the electronic spectra of partially reacted reaction mixtures at various time intervals, depending on the speed of the reaction. Similar runs were made for reactants separately in each case. The spectra were examined for any shift in the wavelength of maximum absorption (λmax), appearance of new absorption bands, or significant enhancement of existing peaks, which could indicate the formation of intermediate species. The presence or absence of intermediate complex formation was further assessed using Michaelis–Menten plots of 1/kobs versus 1/[reductant]. A finite intercept on the ordinate would indicate intermediate complex formation, whereas a linear plot passing through the origin would suggest its absence. (Adetoro *et al.,* 2011, 2024). All kinetic measurements were performed at least in triplicate. Reported rate constants represent mean values, and the associated uncertainties were within ±5% of the mean values.

3.0 Results and Discussion

Stoichiometric investigations revealed that one mole of Fe2O4+ consumed one mole of each thiourea derivative (MTU and ATU), indicating a 1:1 oxidant-to-reductant stoichiometric ratio. This observation suggests that the oxidation process involves the transfer of two electrons per molecule of reductant, resulting in the reduction of the binuclear iron(III) complex to Fe2+. Consequently, the stoichiometric equations for the two systems can be represented by equations 1 and 2 below:

$$Fe_2O^{4+} + CH_3NH(NH_2)C{=}S \rightarrow 2Fe^{2+} + CH_3NH(NH_2)C{=}O + S \qquad (1)$$

$$Fe_2O^{4+} + H_2N(NHR)C{=}S \rightarrow 2Fe^{2+} + H_2N(NHR)C{=}O + S \qquad (2)$$

where R = $CH_2CH{=}CH_2$

A similar stoichiometry has been reported for the electron transfer reactions of thiourea, 1,-methyl-2-thiourea, 1,3-dimethyl-2-thiourea, 1,1,3,3-tetramethyl-2-thiourea, and 1-allyl-thiourea with μ-superoxobinuclear cobalt(III) complex (Osunlaja *et al*., 2013a, b ; Osunlaja, 2014), and reactions of 1,2 and 1,3 benzenediol with Fe_2O^{4+} (Idris *et al.,* 2004; Idris, 2005). Stoichiometries of 1:2 (Ru_2O^{4+}: reductant) were found for reaction of Ru_2O^{4+} (diaquotetrakis (2, 2′-bipyridine) – *μ*-oxodiruthenium(III) ion) with (thiourea, methylthiourea, allylthiourea and dimethyl thiourea) (Mohammed *et al*., 2014a, b; Mohammed, 2015). The observed stoichiometry is consistent with the stepwise two-electron oxidation of thiourea derivatives to their corresponding urea derivatives, accompanied by sulfur formation. The appearance of an absorption maximum at 520nm in all Fe_2O^{4+} reactions in this study confirmed the formation of Fe^{2+} (Yusuf *et al.,* 2004; Iyun, 2004; Idris *et al.,*2004; Idris, 2005). Also, the absence of aa band absorption peak at 620 nm negates the presence of ma ononuclear complex of iron(III) in the reaction medium. Treatment of the reaction products with sodium nitroprusside produced a violet coloration, confirming the presence of sulfur-containing species among the reaction products. This observation supports the proposed oxidation pathway involving sulfur extrusion from the thiourea derivatives. (Murugan, 2013), as one of the products as seen in stoichiometric equations. A similar result wwas obtainedin the reaction of thiourea with chlorite ion in acidic medium (Alamgir and Epstein, 1985; Anweting *et al.,* 2017). From kinetic studies, the reaction between Fe_2O^{4+} and the reductants was first-order dependence on eeach of thereductant concentrations. Pseudo-first-order plots of log(A∞ − At) versus time were linear over more than 70% of the reaction course, indicating ffirst order dependence on $[Fe_2O^{4+}]$ concentration. Furthermore, plots of log kobs versus log[MTU] and log kobs versus log[ATU] (Fig. 1) were linear with slopes approximately equal to unity, demonstrating first-order dependence on reductant concentration. Consequently, the reactions are second order overall, being first order with respect to both oxidant and reductant concentrations.

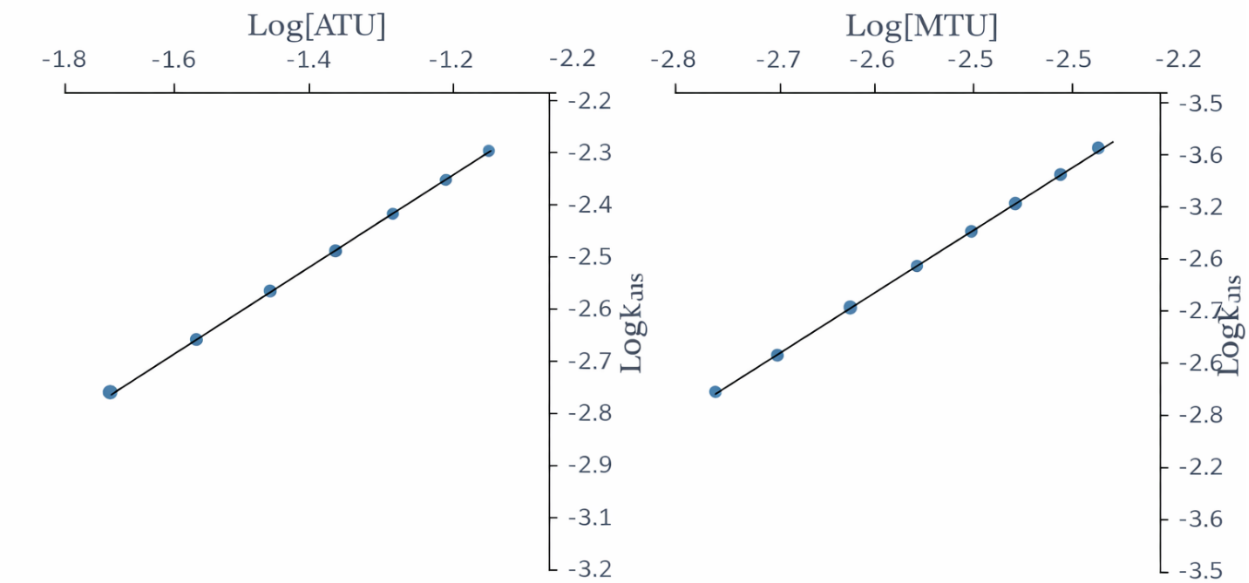

Fig. 1: Pseudo Order Plots for the Redox Reaction of $Fe_2O_4^+$ with MTU and ATU at $[Fe_2O_4^+] = 2 \times 10^{-4}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 0.3 mol dm^{-3} (NaCl), T = 27.0 ± 1.0 °C, $\lambda_{max} = 520$ nm

Thus, these reactions fit into equation 3

$$\frac{-d}{dt}[Fe_2O^{4+}] = k_2[Fe_2O^{4+}][thioureas] \qquad (3)$$

The values of k_2 for the two systems at $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = .3 mol dm^{-3}, T = 27 ± 3°C and $\lambda_{max} = 520$ nm are as follows:

Fe_2O^{4+}- MTU system = (27.99 ± 0.03) ×10^{-2} dm^{3}mol^{-1} s^{-1} with $[Fe^2O^{4+}]$= 2.0×10^{-4} mol dm^{-3}

Fe_2O^{4+}- ATU system = (6.25 ± 0.02) ×10^{-2} dm^{3}mol^{-1} s^{-1} with $[Fe^2O^{4+}]$=2.0×10^{-4} mol dm^{-3}

The observed independence of the reaction rate on hydrogen ion concentration (Tables 1 snd 2) indicates that protonation does not participate in the rate-determining step. This suggests that the reactive forms of both oxidant and reductant remain unchanged within the investigated acid concentration range. This observed acid independence is in accordance with the result obtained by Osunlaja (2014), in the oxidation reaction of TU, MTU, ATU, DMTU and TMTU by $CoCo_2O^{5+}$. Comparison of the second-order rate constants shows that the oxidation of MTU (k2 = 27.99 × 10_{-2} dm3 mol$_{-1}$ s$_{-1}$) proceeds approximately 4.5 times faster than that of ATU (k2 = 6.25 × 10^{-2} dm3 mol−1 s^{-1}). The lower reactivity of ATU may be attributed to the electron-donating allyl substituent and possible steric effects that reduce the susceptibility of the sulfur centre toward oxidation. Varying the ionic strength of the reaction media between 0.1 – 0.6 mol dm^{-3} (NaCl), had no effect on the rates of reaction as shown in Tables 1 – 2.

The negligible effect of ionic strength on the reaction rate suggests that the activated complex is formed between a charged species and a neutral molecule, or that charge development during the transition state is minimal. According to the Brønsted–Bjerrum theory, such behaviour is characteristic of reactions involving neutral species or species of low effective charge. (Idris, 2005; Idris *et al.,* 2004). And in the reaction of Ru_2O^{4+} with TU, MTU, ATU and DMTU (Mohammed *et al.,* 2014a, b; Mohammed, 2015).

Table 1: Pseudo-first and second order rate constants for the redox reaction of MTU by Fe_2O^{4+} in aqueous HCl medium, T = 27.0 ±1.0°C, I = 0.30 mol dm^{-3} (NaCl), [Fe_2O^{4+}] = 2 × 10^{-4} mol dm^{-3} , λ_{max} = 520nm

10^3[MTU] (mol dm^{-3})	10^3[H$^+$] (mol dm^{-3})	10[I$^-$] (mol dm^{-3})	10^4kobs (s^{-1})	k$_2$ (dm^{3}mol^{-1} s^{-1})
2.0	1.0	3.0	5.58	0.279
3.0	1.0	3.0	8.37	0.279
4.0	1.0	3.0	11.20	0.280
5.0	1.0	3.0	14.00	0.280
6.0	1.0	3.0	16.70	0.278
7.0	1.0	3.0	19.40	0.277
8.0	1.0	3.0	22.90	0.286
5.0	0.4	3.0	14.20	0.284
5.0	0.6	3.0	14.30	0.286
5.0	0.8	3.0	14.50	0.290
5.0	1.0	3.0	14.30	0.286
5.0	1.2	3.0	14.30	0.286
5.0	1.4	3.0	13.00	0.260
5.0	1.0	1.0	14.30	0.286
5.0	1.0	2.0	13.70	0.274
5.0	1.0	3.0	14.10	0.282
5.0	1.0	4.0	14.10	0.282
5.0	1.0	5.0	13.40	0.268
5.0	1.0	6.0	13.70	0.274

Table 2: Pseudo-first and second order rate constants for the redox reaction of ATU by Fe_2O^{4+} in aqueous HCl medium, T = 27.0 ±1.0°C, I = 0.30 mol dm^{-3} (NaCl), [Fe_2O^{4+}]= 2 × 10^{-4} mol dm^{-3}, λ_{max} = 520nm

10^3[ATU] (mol dm^{-3})	10^3[H$^+$] (mol dm^{-3})	10[I$^-$] (mol dm^{-3})	10^4kobs (s^{-1})	10^2k$_2$ (dm^3 mol^{-1} s^{-1})
2.0	1.0	3.0	12.50	6.25
3.0	1.0	3.0	18.90	6.30
4.0	1.0	3.0	24.90	6.22
5.0	1.0	3.0	30.80	6.16
6.0	1.0	3.0	37.30	6.22
7.0	1.0	3.0	44.20	6.31
8.0	1.0	3.0	50.20	6.28
5.0	0.4	3.0	31.70	6.34
5.0	0.6	3.0	30.50	6.10

5.0	0.8	3.0	30.90	6.18
5.0	1.0	3.0	31.20	6.24
5.0	1.2	3.0	31.10	6.22
5.0	1.4	3.0	30.70	6.14
5.0	1.0	1.0	29.90	5.98
5.0	1.0	2.0	30.70	6.14
5.0	1.0	3.0	30.20	6.04
5.0	1.0	4.0	31.00	6.20
5.0	1.0	5.0	30.30	6.06
5.0	1.0	6.0	29.80	5.96

The observed decrease in kobs with increasing sulfate and acetate concentrations indicates inhibition by the added anions. Such behaviour may arise from electrostatic interactions between the added anions and the positively charged Fe2O4+ species, thereby reducing the probability of productive collisions between the reactants. (Tables 3-4). Inhibition of the reaction rate by the added anions shows that the added ions have hindered the approach of the reactant species in a simple collision process. The observed inhibition in reaction rate by the added anions in effect suggests that the reactant species are not linked together in the activated complex (Onu, 2010).

Table 3: Dependence of rate constant on added anions for the redox reaction of $[Fe_2O^{4+}]$ and [MTU] at I = 0.3 mol dm^{-3} (NaCl), [MTU] = 5.0 × 10^{-3} mol dm^{-3}, $[Fe_2O^{4+}]$ = 2.0 × 10^{-4} mol dm^{-3}, λ_{max} = 520 nm, $[H^+]$ = 1.0 × 10^{-3} mol dm^{-3}, T = 27.0 ± 1.0^{o}C

Added Ion	**10^3[Ion] (mol dm^{-3})**	**~~10^4k_{obs} (s^{-1})~~**	**k_2 (dm^3 mol^{-1} s^{-1})**
SO_4^{2-}	0.0	14.40	0.288
SO_4^{2-}	30.0	11.80	0.236
SO_4^{2-}	50.0	9.80	0.196
SO_4^{2-}	70.0	8.30	0.166
SO_4^{2-}	90.0	6.84	0.137
SO_4^{2-}	110.0	5.95	0.119
SO_4^{2-}	130.0	4.92	0.098
CH_3COO^-	0.0	14.20	0.284
CH_3COO^-	30.0	10.40	0.208
CH_3COO^-	50.0	8.50	0.170
CH_3COO^-	70.0	6.10	0.122
CH_3COO^-	90.0	4.84	0.097
CH_3COO^-	110.0	2.64	0.053
CH_3COO^-	130.0	1.29	0.026

Table 4 : Dependence of rate constant on added anions for the redox reaction of $[Fe_2O^{4+}]$ and [ATU] at I = 0.3 mol dm^{-3} (NaCl), [ATU] = 5.0 × 10^{-2} mol dm^{-3}, $[Fe_2O^{4+}]$ = 2.0 × 10^{-4} mol dm^{-3}, λ_{max} = 520 nm, $[H^+]$ = 1.0 × 10^{-3} mol dm^{-3}, T = 27.0 ± 1.0^{o}C

Added Ion	**10^3[Ion] (mol dm^{-3})**	**10^4k_{obs} (s^{-1})**	**10^2k_2 (dm^3 mol^{-1} s^{-1})**

SO_4^{2-}	0.0	30.10	6.02
SO_4^{2-}	10.0	26.20	5.24
SO_4^{2-}	25.0	25.30	5.06
SO_4^{2-}	50.0	21.20	4.24
SO_4^{2-}	75.0	19.00	3.80
SO_4^{2-}	100.0	18.05	3.60
SO_4^{2-}	120.0	16.00	3.20
CH_3COO^-	0.0	30.70	6.14
CH_3COO^-	10.0	25.00	5.00
CH_3COO^-	25.0	22.30	4.46
CH_3COO^-	50.0	15.60	3.12
CH_3COO^-	75.0	10.45	2.09
CH_3COO^-	100.0	4.59	0.92
CH_3COO^-	120.0	1.55	0.31

No gel formation was observed upon addition of acrylamide, indicating the absence of detectable free-radical intermediates during the reaction. This observation suggests that electron transfer proceeds through a non-radical pathway.

To ascertain the presence or absence of the formation of intermediate complexes in the course of the reactions of Fe_2O^{4+} and the thioureas, Michaelis-Menten plots of 1/ k_{obs} versus 1/ [reductant] were made, as applied by Adetoro *et al.* (2011). The Michaelis–Menten plots (shown in Figs. 2 and 3) were linear with negligible intercepts, indicating the absence of kinetically significant precursor complexes. The results suggest that electron transfer occurs without the accumulation of a detectable intermediate species. This conclusion is further supported by the absence of new absorption bands or significant shifts in λmax during spectral monitoring of the reaction mixtures.

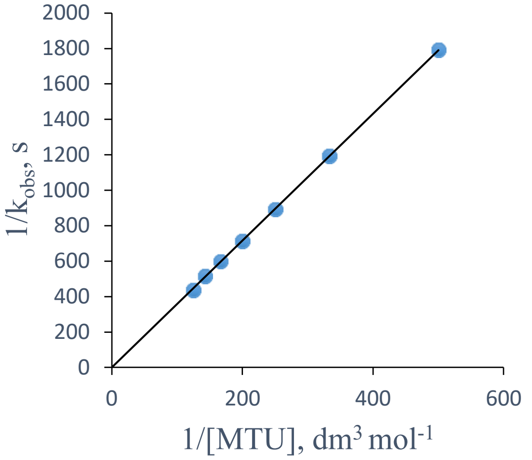

Fig. 3: Michealis-Menten plot of $1/k_{obs}$ versus 1/[MTU] for the oxidation of MTU by Fe_2O^{4+} at $[Fe_2O^{4+}] = 2.0 \times 10^{-4}$ mol dm^{-3}, [MTU] = $(2.0 – 8.0) \times 10^{-3}$ mol dm^{-3}, $[H^+]$ = 1.0×10^{-3} mol dm^{-3}, I = 0.3 mol dm^{-3} (NaCl), T = 27.0 ± 1.0°C and λ_{max} = 520 nm

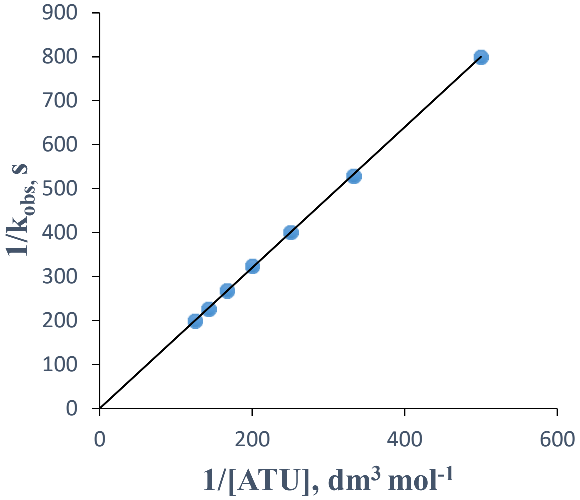

Figure 4: Michealis-Menten plot of $1/k_{obs}$ versus 1/[ATU] for the oxidation of ATU by Fe_2O^{4+} at $[Fe_2O^{4+}] = 2.0 \times 10^{-4}$ mol dm^{-3}, [ATU] = $(2.0 – 8.0) \times 10^{-2}$ mol dm^{-3} $[H^+]$ = 10×10^{-3} mol dm^{-3}, I = 0.3 mol dm^{-3} (NaCl), T = 27.0 ± 1.0°C and λ_{max} = 520 nm.

Based on the observed first-order dependence on both reactants, the absence of ionic-strength effects, inhibition by added anions, the negative results of free-radical tests, and the absence of detectable intermediate complexes, the reactions are proposed to proceed through an outer-sphere electron-transfer mechanism. In the proposed pathway, electron transfer occurs from the sulfur centre of the thiourea derivative to the Fe(III) centres of the μ-oxodiiron(III) complex, resulting in reduction of the oxidant to Fe2+ and oxidation of the thiourea derivative to its corresponding urea derivative. The conversion of the C=S group to a C=O group is consistent with sulfur replacement during the oxidation process and agrees with observations reported for related thiourea oxidation reactions.

4.0 Conclusion

The redox reactions of tetrakis(2,2′-bipyridine)-μ-oxodiiron(III) complex (Fe2O4+) with N-methylthiourea (MTU) and N-allylthiourea (ATU) were successfully investigated in aqueous acidic medium. Stoichiometric studies revealed a 1:1 oxidant-to-reductant ratio for both systems. Kinetic investigations showed that the reactions were first order with respect to both Fe2O4+ and the reductants, resulting in an overall second-order rate law. The reactions were independent of hydrogen ion concentration and ionic strength within the investigated ranges, while added sulfate and acetate ions inhibited the reaction rates, whereas added cations had negligible effects.

The second-order rate constants indicated that MTU reacted faster than ATU, with k2(MTU) > k2(ATU). This difference in reactivity is attributed to the nature of the substituents attached to the thiourea moiety, although the oxidation process remained centred on the sulfur atom in both reductants. The absence of gel formation during acrylamide polymerization tests ruled out the participation of free-radical intermediates, while Michaelis–Menten and spectroscopic studies provided no evidence for the formation of detectable intermediate complexes.

Taken together, the stoichiometric, kinetic, and spectroscopic results support an outer-sphere electron-transfer mechanism for the oxidation of MTU and ATU by Fe2O4+. The study contributes to the understanding of the redox behaviour of thiourea derivatives toward binuclear iron(III) complexes and provides additional mechanistic information on electron-transfer reactions involving sulfur-containing reductants.

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