



## Kinetics of the Oxidation of Thiourea by Tris(1,10-Phenanthroline)Iron(III) Complex Ion in Aqueous Perchloric Acid Media

\*Busari A.<sup>1</sup>, Idris S. O.<sup>2</sup>, Onu A. D.<sup>3</sup>, Abdulkadir I.<sup>2</sup>

<sup>1</sup>Department of Chemistry, Sule Lamido University, Kafin Hausa, Jigawa State, Nigeria.

<sup>2</sup>Department of Chemistry, Ahmadu Bello University, Zaria

<sup>3</sup>Department of Chemistry, Federal College of Education, Zaria.

### ABSTRACT

The redox reaction between tris(1,10-phenanthroline)iron(III) complex ion,  $[Fe(phen)_3]^{3+}$ , and thiourea ( $H_2NCSNH_2$ ) in aqueous perchloric acid media was investigated at temperature of  $26.0 \pm 1.0$  °C over the hydrogen ion concentration range  $0.50-1.0$  mol  $dm^{-3}$  using a UNICO UV-2102PC Spectrophotometer at 510 nm, the visible absorption maximum ( $\lambda_{max}$ ) of the product iron species,  $[Fe(phen)_3]^{2+}$  (tris(1,10-phenanthroline)iron(II) complex ion). The ionic strength was maintained at  $1.0$  mol  $dm^{-3}$  using sodium perchlorate salts, except for the determination of the effect of ionic strength on the rate of the reaction were it was varied between  $0.50$  and  $1.0$  mol  $dm^{-3}$ . One mole of thiourea was consumed per mole of  $[Fe(phen)_3]^{3+}$  with the formation of  $[Fe(phen)_3]^{2+}$  and formamidine disulphide ( $(H_2N)HN=C-S-S-C=NH(NH_2)$ ) as products. Under the conditions in which the reaction was carried out, the reaction is of the first order in each of the reactants in aqueous perchloric acid solutions, and second orders overall. The kinetics of the oxidation obeys the empirical rate law:  $-\frac{d[Fe(phen)_3]^{3+}}{dt} = k_2[Fe(phen)_3]^{3+}[H_2NCSNH_2]$  with the rate constant,  $k_2$ , found to be  $19.01 \pm 0.21$   $dm^3$   $mol^{-1}$   $s^{-1}$ . Taking into account the kinetic data and general observations, a five-step outer-sphere mechanism which lack intermediate complex was proposed for the redox reaction.

### ARTICLE INFO

Article History

Received: March, 2019

Received in revised form: April, 2019

Accepted: May, 2019

Published online: July, 2019

### KEYWORDS

Formamidine disulphide, ionic strength, outer-sphere mechanism, redox reaction, thiourea.

### INTRODUCTION

1, 10-phenanthroline and related compounds are collectively known as 1, 10-phenanthrolines or orthophenanthrolines (Skoog *et al.*, 2014). They bind strongly to most metal ions, especially the first row transition metals, due to the presence of two nitrogen ring atoms at positions 1 and 10 which are used to form heterocyclic metal chelates (Agwara *et al.*, 2010; Wang *et al.*, 2012). These nitrogen atoms have non-conjugated, localized pair of electrons which bears no substituents, but have affinity for these metal atoms, forming complex with octahedral coordination geometry (Busari and Musa, 2018). The stability constants of the metal complexes of 1, 10-phenanthrolines are significantly large which explains why they form quantitatively even if the metal is present in trace amount (Schilt, 1969). Although certain distinctive property of a given metallic element persists through drastic ligand changes, ligands like 1, 10-phenanthroline are known to have a profound effect on the chemical properties of metal ions in coordination complexes.

These include stabilization of different oxidation states and modulation of the electrophilic and nucleophilic properties of the metals (Adeloye and Ajibade, 2010).

Metal ion complexes of phenanthrolines have been known for almost a century (Schilt, 1969; Berkheiser and Mortland, 1977; Plowman *et al.*, 1984). They are known to have high formation constants in aqueous solutions and some like,  $[Fe(phen)_3]^{2+}$ , are also known for high absorptivity (Berkheiser and Mortland, 1977). 1, 10-phenanthroline as well as some of their derived complexes were observed to show antimicrobial activity (Adeloye and Ajibade, 2010; Agwara *et al.*, 2010; Aljahdali *et al.*, 2013) and anticancer (Sammes and Yahiolglu, 1994).

Several kinetic studies of the reduction of the strong one-electron oxidant  $[Fe(phen)_3]^{3+}$  (Beller *et al.*, 2010) have been reported by different authors (Sutin and Gordon, 1961; Carlyle, 1972; Nord and Wernberg, 1975; Pelizzetti and Mentasti, 1977a; Pelizzetti and Mentasti, 1977b; Kimura and Wada, 1978; Yao-Chu *et al.*, 1992; Ayoko *et al.*, 1993b; Vani

\*Corresponding author: Busari, A. ✉ [abdulakeemkekule@yahoo.com](mailto:abdulakeemkekule@yahoo.com) ✉ Department of Chemistry, Sule Lamido University, Kafin Hausa, Jigawa State, Nigeria. © 2019 Faculty of Technology Education, ATBU Bauchi. All rights reserved



*et al.*, 2001; Balakumar *et al.*, 2012; Al Mahdi *et al.*, 2014; Balakumar *et al.*, 2015). Most of these were carried out by following the formation of  $[\text{Fe}(\text{phen})_3]^{2+}$  complex produced at 510 nm, its wavelength of maximum absorption (Ford–Smith and Sutin, 1961; Mentasti and Pelizzetti, 1977; Adedinsewo and Adegite, 1979) and were found to be first order with respect to the concentration of  $[\text{Fe}(\text{phen})_3]^{3+}$  (Ford–Smith and Sutin, 1961; Pelizzetti and Mentasti, 1977a; Mentasti and Pelizzetti, 1977; Adedinsewo and Adegite, 1979; Ayoko *et al.*, 1993).

Reactions of  $[\text{Fe}(\text{phen})_3]^{3+}$  are mainly observed to occur via the outer–sphere mechanism (Mentasti and Pelizzetti, 1977; Adedinsewo and Adegite, 1979; Ayoko *et al.*, 1993; Yao–Chu *et al.*, 1992). Some of these are reported to be acid dependent (Sutin and Gordon, 1961; Kimura and Wada, 1978; Ayoko *et al.*, 1993), while others were independent of acidity (Mentasti and Pelizzetti, 1977; Pelizzetti and Mentasti, 1977a; Pelizzetti and Mentasti, 1977b). Stoichiometries of 1:1 (Ayoko *et al.*, 1993; Mehrotra and Mehrotra, 2003), 2:1 (Mentasti and Pelizzetti, 1977; Pelizzetti and Mentasti, 1977a; Pelizzetti and Mentasti, 1977b) have all been reported for the redox reactions of  $[\text{Fe}(\text{phen})_3]^{3+}$  with different reductants.

Oxidation of sulfur compounds is usually complex (Simoyi *et al.*, 1991; Jonnalagadda *et al.*, 2002; Gao *et al.*, 2008) with the study of sulphur and sulphur containing compounds like thiourea, hereafter designated TU, being important because they have numerous applications (Sahoo *et al.*, 2010; Sharma *et al.*, 2011; Asghari *et al.*, 2015). Thiourea reactions are important in the study of nonlinear chemical kinetics and depending on the reaction conditions, it exhibits exotic behaviors (Mundoma and Simoyi, 2000; Sahoo *et al.*, 2010).

A search in the literature for data about the reaction of  $[\text{Fe}(\text{phen})_3]^{3+}$  with thiourea failed. Our work will cover investigation of the redox reactivity of  $[\text{Fe}(\text{phen})_3]^{3+}$  to throw more light on its mechanistic behaviour. Moreover, iron is an important component of almost all living systems, serving multiple functions, depending on their location and the form in which they exist within the biological system (Pradyot, 2003; Tanvir *et al.*, 2013). Therefore basic knowledge about its redox behaviour in the presence of different ligands and at different pH values is very important. Because of their importance to medicine, many of these iron compounds that are found in nature have been studied in great detail and model systems have been

synthesized in efforts to reproduce their properties and understand the mode of their actions (Buchanan *et al.*, 1994; Bhattacharyya and Mukhopadhyay, 2005; Bhattacharyya *et al.*, 2007). Progress in medicinal coordination chemistry is heavily dependent on the understanding of the thermodynamics and the kinetics and mechanisms of reactions of metal complexes, especially under biologically relevant conditions (Guo and Sadler, 1999). Also information on thiourea reactivity patterns could be beneficial for the studies of the biological role of sulphur compounds in living systems.

## MATERIALS AND METHODS

Thiourea,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ , 1, 10–phenanthroline monohydrate, sulphuric acid, sodium perchlorate and perchloric acid were all used without further purification. The  $[\text{Fe}(\text{phen})_3]^{3+}$  complex ion was prepared by the oxidation of dilute sulphuric acid solution of  $[\text{Fe}(\text{phen})_3]^{2+}$  with  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ , ceric ammonium nitrate, as reported by several researchers (Ford–Smith and Sutin, 1961; Ng and Henry, 1977; Chowdhury and Ali, 2005; Adhikamsetty *et al.*, 2008; Al Mahdi *et al.*, 2014). Solutions of  $[\text{Fe}(\text{phen})_3]^{2+}$  ion was prepared in sulphuric acid solution by adding known excess stoichiometric amounts of 1, 10–phenanthroline to  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ . The perchlorate salts of the  $[\text{Fe}(\text{phen})_3]^{3+}$  ion was precipitated as blue powder from the sulphate solutions by adding concentrated perchloric acid. The salt was confirmed to be pure from the agreement of their spectral characteristics with previously published values (Schilt and Taylor, 1959). The molar absorption coefficient of  $[\text{Fe}(\text{phen})_3]^{3+}$  in concentrated  $\text{HClO}_4$  was found to be  $830 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  at its absorption maximum of 600 nm (Adhikamsetty *et al.*, 2008).

Stock solution of the  $[\text{Fe}(\text{phen})_3]^{3+}$  complex was prepared daily by dissolving its perchlorate salt in concentrated perchloric acid and this was stored at  $0^\circ\text{C}$  in a refrigerator between use. Suitable volumes of this solution were taken for kinetic runs immediately before the reactions were initiated.

The kinetics of the redox reaction of tris(1,10–phenanthroline)iron(III) complex ion with TU in aqueous perchloric acid media was investigated at temperature of  $26.0 \pm 1.0^\circ\text{C}$  over the hydrogen ion concentration range 0.50 – 1.0 mol  $\text{dm}^{-3}$  using a UNICO UV–2102PC Spectrophotometer at 510 nm, the visible absorption maximum ( $\lambda_{\text{max}}$ ) of the product iron specie,  $[\text{Fe}(\text{phen})_3]^{2+}$ , obtained in

\*Corresponding author: Busari, A. ✉ [abdulakeemkekule@yahoo.com](mailto:abdulakeemkekule@yahoo.com) ✉ Department of Chemistry, Sule Lamido University, Kafin Hausa, Jigawa State, Nigeria. © 2019 Faculty of Technology Education, ATBU Bauchi. All rights reserved

the reaction. The ionic strength was maintained at  $1.0 \text{ mol dm}^{-3}$  using sodium perchlorate salts, except for the determination of the effect of ionic strength on the rate of the reaction where it was varied between  $0.50$  and  $1.0 \text{ mol dm}^{-3}$ .

Under the kinetic conditions,  $[\text{Fe}(\text{phen})_3^{3+}] = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{TU}] = 4.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{H}^+] = 0.50 \text{ mol dm}^{-3}$  ( $\text{HClO}_4$ ),  $I = 1.0 \text{ mol dm}^{-3}$  ( $\text{NaClO}_4$ ) and  $T = 26.0 \pm 1.0 \text{ }^\circ\text{C}$ , with  $[\text{Fe}(\text{phen})_3^{3+}]$  as the limiting reagent and using the Beer–Lambert's equation ( $A = \epsilon cl$ ), where  $\epsilon$  of  $[\text{Fe}(\text{phen})_3^{2+}]$  was taken to be  $11,100 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  (Bhattacharyya and Mukhopadhyay, 2005; Bhattacharyya *et al.*, 2007; Adhikamsetty *et al.*, 2008), the concentration of  $[\text{Fe}(\text{phen})_3^{2+}]$  was quantified spectrophotometrically at  $510 \text{ nm}$  after the reaction was confirmed to have been complete. Formamidine disulphide,  $(\text{H}_2\text{N})\text{HN}=\text{C}-\text{S}-\text{S}-\text{C}=\text{NH}(\text{NH}_2)$ , was qualitatively confirmed as the organic product of thiourea oxidation.

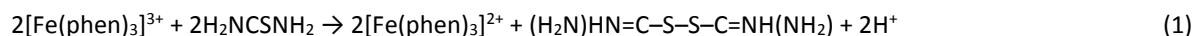
The effect of the variation of  $[\text{TU}]$  on rate is investigated at several initial concentrations ( $2.0 \times 10^{-4}$ ,  $2.5 \times 10^{-4}$ ,  $2.75 \times 10^{-4}$ ,  $3.0 \times 10^{-4}$ ,  $3.25 \times 10^{-4}$ ,  $3.5 \times 10^{-4}$ ,  $3.75 \times 10^{-4}$  and  $4.0 \times 10^{-4} \text{ mol dm}^{-3}$ ) of thiourea but at constant  $[\text{Fe}(\text{phen})_3^{3+}]$ ,  $[\text{H}^+]$ , ionic strength and temperature of  $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $0.50 \text{ mol dm}^{-3}$  ( $\text{HClO}_4$ ),  $1.0 \text{ mol dm}^{-3}$  ( $\text{NaClO}_4$ ) and  $26.0 \pm 1.0^\circ\text{C}$  respectively, unless stated otherwise. The reaction was studied by following the formation of  $[\text{Fe}(\text{phen})_3^{2+}]$ , the product of the reaction, at  $510 \text{ nm}$ , its wavelength of absorption maximum ( $\lambda_{\text{max}}$ ) using a UNICO UV–2102PC Spectrophotometer with a  $1 \text{ cm}$  cell compartment. Pseudo first order rate constants,  $k_{\text{obsd}}$ , were obtained from the slopes of  $\log (A_\infty - A_t)$  versus time plot ( $A_\infty$  and  $A_t$  are the absorbances at the end of the reaction and after time  $t$  respectively). The effect of variation of  $[\text{H}^+]$  ( $0.50$ – $1.0 \text{ mol dm}^{-3}$ ) and ionic strength ( $0.50$ – $1.0 \text{ mol dm}^{-3}$ ) were investigated at  $26.0 \pm 1.0^\circ\text{C}$ ,  $[\text{TU}]$  of  $2.0 \times 10^{-4} \text{ mol dm}^{-3}$  and  $[\text{Fe}(\text{phen})_3^{3+}]$  of  $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ .

In order to find out whether spectroscopically determinable intermediate complex is formed between the complex and thiourea, the spectra of the reaction mixture was

taken at intervals over the  $400$ – $700 \text{ nm}$  range immediately after the reactions were initiated. The formation of an intermediate complex will be indicated by an increase in peak height or a shift in  $\lambda_{\text{max}}$  of the binuclear complex (Osunlaja *et al.*, 2012). Also aliquot of the mixture of  $1.0 \times 10^{-4} \text{ mol dm}^{-3}$   $[\text{Fe}(\text{phen})_3^{3+}]$  at  $[\text{H}^+] = 0.50 \text{ mol dm}^{-3}$  and ionic strength  $1.0 \text{ mol dm}^{-3}$  was mixed with  $10 \text{ w/v\%}$  acrylamide solution and allowed to stand for some time before  $2.0 \times 10^{-4} \text{ mol dm}^{-3}$   $[\text{TU}]$  was added to initiate the reaction, after which large excess methanol was then added. The formation of a gel/polymer will indicate the presence of a free radical intermediate (Sen Gupta *et al.*, 1999; Idris *et al.*, 2014). Blank experiments from which TU was excluded were also carried out.

## RESULTS AND DISCUSSION

After the completion of the reactions between solutions of  $1.0 \times 10^{-4} \text{ mol dm}^{-3}$   $[\text{Fe}(\text{phen})_3^{3+}]$  and  $4.0 \times 10^{-4}$  thiourea at  $[\text{H}^+] = 0.50 \text{ mol dm}^{-3}$  and  $I = 1.0 \text{ mol dm}^{-3}$ ,  $20 \text{ cm}^3$  of ethanol and  $5 \text{ cm}^3$  of concentrated HCl were added to the reaction mixture, which resulted in the formation of white crystals of formamidine dihydrochloride (McAuley and Gomwalk, 1969). This confirmed the oxidation product of thioureas as formamidine disulfide and the dihydrochloride salt is formed in presence of concentrated hydrochloric acid (McAuley and Gomwalk, 1969; Olatunji and Okechukwu, 1987). The reduction product was characterized to be  $[\text{Fe}(\text{phen})_3^{2+}]$  by comparing the spectra of the spent reaction mixture with that already published. The  $[\text{Fe}(\text{phen})_3^{2+}]$  produced was found spectrophotometrically using Beer's law to be  $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ . These gives credence to 1:1 stoichiometry for the system i.e. one mole of the reductants are consumed by one mole of the oxidant, with the formation of one mole of  $[\text{Fe}(\text{phen})_3^{2+}]$  and one-half mole of formamidine disulphide,  $(\text{H}_2\text{N})\text{HN}=\text{C}-\text{S}-\text{S}-\text{C}=\text{NH}(\text{NH}_2)$ , as product for the  $[\text{Fe}(\text{phen})_3^{3+}$ –thiourea redox reaction. Thus the overall reaction may be represented by equation (1):



$[\text{Fe}(\text{CN})_6^{3+}]$  (Lilani *et al.*, 1986),  $\text{KMnO}_4$  (Khan *et al.*, 2007), Chloramine–T (Shubha and Puttaswamy, 2009) and  $\text{IrCl}_6^{2-}$  (Po *et al.*, 1979), which are all known typical outer-sphere oxidant just like  $[\text{Fe}(\text{phen})_3^{3+}]$ , were also found to oxidize thiourea to

formamidine disulfide. Several researchers have reported the formation of formamidine disulfide when excess thiourea was reacted with some oxidants at low pH (Bowley *et al.*, 1986; Saradamba

\*Corresponding author: Busari, A. ✉ [abdulakeemkekule@yahoo.com](mailto:abdulakeemkekule@yahoo.com) ✉ Department of Chemistry, Sule Lamido University, Kafin Hausa, Jigawa State, Nigeria. © 2019 Faculty of Technology Education, ATBU Bauchi. All rights reserved

*et al.*, 1988; Arifoglu *et al.*, 1992; Martincigh *et al.*, 2013).

The initial rate method was used in analyzing the pseudo-first order plots of  $\log(A_{\infty}-A_t)$  versus time. This suggests a first order dependence of rate on  $[\text{Fe}(\text{phen})_3]^{3+}$  for the system. The typical plot is shown in Figure 1. The pseudo first order rate constants,  $k_{\text{obsd}}$ , determined at various initial concentrations of [TU] and at constant  $[\text{Fe}(\text{phen})_3]^{3+}$ ,  $[\text{H}^+]$  and ionic strength are reported in Table 1. Least square plot of respective  $k_{\text{obsd}}$  values against the

$$-\frac{d[\text{Fe}(\text{phen})_3]^{3+}}{dt} = k_2[\text{Fe}(\text{phen})_3]^{3+}[\text{H}_2\text{NCSNH}_2] \quad (2)$$

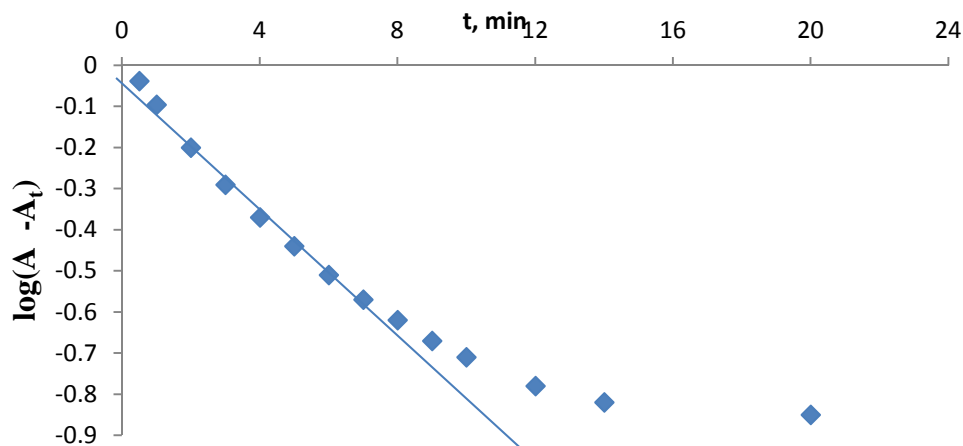
Solution of  $[\text{Fe}(\text{phen})_3]^{3+}$  undergoes slow photodecomposition in weakly acidic solutions of pH above 1.4 (Novak and Arend, 1964; Al Mahdi *et al.*, 2014), therefore our work was carried out at pH 0–0.3 ( $[\text{H}^+] = 0.50\text{--}1.0 \text{ mol dm}^{-3}$ ). The variation of  $[\text{H}^+]$  in the range  $0.50\text{--}1.0 \text{ mol dm}^{-3}$  was observed to have no effect on the observed rate constants of the reactions. Similar results have been reported for the redox reaction of  $[\text{Fe}(\text{phen})_3]^{3+}$  with 1,1'-biphenyl-4,4'-diol (Pelizzetti and Mentasti, 1977b). This can be supported by the fact that the protonation of  $[\text{Fe}(\text{phen})_3]^{3+}$  in equation (3) of the proposed plausible mechanism is of similar rate with the deprotonation of  $\text{H}_2\text{NCSNH}_2$  in equation (4).

Rate constants of the redox reaction were found to decrease with increase in ionic strength from  $0.50$  to  $1.0 \text{ mol dm}^{-3}$  (Table 1). This is an indication that both species at the activated complex are of opposite charges (equation 6) and the product

corresponding initial concentrations of [TU] (Figure 2) is linear with  $r$  equal to 0.999, meaning the reactions is also first order with respect to [TU]. This was further corroborated by slopes of 1.00 obtained from the plot of  $\log k_{\text{obsd}}$  vs.  $\log[\text{TU}]$  (Figure 3). Therefore the reaction is second order overall and the second order rate constant were determined as  $k_{\text{obsd}}/[\text{TU}]$  and were found to be fairly constant at  $19.01 \pm 0.21 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  (Table 1). The rate law of the reaction can be fitted into equation (2).

of their charges was found to be  $-0.58$  from the plot. The non-integral value of the product of the species at the activated complexes indicates that some other interaction might be occurring during the reaction (Ayoko *et al.*, 1992). Spectroscopic evidence and Michaelis-Menten's plot of  $1/k_{\text{obsd}}$  versus  $1/[\text{TU}]$  suggests that intermediates may be unimportant in the rate determining step.

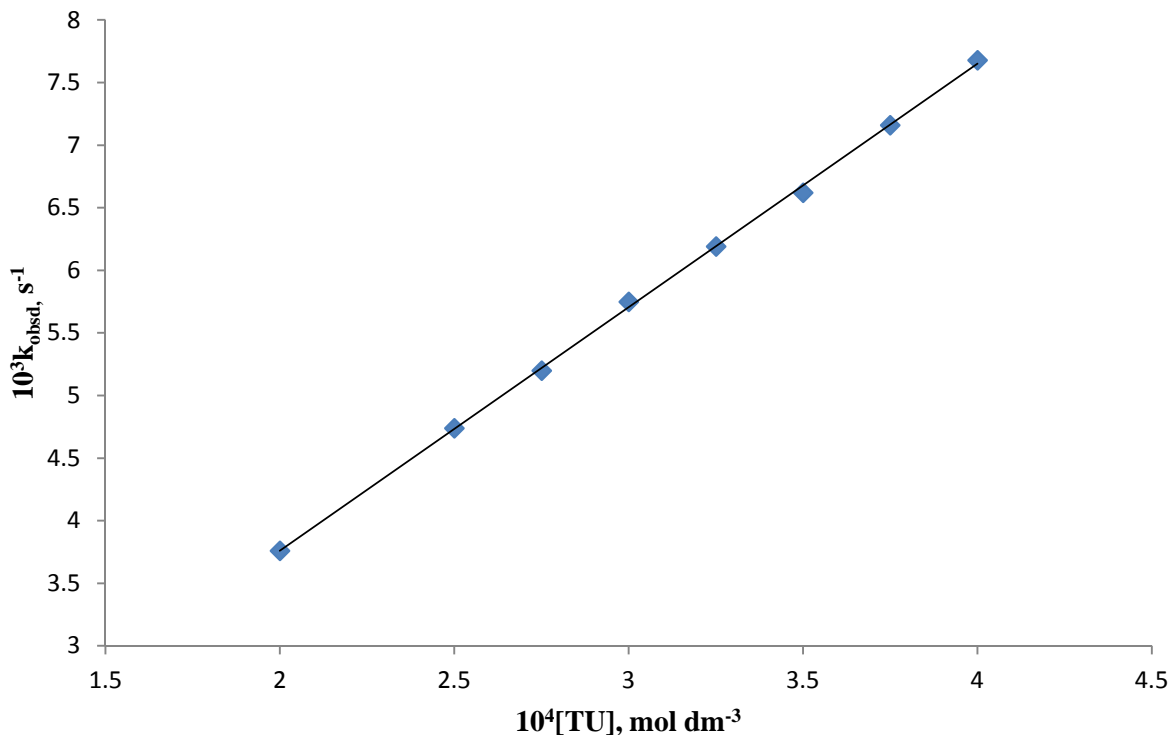
Since  $\text{H}_2\text{NCSNH}_2$  requires two electrons to be converted into  $(\text{H}_2\text{N})\text{HN}=\text{C}-\text{S}-\text{S}-\text{C}=\text{NH}(\text{NH}_2)$ , and with  $[\text{Fe}(\text{phen})_3]^{3+}$  being a well-known one-electron oxidants (Ng and Henry, 1977), the reaction was proposed to occur via two successive univalent changes generating the reactive  $(\text{RHN})\text{HN}=\text{C}-\text{S}^{\cdot}$  radical, which is a well established intermediate in thiourea reactions (Rabai *et al.*, 1993). The polymerization of acrylamide provides support for the existence of free radical in this reaction.



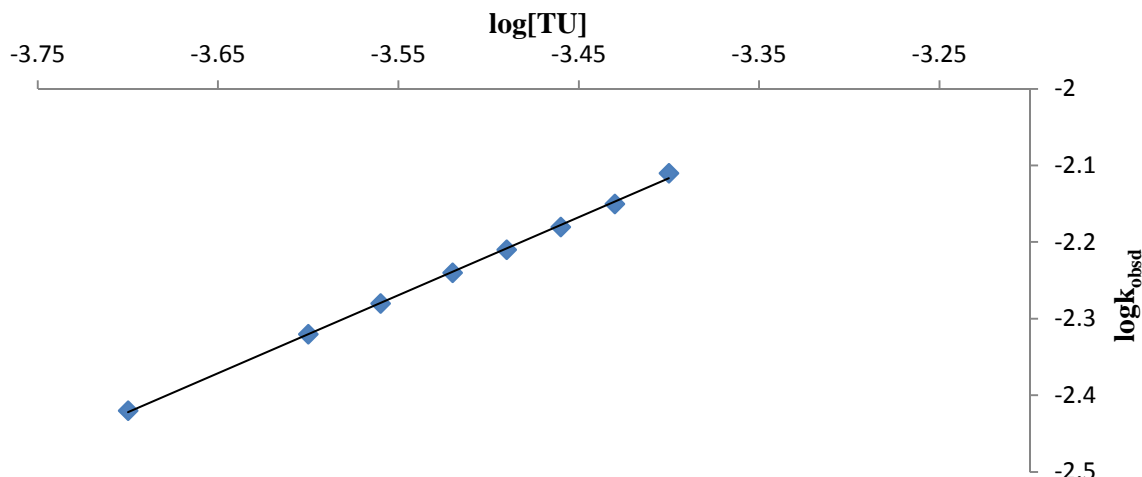
**Figure 1:** Typical Pseudo-first order plot for the redox reaction of  $[\text{Fe}(\text{phen})_3]^{3+}$  with thiourea at  $[\text{H}^+] = 0.50 \text{ mol dm}^{-3}$ ,  $I = 1.0 \text{ mol dm}^{-3}$  ( $\text{NaClO}_4$ ) and  $T = 26 \pm 1.0^\circ\text{C}$ .

**Table 1:** Pseudo first order and second order rate constants for the redox reaction of  $[\text{Fe}(\text{phen})_3]^{3+}$  and TU in aqueous perchloric acid media at  $[\text{Fe}(\text{phen})_3]^{3+} = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $T = 26.0 \pm 1.0 \text{ }^\circ\text{C}$  and  $\lambda_{\text{max}} = 510 \text{ nm}$ .

$10^4[\text{TU}], \text{ mol dm}^{-3}$	$[\text{H}^+], \text{ mol dm}^{-3}$	$I (\text{NaClO}_4), \text{ mol dm}^{-3}$	$10^3 k_{\text{obsd}}, \text{ s}^{-1}$	$k_2, \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
2.0	0.50	1.0	3.76	18.80
2.5	0.50	1.0	4.74	18.96
2.75	0.50	1.0	5.20	18.91
3.0	0.50	1.0	5.75	19.17
3.25	0.50	1.0	6.19	19.05
3.50	0.50	1.0	6.61	18.89
3.75	0.50	1.0	7.16	19.09
4.0	0.50	1.0	7.68	19.20
2.0	0.50	1.0	3.90	19.50
2.0	0.60	1.0	3.96	19.75
2.0	0.70	1.0	3.78	18.90
2.0	0.80	1.0	3.81	19.05
2.0	0.90	1.0	3.92	19.60
2.0	1.0	1.0	3.90	19.50
2.0	0.50	0.50	6.91	34.55
2.0	0.50	0.60	6.29	31.45
2.0	0.50	0.70	5.92	29.60
2.0	0.50	0.80	5.50	27.50
2.0	0.50	0.90	5.00	25.00
2.0	0.50	1.0	4.21	21.05



**Figure 2:** Plot of  $k_{\text{obsd}}$  versus  $[\text{TU}]$  for the reduction of  $[\text{Fe}(\text{phen})_3]^{3+}$  by TU.

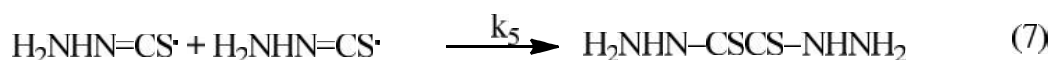
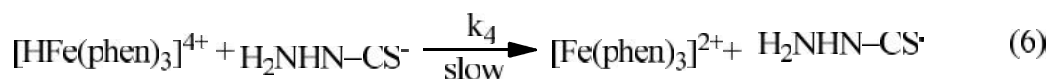
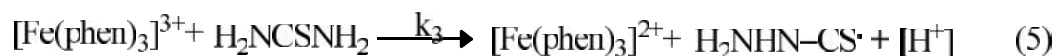
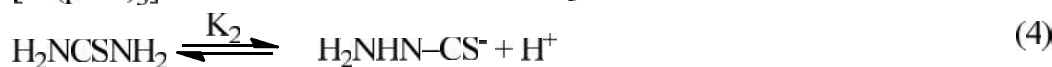


**Figure 3:** Plot of  $\log k_{\text{obsd}}$  versus  $\log[\text{TU}]$  for the reduction of  $[\text{Fe}(\text{phen})_3]^{3+}$  by TU.

### Proposed Mechanism

Based on the observations made, a five-step, outer-sphere transfer mechanism with intermediate radical formation and with equation 6 as rate determining is proposed for this system. The

formation of  $\text{H}[\text{Fe}(\text{phen})_3]^{4+}$  in acidic medium has been previously reported by several authors (Sutin and Gordon, 1961; Kimura and Wada, 1978; Ayoko *et al.*, 1993).



$$-\frac{d[\text{Fe}(\text{phen})_3]^{3+}}{dt} = k_4[\text{HFe}(\text{phen})_3]^{4+}[(\text{RNH})\text{HN}=\text{CS}^-] \quad (8)$$

$$K_1 = \frac{[\text{HFe}(\text{phen})_3]^{4+}}{[\text{Fe}(\text{phen})_3]^{3+}[\text{H}^+]} \quad (9)$$

$$[\text{HFe}(\text{phen})_3]^{4+} = K_1[\text{Fe}(\text{phen})_3]^{3+}[\text{H}^+] \quad (10)$$

$$K_2 = \frac{[(\text{RNH})\text{HN}=\text{CS}^-][\text{H}^+]}{[\text{RNHCSNH}_2]} \quad (11)$$

$$[(\text{RNH})\text{HN}=\text{CS}^-] = \frac{K_2[\text{RNHCSNH}_2]}{[\text{H}^+]} \quad (12)$$

$$-\frac{d[\text{Fe}(\text{phen})_3]^{3+}}{dt} = \frac{k_4 K_1 K_2 [\text{Fe}(\text{phen})_3]^{3+} [\text{RNHCSNH}_2] [\text{H}^+]}{[\text{H}^+]} \quad (13)$$

$$-\frac{d[\text{Fe}(\text{phen})_3]^{3+}}{dt} = k_4 K_1 K_2 [\text{Fe}(\text{phen})_3]^{3+} [\text{RNHCSNH}_2] \quad (14)$$

$$k_o = k_4 K_1 K_2 \quad (15)$$

$$-\frac{d[\text{Fe}(\text{phen})_3]^{3+}}{dt} = k_o [\text{Fe}(\text{phen})_3]^{3+} [\text{RNHCSNH}_2] \quad (16)$$



## CONCLUSION

The kinetics of  $[\text{Fe}(\text{phen})_3]^{3+}$  reduction by thiourea in aqueous perchloric acid solution at different reductant concentrations was studied. The reaction order, rate constant and rate law were determined. Taking into account the results of the kinetic studies and the observations made, a plausible reaction mechanism was proposed for the system. The initial reaction is first order with respect to each reactant. The complication that arise towards the end of the reaction was most likely due to the slow decomposition of both  $[\text{Fe}(\text{phen})_3]^{3+}$  and  $[\text{Fe}(\text{phen})_3]^{2+}$ .

## REFERENCES

- Adedinsowo, C. O., and Adegite, A. (1979). Linear free energy relations in redox reactions. Oxidation of iodide ion by poly(pyridine)iron(III) complexes and hexachloroiridate(IV) ion, *Inorganic Chemistry*, 18(12), 3597–3601.
- Adeloye, A. O., and Ajibade, P. A. (2010). Synthesis and characterization of a Ru(II) complex with functionalized phenanthroline ligands having single-double linked anthracenyl and 1-methoxy-1-buten-3-yne moieties, *Molecules*, 15, 7570–7581.
- Adhikamsetty, R. K., Gollapalli, N. R., and Jonnalagadda, S. B. (2008). Complexation kinetics of  $\text{Fe}^{2+}$  with 1,10-phenanthroline forming ferriox in acidic solutions, *International Journal of Chemical Kinetics*, 40, 515–523.
- Agwara, M. O., Ndifon, P. T., Ndosiri, N. B., Paboudam, A. G., Yufanyi, D. M., and Mohamadou, A. (2010). Synthesis, characterisation and antimicrobial activities of cobalt(II), copper(II) and zinc(II) mixed-ligand complexes containing 1,10-phenanthroline and 2,2'-bipyridine, *Bulletin of Chemical Society of Ethiopia*, 24(3), 383–389.
- Aljahdali, M. S., El-Sherif, A. A., Hilal, R. H., and Abdel-Karim, A. T. (2013). Mixed bivalent transition metal complexes of 1, 10-phenanthroline and 2-aminomethylthiophenyl-4-bromosalicylaldehyde Schiff base: Spectroscopic, molecular modeling and biological activities, *European Journal of Chemistry*, 4(4), 370–378.
- Al Mahdi, A. A. G. A., Hussein, M. A., Joubert, C. C., Swarts, J. C., and Dennis, C. R. (2014). A kinetic study of the oxidation of hydrazine by tris(1,10-phenanthroline)iron(III) in acidic medium, *Polyhedron*, 81, 409–413.
- Arifoglu, M., Marmer, W. N., and Dudley, R. L. (1992). Reaction of thiourea with  $\text{H}_2\text{O}_2$ :  $^{13}\text{C}$  NMR studies of an oxidative/reductive bleaching process, *Textile Research Journal*, 62(2), 94–100.
- Asghari, A., Ghaderi, O., Rajabi, M., Ameri, M., and Amoozadeh, A. (2015). Mechanistic and electrochemical investigation of catechol oxidation in the presence of thioacetamide: application for voltammetric determination of thioacetamide in aqueous media, *Progress in Reaction Kinetics and Mechanism*, 40(1), 95–103.
- Ayoko, G. A., Iyun, J. F., and Ekubo, A. T. (1993). Oxidation of L-methionine by poly(pyridyl)iron(III) complexes in aqueous solutions, *Journal of Chemical Society Pakistan*, 15(3), 178–182.
- Ayoko, G. A., Iyun, J. F., and El-Idris, I. F. (1992). Electron transfer at tetrahedral cobalt(II), Part III: kinetics of copper(II) ion catalysed reduction of periodate, *Transition Metal Chemistry*, 17, 423–425.
- Balakumar, P., Balakumar, S., and Subramaniam, P. (2012). Application of the Marcus theory to the electron transfer reaction between benzylthioacetic acid and tris(1, 10-phenanthroline)iron(III) perchlorate, *Reaction Kinetics, Mechanism and Catalysis*, 107, 253–261.
- Balakumar, P., Balakumar, S., and Subramaniam, P. (2015). Kinetic study on the oxidation of phenyl vinyl sulfide with iron(III)-polypyridyl complexes in the presence on non-ionic micelle, *International Journal of ChemTech Research*, 8(6), 603–606.
- Beller, G., Lente, G., and Fabian, I. (2010). Central role of phenanthroline mono-N-oxide in the decomposition reaction of tris(1,10-phenanthroline)iron(II) and -(III) complexes, *Inorganic Chemistry*, 49: 3698–3970.
- Berkheiser, V. E., and Mortland, M. M. (1977). Hectorite Complexes with Cu(II) and Fe(II)-1, 10-phenanthroline chelates, *Clays and Clay Minerals*, 25, 105–112.
- Bhattacharyya, J., and Mukhopadhyay, S. (2005). Mechanistic studies on the oxidation of

\*Corresponding author: Busari, A. ✉ [abdulakeemkekule@yahoo.com](mailto:abdulakeemkekule@yahoo.com) ✉ Department of Chemistry, Sule Lamido University, Kafin Hausa, Jigawa State, Nigeria. © 2019 Faculty of Technology Education, ATBU Bauchi. All rights reserved



- nitrite by a  $\mu$ -oxodiiron(III, III) complex in aqueous acidic media, *Helvetica Chimica Acta*, 88, 2661–2674.
- Bhattacharyya, J., Das, S., and Mukhopadhyay, S. (2007). Mechanistic studies on oxidation of L-ascorbic acid by an  $\mu$ -oxo-bridged diiron complex in aqueous acidic media, *Dalton Transaction*, 12, 1214–1220.
- Bowley, H. J., Crathorne, E. A., and Gerrard, D. L. (1986). Quantitative determination of thiourea in aqueous solution in the presence of sulphur dioxide by raman spectroscopy, *Analyst*, 111, 539–542.
- Buchanan, R. M., Cham, S., Richardson, J. F., Bressan, M., Forti, I., Morillo, A., and Fish, R. H. (1994). Biomimetic oxidation studies. 8. Structure of a new MMO active site model,  $[\text{Fe}_2\text{O}(\text{H}_2\text{O})_2(\text{tris}(1\text{-methylimidazo-2-yl)methyl)amine}_2)]^{4+}$  and role of the aqua ligand in alkane functionalization reaction, *Inorganic Chemistry*, 33(5), 3208–3209.
- Busari A. and Musa I. (2018). 1, 10-Phenanthroline: A Spectrophotometric Reagent for Iron Estimation, *Jigawa Journal of Multidisciplinary Studies*, 1(1): 98–105.
- Carlyle D. W. (1972). Electron transfer between sulphur(IV) and tris(1, 10-phenanthroline iron(III) ion in aqueous solution, *Journal of American Chemical Society*, 94(13), 4525–4529.
- Chowdhury, P., and Ali, Md. A. (2005). Role of 1,10-phenanthroline and ortho phosphoric acid on graft polymerization of vinyl monomers from poly (vinyl alcohol) in the presence of fenton's reagent, *Journal of Applied Polymer Science*, 97(6), 2335–2339.
- Cyfert, M., Latko, B., and Wawrzenczyk, M. (1996). Oxidation of tris(1, 10-phenanthroline)iron(II) ion by iodate and periodate ions in neutral medium, *International Journal of Chemical Kinetics*, 28(2), 103–108.
- Ford-Smith, H., and Sutin, N. (1961). The kinetics of the reactions of substituted 1, 10-phenanthroline, 2,2'-dipyridine and 2,2',2''-tripyridine complexes of iron(III) with iron(II) ions, *Journal of American Chemical Society*, 83(8), 1830–1834.
- Gao, Q., Wang, G., Sun, Y., and Epstein, I.R. (2008). Simultaneous tracking of sulphur species in the oxidation of thiourea by hydrogen peroxide, *Journal of Physical Chemistry A*, 112, 5771–5773.
- Guo, Z., and Sadler, P. J. (1999). Metals in Medicine, *Angewandte Chemie International Edition*, 38, 1512–1531.
- Idris, S. O., Bako, B., Iyun, J. F. and Myek, B. (2014). Kinetics and mechanism of the oxidation of bromopyrogallol red by bromate ion in aqueous hydrochloric acid medium, *International Journal of Modern Chemistry*, 6(2): 87-95
- Jonnalagadda, S. B., Chinake, C. R., Olojo, R., and Simoyi, R. H. (2002). Kinetics and mechanism of the oxidation of 4-methyl-3-thiosemicarbazide by acidic bromate, *International Journal of Chemical Kinetics*, 34(4), 237–247.
- Khan, S. A., Kumar, P., Saleem, K., and Khan, Z. (2007). A kinetic study of water-soluble colloidal  $\text{MnO}_2$  formed by the reduction of permanganate by thiourea, *Colloids and surfaces A: Physicochemical and Engineering Aspects*, 302, 102–106.
- Kimura, M., and Wada, G. (1978). Kinetics of the oxidation reactions of iodide and iron(II) ions by tris(1, 10-phenanthroline)iron(III) ion in aqueous mixtures of methanol and ethanol, *Inorganic Chemistry*, 17, 2239.
- Lilani, M.D. Sharma, G.K. and Shanker, R. (1986). Kinetics and mechanism of oxidation of thiourea and N-substituted thioureas by hexacyanoferrate(III) under acidic conditions, *Indian Journal of Chemistry*, 25(4), 370–372.
- Martincigh, B. S., Mhike, M., Morakinyo, K., Adigun, R. A., and Simoyi, R. H. (2013). Oxyhalogen sulfur chemistry: Oxidation of a thiourea dimer, formamidine disulfide, by chlorine dioxide, *Australian Journal of Chemistry*, 66, 362–369.
- McAuley, A., and Gomwalk, U. D. (1969). Metal-ion oxidations in solution. Part VI: Oxidation of thiourea and its N-substituted derivatives by cobalt(III), *Journal of Chemical Society (A)*, 977–980.
- Mentasti, E., and Pelizzetti, E. (1977). Kinetics and mechanism of oxidation of quinols by tris(1, 10-phenanthroline)iron(III) complexes in aqueous acidic perchlorate media, *International Journal of Chemical Kinetics*, 9, 215–222.

\*Corresponding author: Busari, A. ✉ [abdulakeemkekule@yahoo.com](mailto:abdulakeemkekule@yahoo.com) ✉ Department of Chemistry, Sule Lamido University, Kafin Hausa, Jigawa State, Nigeria. © 2019 Faculty of Technology Education, ATBU Bauchi. All rights reserved





- Ng, F. T. T., and Henry, P. M. (1977). Kinetics and mechanism of the oxidation of several ketones by tris(1, 10-phenanthroline)Fe(III) in aqueous acid medium, *Canadian Journal of Chemistry*, 55, 2900–2908.
- Nord, G., and Wernberg, O. (1975). Reduction of tris(2,2'-bipyridyl) and tris(1, 10-phenanthroline) complexes of iron(III) and osmium(III) by hydroxide ion, *Journal of Chemical Society Dalton Transaction*, 10, 845–849.
- Novak, J., and Arend, H. (1964). The photosensitivity of the complex of iron<sup>III</sup> with 1, 10-phenanthroline, *Talanta*, 11(5), 898, 899.
- Olatunji, M. A. and Okechukwu, R. C. (1987). Oxidation of thiourea and thioacetamide by octacyanomolybdate(V) anion in perchloric acid, *Transition Metal Chemistry*, 12, 205–209.
- Osunlaja, A. A., Idris, S. O. and Iyun, J. F. (2012). Kinetics and mechanism of methylene blue-permanganate ion reaction in acidic medium. *Archives of Applied Science Research*. 4(2): 772– 780.
- Pelizzetti, E., and Mentasti, E. (1977a). Kinetics and mechanism of oxidation of catechols by tris(1, 10-phenanthroline)iron(III) and its derivatives in aqueous acidic perchlorate media, *Zeitschrift fur Physikalische Chemie Neue Folge*, Bd. 105, S. 21–34.
- Pelizzetti, E., and Mentasti, E. (1977b). Kinetics and mechanism of oxidation of 1, 1'-biphenyl-4, 4'-diol by tris(1,10-phenanthroline)iron(III) and its derivatives in aqueous acidic perchlorate media, *Journal of Inorganic and Nuclear Chemistry*, 39, 2227–2230.
- Plowman, J. E., Loehr, T. M., Schauer, C. K., and Anderson, O. P. (1984). *Inorganic Chemistry*, 23, 3553–3559.
- Po, H. N., Eran, H., Kim, Y., and Byrd, J. E. (1979). Oxidation of thiourea and N, N'-dialkylthioureas by hexachloroiridate(V) ion, *Inorganic Chemistry*, 18(1), 197–201.
- Pradyot, P. (2003). *Handbook of Inorganic Chemicals*, New York, McGraw-Hill, pp 410, 411.
- Rabai, G. Wang, R. T., and Kustin, K. (1993). Kinetics and mechanism of the oxidation of thiourea by chlorine dioxide, *International Journal of Chemical Kinetics*, 25, 53–62.
- Sahoo, P. R., Sahu, S., Patel, S., and Mishra, B. K. (2010). Oxidation kinetics of arylthioureas by cetyltrimethylammonium dichromate, *Indian Journal of Chemistry*, 49A, 1483–1487.
- Sammes, P. G., and Yahioglu, G. (1994). 1, 10-Phenanthroline: A versatile ligand, *Chemical Society Reviews*, 327–334.
- Saradamba, G.V. Ramakrishna, K., and Raju, K.N. (1988). Kinetics of oxidation of thiourea by iron(III) in the presence of 2, 2'-bipyridyl, *Revue Roumaine de Chimie*, 33(5), 547–554.
- Schilt, A. A. (1969). *Analytical applications of 1, 10-phenanthroline and related compounds*, Oxford, Pergamon, pp 10–26, 54–55, 102.
- Schilt A. A., and Taylor, R. C. (1959). Infra-red spectra of 1, 10-phenanthroline metal complexes in the rock salt region below 2000 cm<sup>-1</sup>, *Journal of Inorganic and Nuclear Chemistry*, 9, 211–221.
- Sen Gupta, K. K., Pal, B. and Sen, P. K. (1999). Kinetics and mechanism of the oxidation of some  $\alpha$ -hydroxy acids by tetrachloroaurate(III) in acetic acid-sodium acetate buffer medium, *International Journal of Chemical Kinetics*, 31: 873–882.
- Sharma, V. K., Luther, G. W., and Millero, F. J. (2011). Mechanisms of oxidation of organosulfur compounds by ferrate(VI), *Chemosphere*, 82, 1083–1089.
- Shubha, J. P., and Puttaswamy, A. S. (2009). Oxidative conversion of thiourea and N-substituted thioureas into formamidine disulphides with acidified chloramines-T: A kinetic and mechanistic approach, *Journal of Sulphur Chemistry*, 30(5), 490–499.
- Simoyi, R. H., Masere, J. Muzimbaranda, C., Manyonda, M., and Dube, S. (1991). Travelling wave in the chlorite-thiourea reaction, *International Journal of Chemical Kinetics*, 23(5), 419–429.
- Skoog, D. A., West, D. M., Holler, F. J., and Crouch, S. R. (2014). *Fundamentals of Analytical Chemistry*, (9<sup>th</sup> Ed.). Brooks/Cole, Cengage Learning, p 504.
- Sutin, N., and Gordon, B. M. (1961). The kinetics of the oxidation of the iron(II) ion by the tris-(1, 10-phenanthroline)-iron(III) ion, *Journal American Chemical Society*, 83(1), 70–73.
- Tanvir, T. A., Hossain, Md. E., Al Mamun, M., and Ehsan, M. Q. (2013). Preparation and

\*Corresponding author: Busari, A. ✉ [abdulakeemkekule@yahoo.com](mailto:abdulakeemkekule@yahoo.com) ✉ Department of Chemistry, Sule Lamido University, Kafin Hausa, Jigawa State, Nigeria. © 2019 Faculty of Technology Education, ATBU Bauchi. All rights reserved



- characterization of iron(III) complex of saccharin, *Journal of Bangladesh Academy of Sciences*, 37(2), 195–203.
- Vani, P., Kishore, K. K., Rambabu, R., and Dikshitulu, L. S. A. (2001). Mechanism of oxidation of L-methionine by iron(III)–1,10–phenanthroline complex—A kinetic study, *Proceeding of Indian Academy of Science (Chemical Science)*, 113(4), 351–359.
- Wang, S., Vincent, J. H., Janice, R. A., and Ming, J. W. (2012). Identification of the molecular mechanisms underlying the cytotoxic action of a potent platinum metallointercalator. *Journal of Chemical Biology*, 5.2, 51-61.
- Yao-Chu, C., Hong-Ping L., Shih S. S. and Jing-Jer J. (1992). Kinetic study of the ferriin oxidation of malonic acid and its derivatives. Implication in the Belousov-Zhabotinsky reaction, *Journal of Physical Chemistry*, 97, 8450–8451.