

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

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ABSTRACT

The kinetics of the redox reaction between tannic acid (TA) and potassium trisoxalatoferate (III) trihydrate, $(K_3[Fe(C_2O_4)_3] \cdot 3H_2O)$ has been studied in aqueous hydrochloric acid medium. The stoichiometry of the reaction determined by the mole ratio method was observed to be 1:1. The kinetic results showed first order dependence with respect to complex and tannic acid concentrations. The experimental data for the reaction system are consistent with the following rate law:

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

where $a = 2.0 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ and $b = 2.1 \times 10^{-3} \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$ at 420 nm and $27.0 \pm 1.0^\circ \text{C}$.

The rate of reaction was found to increase with increase in $[H^+]$ in the acid range used, but decreased with increase in ionic strength of the reaction medium. While the rate of reaction was observed to decrease with increasing dielectric constant of the reaction medium, the addition of CH_3COO^- , $HCOO^-$, Ni^{2+} and K^+ catalyzed the rate of the reaction. The Michaelis-Menten plot of $1/k_{obs}$ versus $1/[\text{oxidant}]$ gave a straight line with an insignificant positive intercept. The addition of acrylamide to the partially oxidized reaction mixture did gave a gel in the presence of excess methanol. Based on the experimental data, a plausible mechanism involving outer sphere electron transfer has been proposed for the redox reaction between tannic acid and potassium trisoxalatoferate (III) trihydrate.

Keywords: Kinetics, tannic acid, potassium trisoxalatoferate (III) trihydrate, outer-sphere mechanism

INTRODUCTION

Tannic acid is a major pollutant present in the wastewater generated from vegetable tannery processes and food processing [1]. Tannic acid is considered as one of the polyphenolic pollutants which may cause several threats to the environment. For example, it can react with chlorine disinfectants during drinking water treatment and these chlorinated intermediates can cause serious problems to human health and aquatic life [2]. Since tannic acid is recalcitrant in the environment, it must therefore be removed from water and wastewater so as to protect the environment [3].

Biological, electrocoagulation and autoxidation methods have been used in removing TA from waste waters [2 and 4]. Reports on the oxidation of tannic acid with metal ions and metal complexes are scanty and hence the effort to study its reaction with $Fe(C_2O_4)_3^{3-}$.

Potassium trisoxalatoferate (III) trihydrate, $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ has been reported to play important roles in many aspects of co-ordination chemistry. For instance, it exhibits spectroscopic and kinetic behaviors in solution and its resolution into enantiomers [5]. The complex has also found application in photography, analytical chemistry, medicine and actinometry.

The oxidation-reduction reaction of the complex with $\text{S}_2\text{O}_3^{2-}$, MnO_4^- and SO_4^{2-} , have been reported [5 - 7]. We present, in this paper, the kinetics and mechanism of the oxidation of tannic acid by potassium trisoxalatoferrate (III) trihydrate in aqueous hydrochloric acid medium with the hope that it will give more insight into the redox behavior of this redox system.

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. Reagent grade HCl and NaCl were used to adjust the acidity and ionic strength of the reaction media respectively. All kinetic runs and other runs were carried out on Jenway 6300 UV-visible spectrophotometer.

Synthesis and characterization of potassium trisoxalatoferrate (III) trihydrate

Potassium trisoxalatoferrate (III) trihydrate was synthesized and characterized according to the method of ZivaTronics Laboratory, [8], involving the direct reaction of oxalic acid dihydrate, potassium hydroxide and iron (III) chloride hexahydrate.

Stoichiometric Studies

The stoichiometry for the reaction was determined by spectrophotometric titration using the mole ratio method at $[\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}] = 4.45 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{tannic acid}] = (0.445 - 4.45) \times 10^{-1} \text{ mol dm}^{-3}$, $[\text{H}^+] = 0.2 \text{ mol dm}^{-3}$, $I = 0.5 \text{ mol dm}^{-3}$, $\lambda_{\text{max}} = 420 \text{ nm}$ and $T = 27.0 \pm 0.1^\circ\text{C}$. The reaction mixture was allowed to stand for 24 hours after which the absorbance were taken using the spectrophotometer. The stoichiometry was evaluated from the plot of absorbance against mole ratio [9 and 10].

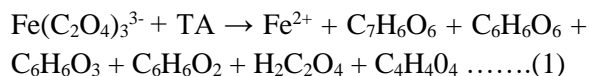
Kinetic Measurements

Rate data for the redox reaction between the oxidant and reductant were obtained by monitoring the increase in absorbance at $\lambda_{\text{max}} = 420 \text{ nm}$. The reaction was conducted under pseudo-first conditions with the reductant in large excess over the oxidant. Under such conditions, kinetics plots were exponential and rate constants were obtained from logarithmic plots of absorbance difference $\log (A_0 - A_t)$ versus time.

RESULTS AND DISCUSSION

Stoichiometry

Spectrophotometric titration revealed that one mole of the oxidant was consumed by one mole of the reductant. These observations are in accord with equation (1).



A similar stoichiometry has been reported [11 and 12].

Product Analysis

Reduction of the iron (III) complex to iron (II) was confirmed by the reaction of acidified solution of the completely reacted mixture with freshly prepared potassium hexacyanoferrate (II) or with freshly prepared potassium hexacyanoferrate (III) as described by [13]. On addition of Fehling's solution to partially reacted mixture of oxidant and reactant, a brick-red precipitate was obtained on warming. This indicated the presence of a reducing sugar. Glucose, resorcinol, oxalic acid, maleic acid and gallic acid have been reported as products of the oxidation of tannic acid [2, 14 and 15].

Determination of Order

Pseudo-first order decay was linear to greater than 97 % of the extent of reaction showing first

order dependence on rate with respect to tannic acid. Pseudo-first order rate constants were obtained and second order rate constant, obtained by dividing k_{obs} by [oxidant] and were found to be fairly constant, indicating first order also in tannic acid giving an overall second order. The values of the rate constants are presented in Table 1. Plot of $\log k_{\text{obs}}$ versus $\log [\text{TA}]$ ($R^2 = 0.96$), gave a slope of 0.95, which agrees to first-order dependence of rates of reaction on tannic acid. Similar observation for first order dependence on rate has been reported by [2, 11, 12, and 16]. The rate law for the reaction is given by equation (2):

$$-d[\text{TA}]/dt = k_2[\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}][\text{TA}] \quad \dots\dots\dots (2)$$

$$k_2 = 3.56 \pm 0.37 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

Acid Dependence

The effect of $[\text{H}^+]$ on the reaction rate was investigated by varying the concentration of HCl

within the range of (0.089 – 0.534) mol dm^{-3} , $[\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}] = 4.45 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{TA}] = 0.0445 \text{ mol dm}^{-3}$, $I = 0.5 \text{ mol dm}^{-3}(\text{NaCl})$, $\lambda_{\text{max}} = 420 \text{ nm}$ and $T = 27.0 \pm 0.1^\circ\text{C}$. Under these conditions, the rate of the reactions increased with increase in concentration of H^+ . This acid catalysis has been interpreted to be arising from a pre-equilibrium step before the electron transfer reaction [5 and 13]. Acid dependent rate constants are shown in Table 1. Acid dependent rate constant is given as:

$$k_2 = a + b [\text{H}^+] \quad \dots\dots\dots (3)$$

From the least square fit ($R^2 = 0.98$), for plot of $\log k_{\text{H}}$ versus $\log[\text{H}^+]$ (Fig. 1) the value of $a = 2.45 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $b = 1.2 \text{ dm}^6 \text{ mol}^2 \text{ s}^{-1}$. The rate equation for the reaction can therefore be represented as:

$$-d[\text{TA}]/dt = \{a + b[\text{H}^+]\}[\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}][\text{TA}] \quad \dots (4)$$

Table 1: Pseudo-first order and second order rate constants for the oxidation of tannic acid by $[\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}]$ in aqueous hydrochloric acid medium at $[\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}] = 4.45 \times 10^{-3} \text{ mol dm}^{-3}$, $I = 0.5 \text{ mol dm}^{-3}(\text{NaCl})$, $[\text{H}^+] = 0.2 \text{ mol dm}^{-3}$, $\lambda_{\text{max}} = 420 \text{ nm}$ $T = 27.0 \pm 0.1^\circ\text{C}$.

$10^2[\text{TA}]$, mol dm^{-3}	$10^2[\text{H}^+]$, mol dm^{-3}	10^2I , mol dm^{-3} NaCl	10^4k_{obs} , s^{-1}	10^3k_2 , $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
4.45	20	50	1.8	4.0
8.90	20	50	2.6	3.0
13.4	20	50	5.2	3.9
17.8	20	50	6.8	3.8
22.3	20	50	7.9	3.5
26.7	20	50	8.5	3.2
4.45	8.90	50	1.8	2.0
4.45	17.8	50	5.2	2.9
4.45	26.7	50	6.4	2.4
4.45	35.6	50	9.8	2.8
4.45	44.5	50	13.5	3.0
4.45	53.4	50	16.8	3.1
4.45	20	17.8	4.8	2.7
4.45	20	35.6	6.5	1.8
4.45	20	51.0	8.2	1.6
4.45	20	71.2	9.4	1.3
4.45	20	89.0	9.6	1.1
4.45	20	106.8	10.8	1.0

Effect of Ionic Strength

The effect of ionic strength on the reaction rate was studied between 0.178 to 1.068 mol dm⁻³ using various amounts of NaCl at [TA] = 0.0445 mol dm⁻³, [Fe(C₂O₄)₃³⁻] = 4.45×10⁻³ mol dm⁻³ [H⁺] = 0.2 mol dm⁻³, and, λ_{max} = 420 nm and T = 27.0 ± 0.1°C. The results as shown in Table 1 indicated that the rate of the reaction decreased with increase in ionic strength which is attributed to the fact that the redox species are oppositely charged. A plot of log k₂ versus √I was linear showing a negative Brønsted-Debye salt effect and suggesting the absence of intermediate complex

formation and that species carrying opposite charged sign in the activated complex are interacting [17 - 21].

Effect of Dielectric Constant (D)

As other parameters are kept constant, dielectric constant of the reaction media was varied by adding varying portions of acetone-water mixture. Results in this respect show increase in reaction rate as dielectric constant decrease. Plot of log k_{obs} versus 1/D, gave a positive slope which is indicative of a reaction between redox partners of unlike charges [13 and 22].

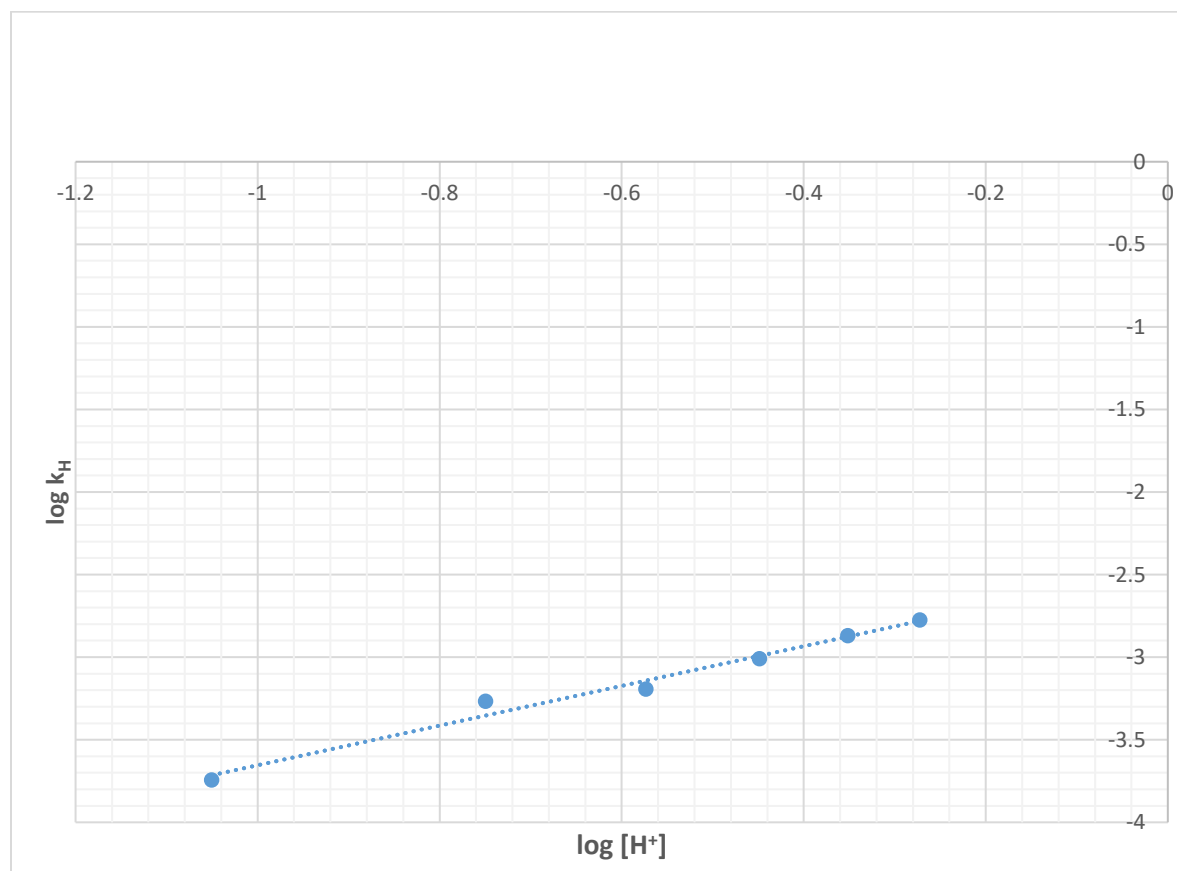


Figure 1: Plot of log k_{obs} versus log [H⁺] at [Fe(C₂O₄)₃³⁻] = 4.45 × 10⁻³ mol dm⁻³, I = 0.5 mol dm⁻³ (NaCl), [TA] = 0.0445 mol dm⁻³, λ_{max} = 420 nm and T = 27.0 ± 0.1°C

Table 2: Effect of dielectric constant on the oxidation of Tannic acid by $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$ in aqueous hydrochloric acid medium at $[\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}] = 4.45 \times 10^{-3} \text{ mol dm}^{-3}$, $I = 0.5 \text{ mol dm}^{-3}(\text{NaCl})$, $[\text{H}^+] = 0.2 \text{ mol dm}^{-3}$, $[\text{TA}] = 0.0445 \text{ mol dm}^{-3}$, $27.0 \pm 0.1^\circ\text{C}$ and $\lambda_{\text{max}} = 420 \text{ nm}$.

Dielectric Constant (D)	$10^3 1/D$	$10^4 k_{\text{obs}}, \text{S}^{-1}$	$10^2 k_2, \text{dm}^3 \text{mol}^{-1} \text{S}^{-1}$
211.6	4.7	1.8	0.1
126.2	7.9	3.6	0.1
86.8	11.5	5.6	0.1
74.0	13.5	7.2	0.1
68.7	14.6	14.8	0.2

Effect of Added Ions

Catalytic effects of added ions was investigated by adding varying concentrations of Ni^{2+} , K^+ , HCOO^- and CH_3COO^- in the range of (0.089 – 0.445) mol dm^{-3} separately into the reaction medium while keeping other parameters constant. The presence of K^+ , Ni^{2+} , CH_3COO^- and HCOO^- was found to enhance the reaction rate. This is an indication that the reaction most probably occurred via an outer-sphere mechanism [5, 13, 20, 23 and 24]. Positive catalysis of the reaction rates by added cations and anions was observed in the redox reactions between $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}/\text{S}_2\text{O}_3^{2-}$ system [5] while negative catalysis on rate is consistent with the report for $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}/\text{SO}_4^{2-}$ and MnO_4^- systems [6 and 7].

Test for Free Radicals

The presence of free radicals was indicated by the positive polymerization test on addition of acrylamide to partially reacted mixture of the

reactants in excess methanol. The methanol was responsible for trapping the polymer as an insoluble precipitate. This is evidence of inner-sphere electron transfer mechanism [25], suggesting that free radicals participated in this reaction [26 and 27]. The acrylamide polymerized the reaction mixture [28]. Polymerization of acrylamide by potassium trisoxalatoferrate (III) trihydrate had earlier been reported [6 and 7].

Michaelis-Menten Plot

Michaelis-Menten type plot of $1/k_{\text{obs}}$ versus $1/[\text{TA}]$ was linear with no significant intercept as shown in Fig. 5. This is in accord with reactions occurring via the outer-sphere paths, suggesting the absence of intermediate or precursor complex formation [6, 26 and 29]. Similar reaction pathway was reported for the redox reaction between $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}/\text{S}_2\text{O}_3^{2-}$ and $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}/\text{SO}_4^{2-}$ systems [5 and 6].

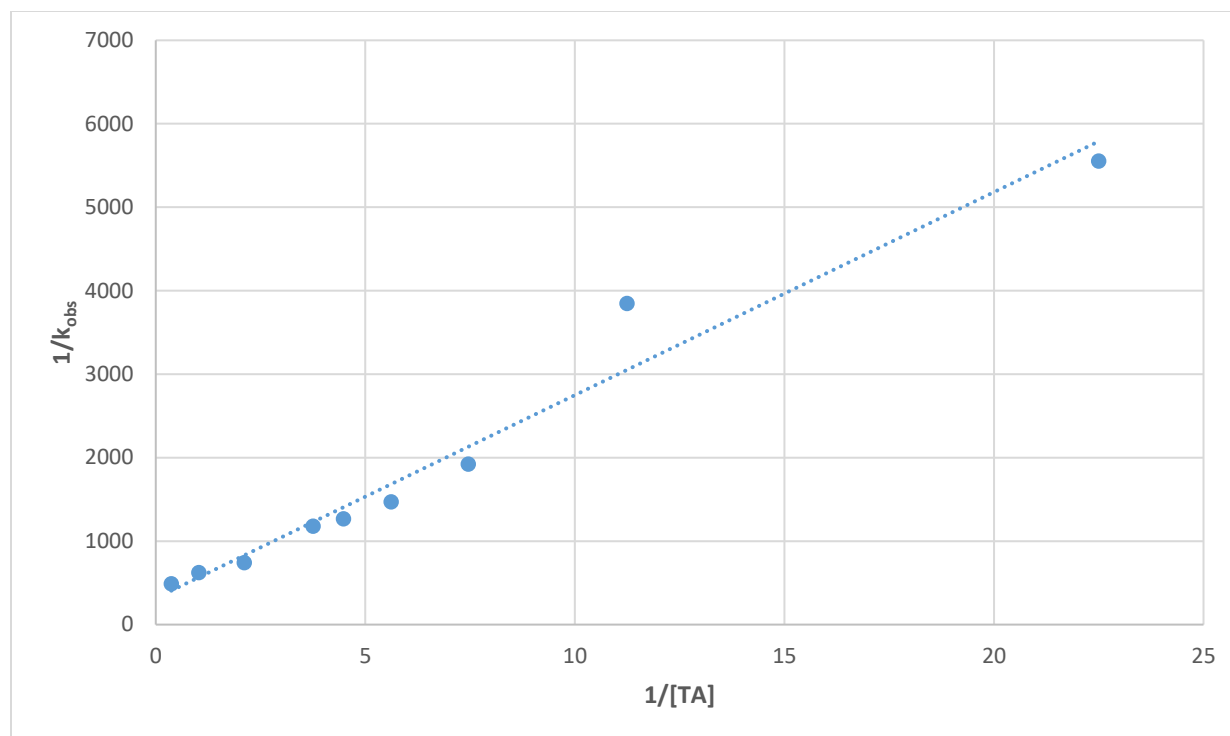
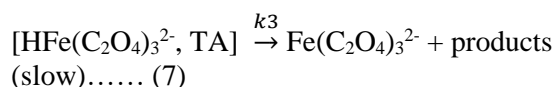
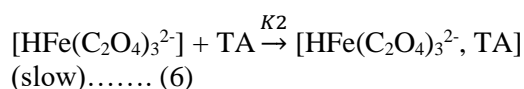
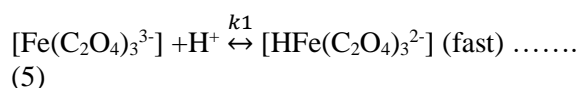


Figure 2: Plot of $1/k_{\text{obs}}$ versus $1/[TA]$ at $[\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}] = 4.45 \times 10^{-3} \text{ mol dm}^{-3}$, $I = 0.5 \text{ mol dm}^{-3}(\text{NaCl})$, $[\text{H}^+] = 0.4 \text{ mol dm}^{-3}$, $\lambda_{\text{max}} = 420 \text{ nm}$, $T = 27.0 \pm 0.1^\circ\text{C}$.

Mechanism of the Reaction

Based on the stoichiometry, observed positive acid dependence, negative ionic strength dependence, anion and cation catalysis, a plausible reaction scheme has been proposed to account for the kinetic data generated for tannic acid - $[\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}]$ system.



From equations (6) and (7), the rate equation can be written as:

$$\text{Rate} = k_2[\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}][\text{TA}] + k_3[\text{TA}][\text{Fe}(\text{C}_2\text{O}_4)_3^{2-}] \dots\dots (8)$$

From equation (5),

$$[\text{HFe}(\text{C}_2\text{O}_4)_3^{2-}] = k_1[\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}][\text{H}^+] \dots\dots (9)$$

Substituting equation (9) into (8), we obtain:

$$\text{Rate} = k_2k_1[\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}][\text{TA}][\text{H}^+] + k_3[\text{TA}][\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}] \dots (10)$$

$$\text{Rate} = (k_3 + k_2k_1[\text{H}^+])[\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}][\text{TA}] \dots (11)$$

Equation (11) is analogous to equation (4), where:

$$a = k_3 = 2.25 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$$

$$b = k_2k_1 = 1.2 \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$$

In order to assign a reaction pathway through which the oxidation of tannic acid by potassium trisoxalatoferrate (III) trihydrate occurred, the following points of interest have to be considered:

- (a) Addition of acrylamide to the partially oxidized mixture gave a gel in excess methanol, suggesting the probable

presence of free radicals in the reaction. This evidence is in support of inner-sphere from electron transfer pathway [7].

- (b) From Table 1, reaction rates decreased with increase in ionic strength. Also, plot of $\log k_2$ versus \sqrt{I} gave a linear graph with a negative slope and intercept showing a negative salt effect. This suggests absence of formation of intermediate complex in the reaction, thus implicating the occurrence of outer sphere reaction pathway [30].
- (c) Plots of $1/k_{\text{obs}}$ versus $1/[TA]$ (using the Lineweaver-Burk modification of Michaelis-Menten equation) was linear without an appreciable intercept (Figure 2). This is in support of an outer sphere reaction mechanism.
- (d) The addition of CH_3COO^- , HCOO^- , K^+ and Ni^{2+} enhanced the reaction rate. Cations and anions catalysis or inhibition has been proposed to support outer sphere reaction pathway in most reactions that has been studied [5].

Owing to the strengths of these kinetic evidence (a) - (d), it can be inferred that the redox reaction between potassium trisoxalatoferrate (III) trihydrate most probably occurred via an outer sphere electron transfer mechanism and is hereby proposed

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