KINETICS AND MECHANISM OF THE REDUCTION OF POTASSIUM TRISOXALATOFERRATE (III) BY THIOUREA IN AQUEOUS HYDROCHLORIC ACID MEDIUM

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Abstract: The kinetics of the reduction of potassium trisoxalatoferrate (III) by thiourea has been studied in aqueous acidic medium. The stoichiometric studies showed that 1 mole of the complex was reduced for every mole of thiourea oxidized. Under pseudo-first order conditions of $[TU] \gg [Fe(C_2O_4)_3^{3-}]$ the reaction was found to have first order dependence on each of the reactants, giving second order overall.

The experimental data are consistent with the rate law:

$$\frac{-d[TU]}{dt} = (a + b[H^+])[TU][Fe(C_2O_4)_3^{3-}]$$

with $a = 0.9 \times 10^{-2}$ dm^3 mol^{-1} s^{-1} b $= 2.1 \times 10^{-3}$ dm^6 mol^{-2} s^{-1} at 420 nm and 20 ± 1.0 °C

The reaction rate was found to be directly dependent on acid concentration and increased with increase in ionic strength of reaction system. It was also evident that increase in dielectric constant of the reaction medium (D) enhanced the reaction rate and addition of CH_3COO^-, $HCOO^-$, Mg^{2+} and K^+ catalyzed the rate of the reaction. The reduction of potassium trisoxalatoferrate (III) by thiourea is rationalized in terms of absence of ion pair complex formation with outer-sphere reaction pathway characteristics.

Keywords: Kinetics, thiourea, potassium trisoxalatoferrate (III), ionic strength, added ions, outer-sphere mechanism

Introduction

Oxidation of sulphur containing compounds (organosulphur) like thiourea, hereafter designated as TU is usually important because of its wide range of applications in both chemical and biological fields (Busari *et al*., 2019; Anweting *et al*., 2017). Most notable among these applications of thiourea is its use as a corrosion inhibitor, plant growth stimulator to break bud dormancy, therapeutic agent in the treatment of thyroid dysfunction and a chaotropic agent. Thiourea been used as a vulcanization accelerator and in drug production such as uracil (Anweting *et al*., 2017). Thiourea reactions are very important in the study of non-linear chemical kinetics. Despite the aforementioned applications of thiourea, which is made possible by its redox properties, the kinetic data for its redox reactions are few.

Potassium trisoxalatoferrate (III), $K_3[Fe(C_2O_4)_3]$ has played vital roles in many aspects of co-ordination chemistry, because of its spectroscopic and kinetic behaviors in solution and in some cases its resolution into enantiomers (Ogori and Lohdip, 2017). For example, the complex has been used in the field of photography, analytical chemistry, medicine and actinometry. The electron-transfer reaction of the complex with $S_2O_3^{2-}$, MnO_4^- and SO_4^{2-}, have been reported (Ogori and Lohdip, 2017; Ogori *et al*, 2016; 2021). In this paper, we report the kinetics and mechanism of the reduction potassium trisoxalatoferrate (III) trihydrate by thiourea in aqueous hydrochloric acid medium as our contribution of providing additional information on the redox pattern of both the oxidant and reductant.

Materials and Methods

Materials and Reagents

All reagents were of analytical grade and were used without further purification unless otherwise stated. Solutions of all the reagents used were dissolved in distilled water. All kinetic runs and other runs were carried out on Jenway 6300 UV-visible spectrophotometer.

Synthesis and Characerization of Potassium Trisoxalatoferrate (III) Trihydrate

The complex, $K_3[Fe(C_2O_4)_3].3H_2O$ was synthesized and characterized according as described by Ogori and Lohdip, (2017) involving the direct reaction of oxalic acid dihydrate, potassium hydroxide and iron (III) chloride hexahydrate.

Stoichiometric Studies

The stoichiometry of the reaction was determined by spectrophotometric titration at a predetermined $\lambda_{max} = 420$ nm using the mole ratio method. The concentration of $Fe(C_2O_4)_3^{3-}$ was kept constant at 5.0×10^{-3} mol dm^{-3} while that of thiourea was varied between $(0.05 - 0.175)$ mol dm^{-3} at $[H^+] = 0.3$ mol dm^{-3} and constant ionic strength of 0.525 mol dm^{-3} (NaCl) at 20.0 ± 1°C. the reactions were allowed to stand until the repeated absorbances of the reaction mixture at $\lambda_{max} = 420$ nm were constant. The stoichiometry was then determined from the plot of absorbance versus mole ratio of $Fe(C_2O_4)_3^{3-}$: TU.

Product Analysis

At the completion of the reaction, the reaction mixture was analyzed for the type of organic and inorganic products formed. Addition of 20 cm^3 of ethanol and 5 cm^3 of

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concentrated HCl were added to the reaction mixture which resulted in the formation of white crystals of formamidine disulphide.

Kinetic Studies
The rate of the reaction was studied under pseudo-first order conditions with [TU] in at least 10-fold excess over $[Fe(C_2O_4)_3^{3-}]$ at the stated conditions by monitoring the change in the absorbance of the complex at 420 nm using Jenway 6300 spectrophotometer.

Acid Dependence
The effect of change in the hydrogen ion concentration on the reaction rate was investigated by keeping the concentration of the other reactants constant while varying the hydrogen ion concentration in the range of $(0.05 – 0.3)$ mol dm^{-3}.

Effect of Ionic Strength
The effect of ionic strength on the rate of the reaction was studied over the range of $(0.15 – 0.9)$ mol dm^{-3} using NaCl, while other reaction conditions were kept constant.

Effect of Dielectric Constant
The effect of medium dielectric constant, D, on the reaction rate investigated by carrying out the reaction in medium of varying dielectric constants. The medium dielectric constants were varied by using a binary solvent mixture of water and acetone while keeping all other reaction conditions constant.

Effect of Added Ions
The influence of added CH_3COO^-, NO_3^-, K^+, and Mg^{2+} on the rate of the reaction were investigated by varying the concentration of these ions while keeping the concentration of other reactants and conditions constant.

Test for the Participation of Free Radicals in the Course of the Reaction
The test for free radicals was done by adding about 2 g of acrylamide to partially reacted mixture containing various concentrations of the other reactants. Excess methanol was also added to the reaction mixture.

Test for the Formation of Intermediate Complex
The test for the presence of stable and detectable intermediate complex formed in the course of the reaction was done by the Michaelis-Menten plot of $1/k_{obs}$ versus $1/[reductant]$. Identification or otherwise of intercepts from this plot would give an idea of the presence or otherwise of intermediate complex formation.

Results and Discussion
Stoichiometry and Product Analysis
The results of the stoichiometric studies for the oxidation of thiourea by $Fe(C_2O_4)_3^{3-}$ revealed that one mole of the reductant was consumed by one mole of the oxidant. The stoichiometric equation can be represented as equation 1.

$2Fe^{3+} + 2(NH_2)_2C=S \rightarrow 2Fe^{2+} + (H_2N)HN=C-S-S-C=NH(NH_2) + 2H^+$ …………..(1)
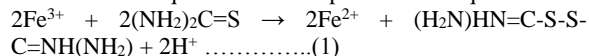
A similar stoichiometry has been reported for the oxidation of thiourea (Anweting *et al*., 2017 and Busari *et al*., 2019) while the formation of urea and formamidine was reported by Anweting *et al*., (2017) and Busari *et al*., (2019) repectively.

Kinetic Study
Pseudo-first order plot of log $(A_0 - A_t)$ versus time was linear to greater than 90 % extent of reaction, indicating first order

with respect to $[Fe(C_2O_4)_3^{3-}]$. The plot of log k_{obs} versus log[TU] was linear with slope approximately equal to one, suggesting that the reaction is first order with respect to [TU] and second order overall as shown in Fig. 1. Second order rate constant k_2, obtained from $k_{obs}/[TU]$ were fairly constant. further suggesting that the reaction is indeed first order with respect to [TU] as seen in Table 1. Similar second order kinetics have been reported elsewhere (Anweting *et al*., 2017 and Busari *et al*., 2019). The rate law of the equation can be fitted into equation 2.

$$-\frac{d[TU]}{dt} = k_2 [TU][Fe(C_2O_4)_3^{3-}]$$
……………………………………………………(2)

Where $k_2 = 1.67 \pm 0.04 \times 10^{-3}$ dm^3 mol^{-1} s^{-1}

Effect of Change in Hydrogen Ion Concentration
Within the $[H^+]$ range of $(0.05 – 0.3)$ mol dm^{-3}, the rate constants increased with increase in $[H^+]$ as indicated in Table 1. This is an indication that the reaction is dependent on $[H^+]$. Plot of $[H^+]$ versus k_2 was linear with a positive slope and intercept as shown in Fig. 2. Non-dependence of $[H^+]$ has been reported elsewhere (Anweting *et al*, 2017 and Busari *et al*., 2019). The acid dependent second order rate constant is presented in equation 3

$$-\frac{d[TU]}{dt} = (a + b[H^+]) [TU][Fe(C_2O_4)_3^{3-}]$$
……………………………………………………(2)

where $a = 0.9 \times 10^{-2}$ dm^3 mol^{-1} s^{-1} and $b = 2.1 \times 10^{-3}$ dm^6 mol^{-2} s^{-1}.

Effect of Ionic Strength on Reaction Rate
Varying the ionic strength of the reaction within the range of $(0.15 – 0.9)$ mol dm^{-3} using NaCl, while other reaction conditions were kept constant, had a positive effect on the rate constant as rate increased with increase in the ionic strength concentration as seen in Table 1. This is pointing to the possibility of an outer-sphere reaction mechanism (Ogori and Lohddip, 2017). This is an indication that both species at the activation complex are of like charge and the product of the charge was found to be 0.76 from the plot of log k_2 versus $\sqrt{I}$ (Fig. 3) (Ukoha *et al*., 2023). Non-dependence of ionic strength on reaction rate has been reported for the oxidation of thiourea by Fe_2O^{4+} (Anweting *et al*., 2017) while increase in ionic strength of the reaction medium resulted in a decrease in reaction rate for the oxidation of thiourea by $[Fe(phen)_3^{3+}]$ (Busari *et al*., 2019).

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Table1: Pseudo-first and second order rate constants for the reduction of $[Fe(C_2O_4)_3^{3-}]$ by thiourea in aqueous hydrochloric acid at medium $[Fe(C_2O_4)_3^{3-}] = 5.0 \times 10^{-3}$ mol dm^{-3}, I = 0.525 mol dm^{-3}(NaCl), [H] = 0.30 mol dm^{-3}, λ_{max} = 420 nm and T = 20 ± 0.1 ºC.

10^2 [TU] mol dm^{-3}	10^1 [H$^+$] mol dm^{-3}	10^1, I mol dm (NaCl)	10^3 k$_{obs}$ s^{-1}	10^2 k$_2$ dm^3 mol^{-1} s^{-1}
5.00	3.0	5.25	0.85	1.70
7.50	3.0	5.25	1.24	1.65
10.00	3.0	5.25	1.60	1.60
12.50	3.0	5.25	2.08	1.70
15.00	3.0	5.25	2.48	1.65
17.50	3.0	5.25	2.98	1.70
7.50	5.0	5.25	0.50	1.00
7.50	10.0	5.25	1.05	1.05
7.50	15.0	5.25	1.90	1.27
7.50	20.0	5.25	2.70	1.35
7.50	25.0	5.25	3.55	1.42
7.50	30.0	5.25	4.50	1.50
7.50	3.0	1.50	0.58	0.39
7.50	3.0	3.00	1.40	0.47
7.50	3.0	4.50	2.80	0.62
7.50	3.0	6.00	4.20	0.70
7.50	3.0	7.50	6.70	0.90
7.50	3.0	9.00	8.85	1.00
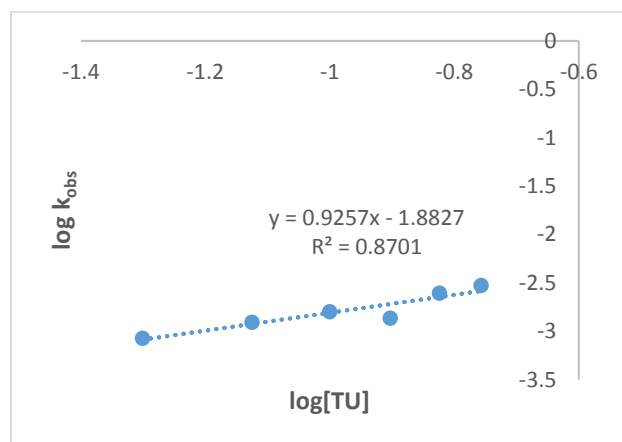
Fig. 1: Plot of log k$_{obs}$ against log [TU] for the reduction of thiourea at $[Fe(C_2O_4)_3^{3-}] = 5.0 \times 10^{-3}$ mol dm^{-3}, I = 0.525 mol dm^{-3} (NaCl), [H$^+$] = 0.3 mol dm^{-3}, λ_{max} = 420 nm and T = 20 ± 0.1 ºC.
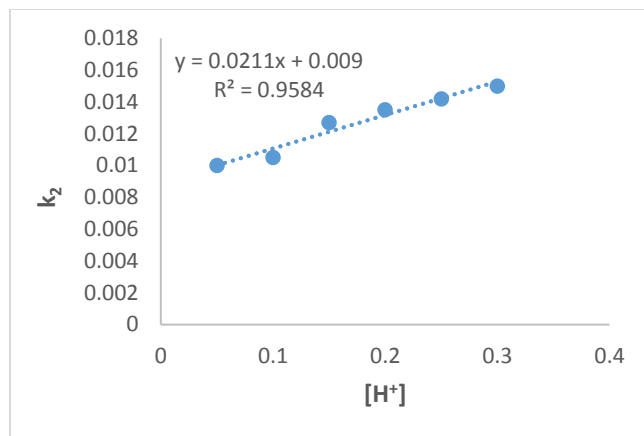
Fig. 2: Plot of k$_2$ against [H$^+$] for the reduction of $[Fe(C_2O_4)_3^{3-}]$ by thiourea at $[Fe(C_2O_4)_3^{3-}] = 5.0 \times 10^{-3}$ mol dm^{-3}, I = 0.525 mol dm^{-3} (NaCl), λ_{max} = 420 nm and T = 20 ± 0.1 ºC.
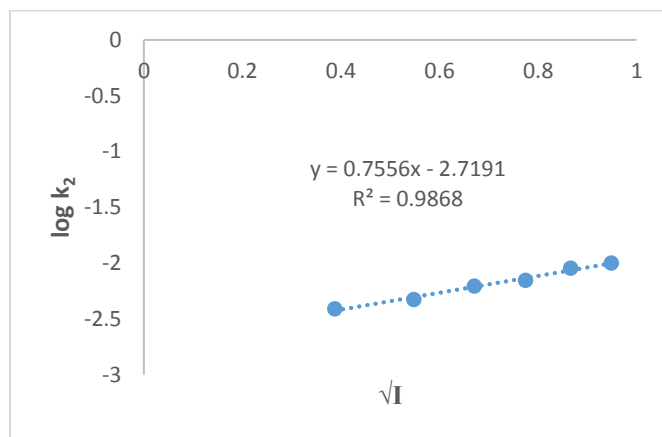
Fig. 3: Plot of log k$_2$ against $\sqrt{I}$ for the reduction of $[Fe(C_2O_4)_3^{3-}]$ by thiourea at $[Fe(C_2O_4)_3^{3-}] = 5.0 \times 10^{-3}$ mol dm^{-3}, [H$^+$] = 0.3 mol dm^{-3}, λ_{max} = 420 nm and T = 20 ± 0.1 ºC.

Effect of Medium Dielectric Constant on Reaction Rate
Reaction rate was enhanced as a function of 1/D as indicated on Table 2. This suggests the participation of redox partners of the same charge.

Table 2: Effect of dielectric constant on the reduction of $[Fe(C_2O_4)_3^{3-}]$ by thiourea in aqueous hydrochloric acid at $[Fe(C_2O_4)_3^{3-}] = 5.0 \times 10^{-3}$ mol dm^{-3}, [TU] = 0.05 mol dm^{-3}, I = 0.525 mol dm^{-3}(NaCl), [H] = 0.3 mol dm^{-3}, λ_{max} = 420 nm and T = 20 ± 0.1 ºC

D	$10^2$1/D	10^3k$_{obs}$, s^{-1}	10^3k$_2$, dm^3 mol^{-1} s^{-1}
69	1.45	1.22	1.02
60	1.67	1.84	1.52
49	2.05	2.54	1.77
38	2.63	3.12	2.45
29	3.45	3.93	2.96
21	4.76	4.66	3.65

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Effect of Added Ions

Addition of CH_3COO^-, NO_3^-, K^+, and Mg^{2+} influenced the rate of the reaction by increasing the rate constants as observed in Table 3. This observed increase in reaction rate as the concentration of the added ions increased suggests that the reaction proceeded via the outer-sphere pathway and that the reactant species are linked together in the activation complex (Busari *et al*., 2019; Myek *et al*., 2014, Osunkwo *et al*., 2018).

Table 3: Effect of added ions on the reduction of $[Fe(C_2O_4)_3^{3-}]$ by thiourea in aqueous hydrochloric acid medium at $[Fe(C_2O_4)_3^{3-}] = 5.0 \times 10^{-3}$ mol dm^{-3}, $[TU] = 0.05$ mol dm^{-3}, $I = 0.525$ mol dm^{-3}(NaCl), $[H] = 0.3$ mol dm^{-3}, $\lambda_{max} = 420$ nm and $T = 20 \pm 0.1$ ºC.

X	$10^1[X]$, mol dm^{-3}	$10^3 k_{obs}$, s^{-1}	$10^2 k_2$, dm^{-3} mol^{-1} s^{-1}
CH₃COO⁻	1.00	0.95	0.95
	1.50	1.93	1.29
	2.00	3.85	1.93
	2.50	6.30	2.52
	3.00	9.10	3.03
NO₃⁻	1.00	0.95	0.95
	1.50	1.90	1.26
	2.00	2.90	1.45
	2.50	4.85	1.94
	3.00	6.55	2.19
Mg²⁺	1.00	0.85	0.85
	1.50	1.50	1.00
	2.00	2.70	1.40
	2.50	4.40	1.80
	3.00	6.10	2.00
K⁺	1.00	0.90	0.90
	1.50	1.75	1.20
	2.00	2.65	1.30
	2.50	5.52	2.10
	3.00	7.90	2.60

*Test for Free Radicals*

Test for free radicals using acrylamide in excess methanol for the reaction gave no gel formation. This confirms the non-participation of free radicals in the reaction, suggesting that the reaction went through the inner-sphere pathway (Nkole *et al*., 2018).

Test for Intermediate Complex Formation

In ascertaining the presence or absence of the formation of intermediate complex in the course of the reaction between thiourea and $[Fe(C_2O_4)_3^{3-}]$, Michaelis-Meten plot of $1/k_{obs}$ versus $1/[TU]$ (Fig.4) was made. The linearity of the plot with negligible intercept, indicated that the intermediates participating in the reaction have no appreciate equilibrium
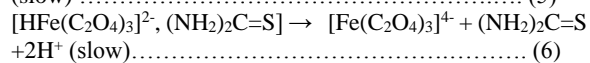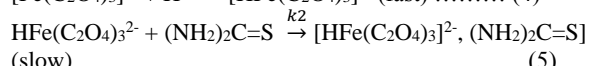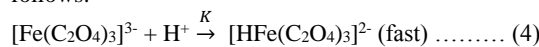
constant and thereby ruling out the formation of intermediate complex formation in the course of the reaction. This is suggestive of an outer-sphere reaction mechanism (Anweting *et al*., 2017).
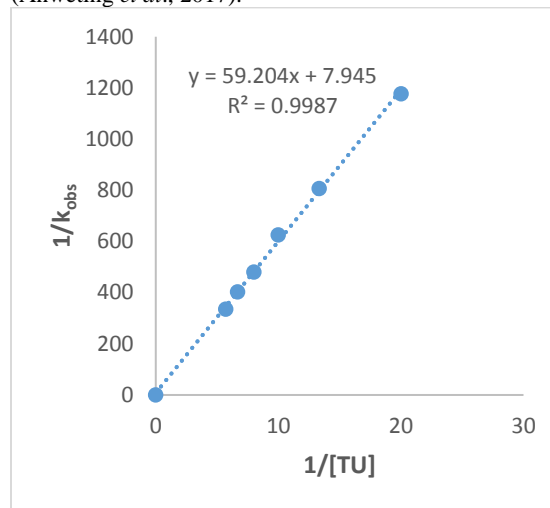
Fig. 4: Plot of $1/k_{obs}$ against $1/[TU]$ for the reduction of $[Fe(C_2O_4)_3^{3-}]$ by thiourea at $[Fe(C_2O_4)_3^{3-}] = 5.0 \times 10^{-3}$ mol dm^{-3}, $I = 0.525$ mol dm^{-3} (NaCl), $[H^+] = 0.3$ mol dm^{-3}, $\lambda_{max} = 420$ nm and $T = 20 \pm 0.1$ ºC.

Mechanism of the Reaction

Within the limit of experimental conditions employed in this research, the mechanism of the reaction is proposed as follows:

$[Fe(C_2O_4)_3]^{3-} + H^+ \overset{K}{\rightarrow} [HFe(C_2O_4)_3]^{2-}$ (fast) ……… (4)

$HFe(C_2O_4)_3^{2-} + (NH_2)_2C=S \overset{k2}{\rightarrow} [HFe(C_2O_4)_3]^{2-}, (NH_2)_2C=S]$ (slow) ……………………………………… (5)

$[HFe(C_2O_4)_3]^{2-}, (NH_2)_2C=S] \rightarrow [Fe(C_2O_4)_3]^{4-} + (NH_2)_2C=S +2H^+$ (slow)……………………………….……… (6)

From equations (4) and (5),

Rate $= k_2 [HFe(C_2O_4)_3^{2-}][(NH_2)_2C=S] + k_3[Fe(C_2O_4)_3^{3-}][(NH_2)_2C=S]$ …………………………...………… (7)

From equation (5):

$[HFe(C_2O_4)_3^{2-}] = k_1[Fe(C_2O_4)_3^{3-}][H^+]$ ……………… (8)

Substituting equation (8) into (7),

Rate $= k_2k_1[Fe(C_2O_4)_3^{3-}][H^+][(NH_2)_2C=S] + k_3[Fe(C_2O_4)_3^{3-}][(NH_2)_2C=S]$ ……………………………………… (9)

Rate $= (k_2 + k_1 [H^+])[Fe(C_2O_4)_3^{3-}][(NH_2)_2C=S]$………………………………………….. (10)

Equation (10) is in agreement with equation (3) where

$k_3 = a = 0.68$ dm^3 mol^{-1} s^{-1} and $k_2k_2 = b = 1.30$ dm^6 mol^{-1} s^{-1}.

Conclusion

A major point of interest as to whether or not the reaction proceeded via outer sphere, inner sphere mechanism or a combination of both was proposed as follows:

(a) Positive cations and anions catalysis is suggestive that the reaction likely proceeded via an outer sphere electron transfer mechanism (Umoru, 2019). Ion catalysis and inhibition has been reported to be a characteristics of an outer sphere reaction mechanism (Osunkwo, *et al*., 2018).

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(b) Absence of free radicals on addition of acrylamide to partially reacted mixture in the presence of excess methanol is pointing to an outer-sphere electron transfer mechanism (Ogori and Lohdip, 2017).

(c) Insignificant positive intercept for Michaelis-Menten plots of $1/k_{obs}$ versus $1/[TU]$ from (Fig. 4) is in support of an outer sphere reaction pathway (Ogori and Lohdip, 2017).

(d) Positive ionic strength dependence and positive slope obtained from plots of log k_2 versus $\sqrt{I}$ (Table 1) correspond reasonably with an outer sphere mechanism (Ukoha *et al*, 2018, 2023).

The evidence (a –d) is in support of the outer sphere mechanism and is hereby proposed for the redox reaction of $[Fe(C_2O_4)_3{}^{3-}]$ /TU system.

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