

KINETICS AND MECHANISM OF OXIDATION OF L-CYSTEINE BY FERROZINEIRON(III) COMPLEX IN AQUEOUS ACIDIC MEDIUM

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تمت دراسة حركية أكسدة مركب السستين كحمض أميني باستخدام متراكب $[\text{Fe}(\text{Fz})_2]^{-1}$ المكون من أيون الحديد الثلاثي مرتبط مع نسيقة الفروزين HFz^{-1} في وسط حمضي، باستخدام الطرق الطيفية عند درجة حرارة 36^oم. استخدمت في الدراسة طريقة سرعة التفاضل تحت ظروف رتبة التفاعل الأولى الكاذبة، كما حسبت قيمة النسبة الجزئية بين النسيقة HFz^{-1} والحديد الثلاثي والحديد الثنائي في وجود وغياب مركب السستين كل على حدة باستخدام طريقة جوب للتغير المستمر. وقد لوحظ أن التفاعل من الدرجة الأولى لكل من الحديد الثلاثي والسستين، ومن الدرجة الثانية بالنسبة لـ HFz^{-1} ، وثنائي رجعي بالنسبة لتركيز أيون الهيدروجين. ولم تؤثر إضافة أملاح مثل NaClO_4 في سرعة أو اتجاه التفاعل، كذلك لم تؤدي إضافة ماسكات الجذر الحر إلى تكوين المبلورات أو أي زيادة في الزوجة وهذا يؤكد سير التفاعل بطريقة غير ميكانيكية الجذر الحر. إن الارتفاع الملحوظ في قيمة k_{obs} لتفاعل الأكسدة المذكور أعلاه بزيادة درجة الحرارة مكننا من دراسة وحساب المتغيرات الحركية له وذلك بتقييم السلوك المثالي للتفاعل في منطقة مثالية الامتصاص. بناء على هذه النتائج تم اقتراح وتدعيم ميكانيكية لهذا التفاعل.

Kinetic oxidation of L-cysteine by $[\text{Fe}(\text{Fz})_2]^{-1}$ complex was carried out in acidic medium under pseudo rate conditions. The molar ratios between iron(III), iron(II) and Ferrozine (HFz) complexes in absence and presence of L-cysteine were individually determined using job's method. The formation of $[\text{Fe}^{2+}\text{-Fz}]$ at $\lambda_{\text{max}} = 562\text{nm}$ was spectrophotometrically followed during this kinetic study. The reaction is found to be first-order with respect to iron(III) and L-cysteine, second-order with respect to HFz^{-1} ligand and reversed second-order with respect to hydrogen ion concentrations. The salts effect was determined and no radical species have been detected. The k_{obs} rose when the temperature was increased which empowered the activation parameters of the rate-determining step calculations. A reaction mechanism and rate law derivation are proposed with a pre-equilibrium of an adduct formation between L-cysteine and $[\text{Fe}^{3+}\text{-Fz}]$ complex.

Keywords: Iron(II) complexes, Kinetic determination, Oxidation, L-Cysteine, Ferrozine ligand.

INTRODUCTION

Transition-metal complexes with ligand systems containing nitrogen-donor atoms have been used successfully to promote the transformation of organic compounds and also to act as

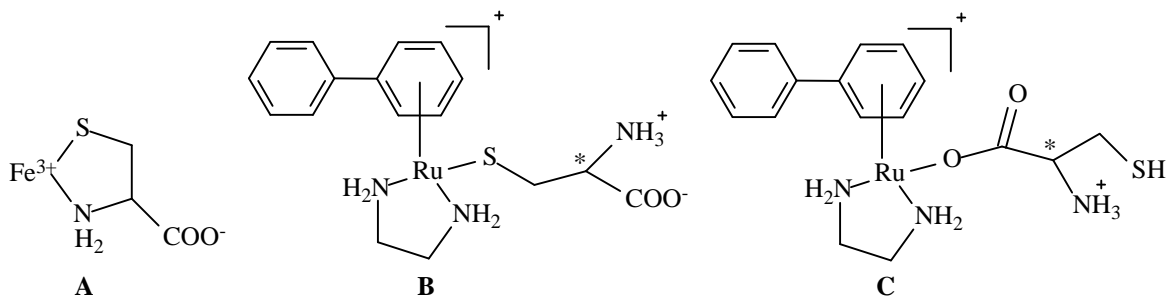
structural mimics of metal centers in enzymes [1-5]. The chemistry of metallacycles using multi-nitrogen ligand components has received growing interest during recent years, as a result of their involvement in catalytic processes [6-8]. A significant progress in the stabilization, isolation,

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and examination of undercoordinated species was achieved by the introduction of multifunctional ligand. Moreover the sterical and electronic properties of these kinds of ligands can be varied in wide range by the employments of different substituents at the coordinated atoms which are in most case phosphorus or nitrogen. Such of these complexes which are in general containing multidentate pure nitrogen or/ and phosphine-donor atoms served as novel catalysts [9-14]. On the other hand it used as good oxidizing reagents in a medium with an appropriate pH value [15-18].

L-Cysteine ($C_3H_7NO_2S$) as sulfur-containing amino acid is a tri-basic compound, it linked together by peptide bonds to form proteins or it

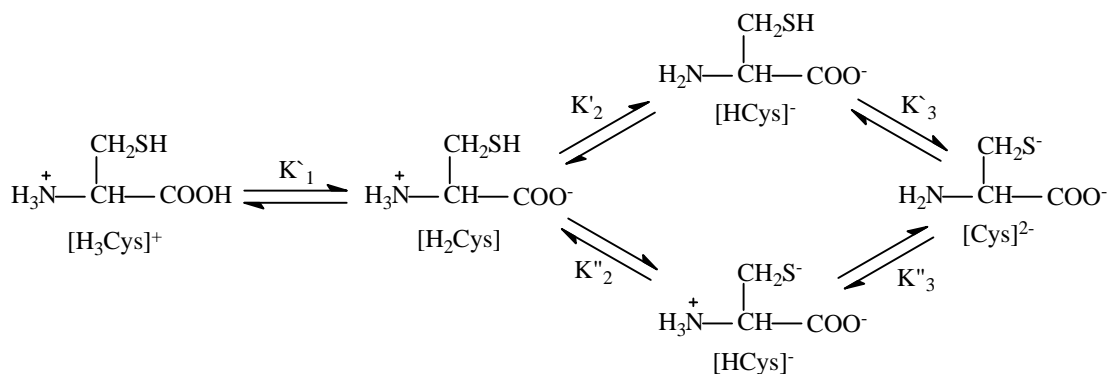
can bind through disulfide bridge to synthesize sulfur-organic compounds such as cystine (RS-SR). It is considered as the primary source of organic sulfurcontaining compounds in the environment, it can be found in human blood, urine and tissues in very small amounts. Micrograms of L- or D-cysteine are essential to control the daily biochemical-bodies activities [15-18]. Due to the presence of multi-atoms (S, O and N) which are ready to coordinate metal center as well as one chiral center in the backbone of L-cysteine compound, it will act as mono or bidentate ligand in coordination chemistry [19-22] as an example see Scheme 1.



Scheme 1: L-Cysteine as bidentate (S, N) ligand as in complex A and monodentate (S or O) ligands as in complexes B and C respectively.

Reactions of L-cysteine appears to play key roles in the biological chemistry of Pt(II) and Pt(IV), Fe(III) and Ru(III) anticancer agents. The reigo-binding selectivity of L-cysteine with transition metal ions which affects the chemical

and biological properties depends directly on the ionization state of cysteine molecule and the reactions medium. Cysteine can be ionized to different forms [22-24] as in Scheme 2.



Scheme 2: Cysteine ionization forms.

The concentration of the cysteine-containing tripeptide glutathione is elevated in some platinum-resistant cell lines, and thiols appear to be involved in the reduction of Pt(IV), Ru(III) and Fe(III) complexes to active Pt(II), Ru(II) and Fe(II) species [19-22].

Many efforts have been constructed to develop what so called the radiolabeled bioactive peptides which found to be attractive vectors for targeting a variety of diseases through interaction with specific cell surface receptors [25,26]. Current approaches make use of tripeptides (such as L-cysteine) that can form chelate complexes with the radiometals [26-29].

In this work, Ferrozine (HFz⁻) has been used as water soluble nitrogen multi-donor ligand. It ionized in water to Fz²⁻ anion. The method is based on mixing HFz ligand with iron(III) to form yellowish Fe³⁺-Fz complex which showed a maximum absorbance at 344 nm. The Fe³⁺-Fz complex in acidic medium served as a good oxidizing agent. Herein, we wish to report a helpful study of reaction kinetics, comparative, mechanism and rate law derivation of L-cysteine oxidation by Fe³⁺-Fz in aqueous acidic medium.

EXPERIMENTAL

Apparatus:

Absorbance measurements in this study were performed using A UNICAM UV2_Shimadzu computerized UV-visible spectrophotometer with a 1 cm length quartz cell. It has got vision software and a circulation thermostat water bath (C-85A) for temperature control. All pH measurements were made using a calibrated HANNA E 18521 pH meter with combined glass electrode. Oxidation product (cystine) was identified as the corresponding amino acid by spot test [30]. Computerized Fourier transform infrared spectrophotometer (Shimadzu FTIR 820PC), with Hypride software were used to characterize the products. Standard buffer solutions were used to standardize the set before any runs have been carried out.

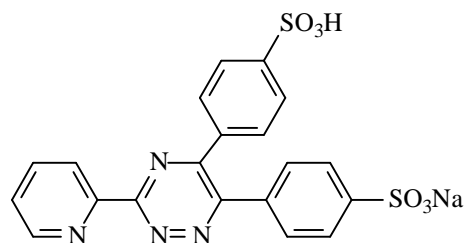
Reagents:

All the chemicals used were analytical reagents or of pure grade; distilled water and 95-100% redistilled ethanol were also used.

FeCl₃.6H₂O and Ferrozine were obtained from Aldrich Company. 1 × 10⁻² M of Fe³⁺ solution and 1 × 10⁻³ M of Ferrozine were prepared in distilled-deionized water and used as stock solutions; other concentrations from Fe³⁺ solution were obtained by dilution. The stock solutions were sealed in brown bottles in black cold place. L-cysteine was purchased from Aldrich, solutions of 1 × 10⁻³ M was daily prepared using deionized oxygen-removed water. The sodium acetate and acetic acid buffer system was prepared according to the literature [31].

Synthesis and procedures:

The structure of Ferrozine [3-(2-pyridyl)-5,6-bis-(4-phenylsulfonic acid)-1,2,4-triazine] as electrons multidentate ligand is shown in Scheme 3.



Scheme 3: The structure of Ferrozine [3-(2-pyridyl)-5,6-bis-(4-phenylsulfonic acid)-1,2,4-triazine] as multifunctional atoms ligand.

The reaction was carried out in the quartz cell of the UV-visible spectrophotometer directly to save the reaction time, care also was taken to exclude walls air bubbles formation. Fixed general procedure was adjusted to get the best reproducibility, taking in consideration the sequence of order which found to be: buffer-water system, Ferrozine ligand, Fe³⁺ followed by L-cysteine respectively. Together by following this sequence of addition and using a suitable acidic medium, absolutely no direct reaction between Fe³⁺ and L-cysteine was observed. The total reaction mixture volume was 10 ml. These reagents concentrations were carefully calculated to be fit with the acceptable absorption range (beer's law) [32].

RESULTS AND DISCUSSION

General investigations under the condition of pseudo-first-order rate, the plots of $\ln(A_\infty - A_t)$ versus time (min.) for more than 3 half lives of the reaction were found to be linear (with slope 0.99 or 1.98 depending on the reagents studied). The pseudo-first-order rate constants, k_{obs} , were calculated by the least-squares method. The rate constants reported here are the averages of 3 independent runs. Deviations in duplicate determinations are generally less than $\pm 5\%$. The complex formation between Fe(III) and HFz^- was performed in aqueous acidic medium. The absorption spectra of the produced complex showed $\lambda_{\text{max}} = 344 \text{ nm}$ which revealed $[\text{Fe}(\text{Fz})_2]^{1-}$ formation.

When this complex was treated with L-cysteine a blue unstable color was detected by eyes for a very short time ($< 1 \text{ sec.}$), this is attributed to $[\text{Fe}^{3+}\text{-Fz-Cysteine}]$ flash-intermediate formation before it is reduced to the stable new violet color of $\text{Fe}^{2+}\text{-Fz}$ complex. The study of L-cysteine oxidation by $\text{Fe}^{3+}\text{-Fz}$ complex was performed spectrophotometrically at $\lambda_{\text{max}} = 562 \text{ nm}$ of the violet $[\text{Fe}(\text{Fz})_3]^{4-}$ complex, λ_{max} was selected from the spectra scanned at suitable pH. The rate of reaction was modified by suitable hydrogen ions concentration to be measurable. The absorption spectra of $[\text{Fe}(\text{Fz})_3]^{4-}$ complex at $\lambda_{\text{max}} = 562 \text{ nm}$ as a function of wavelength (nm) at different time periods were illustrated in Figure 1.

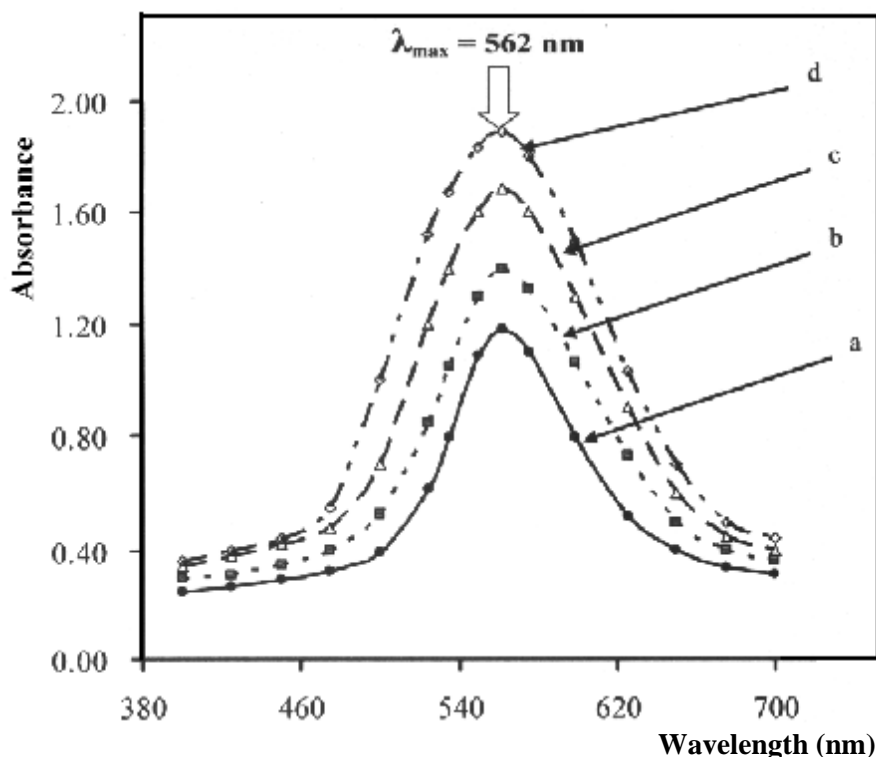


Figure 1: Absorption spectra of the violet $[\text{Fe}^{2+}\text{-Fz}]$ complex at $\lambda_{\text{max}} = 562 \text{ nm}$, $t=28^\circ\text{C}$, $[\text{Fe}^{2+}] = 3 \times 10^{-4} \text{ M}$, $[\text{HFz}^-] = 6 \times 10^{-4} \text{ M}$, $\text{pH} = 4$. (a) after 2 min; (b) after 3 min; (c) after 5 min and (d) after 7 min. from Fe^{2+} addition.

Complexes stoichiometries:

The molar ratios of $\text{Fe}^{3+}\text{-Fz}$, $\text{Fe}^{2+}\text{-Fz}$ and $\text{Fe}^{3+}\text{-Fz}$ in the presence of cysteine have been

studied individually, by using job's continuous variation method [33] to determine the stoichiometry of the iron(III)/(II)-Fz complexes.

The result showed the existence of [1:3] $[\text{Fe}^{2+}:\text{Fz}]$, [1:2] $[\text{Fe}^{3+}:\text{Fz}]$ and [1:2:1] $[\text{Fe}^{3+}:\text{Fz}:\text{Cys}]$ respectively, the result which summarized in Figure 2 and figure 3 are in agree with the literature [15, 22,34-36].

Optimum conditions:

The oxidation rates of L-cysteine to cystine using Fe^{3+} -Fz complex as an oxidizing agent were influenced by the pH of the buffer medium, reagents concentrations, ionic strength, ethanol ratio and temperature. The optimum conditions of the method were investigated as follows.

Effect of pH on the rate of the reaction:

The effect of pH on the initial rate of the reaction was studied at different pH values

between 2.5 and 7.0 at 28 °C as shown in Figure 4. The optimum pH lied between 3.9 and 4.1. The absorption-time curves of the reaction in different H^+ concentration ($0.1\text{-}3.1 \times 10^{-4}$ M, 2.5-4.0 pH) indicated that the reaction rate was increased by increasing pH. The acids acted as inhibitor in this pH range the best straight line was recorded when $1/k_{\text{obs}}$ vs. $[\text{H}^+]^2$ was plotted (Figures 5).

Effect of ionic strength:

The effect of NaClO_4 concentration on the rate of the reaction was studied and the result is presented in Table 1 and Figure 6. It can be seen that the k_{obs} values decreased with increasing the $[\text{NaClO}_4]$. Plot of $-\ln k_{\text{obs}}$ vs. $[(\text{I})^{1/2} / (1 + (\text{I})^{1/2})]$ was linear with a slope = -2.27.

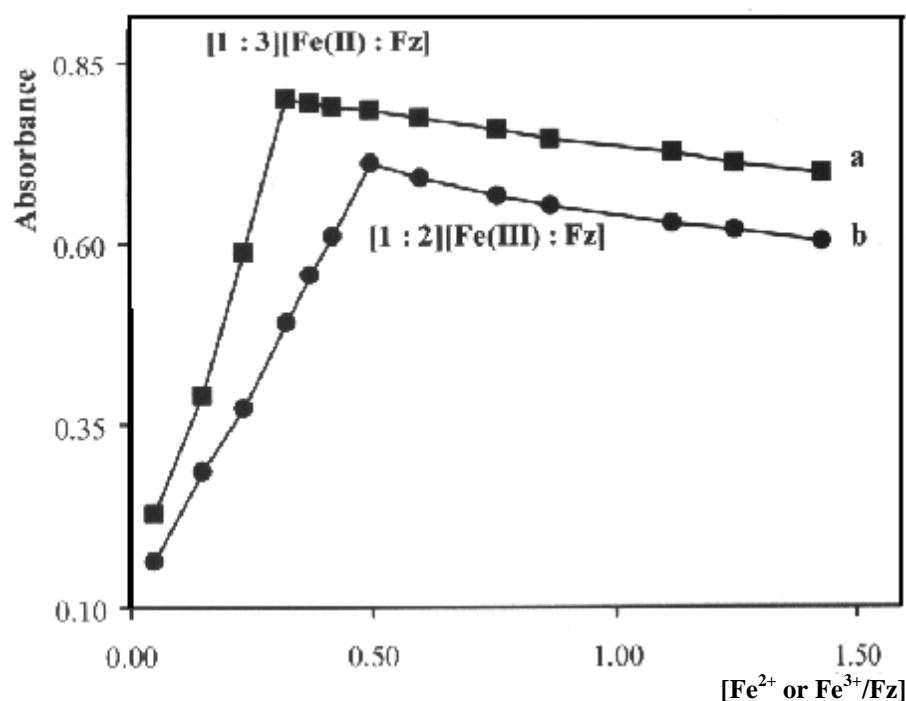


Figure 2: Job's plots to determination the molar ratios at $t = 28$ °C, a) Plot of absorbance vs. $[\text{Fe}^{2+}/\text{HFz}]$ at $\lambda_{\text{max}} = 562$ nm, $[\text{HFz}] = 3 \times 10^{-4}$ M, $[\text{Fe}^{2+}] = 0.1 - 4.0 \times 10^{-4}$ M and pH = 2.50; b) Plot of absorbance vs. $[\text{Fe}^{3+}/\text{HFz}]$ at $\lambda_{\text{max}} = 344$ nm, $[\text{HFz}] = 3 \times 10^{-4}$ M, $[\text{Fe}^{3+}] = 0.10 - 3.0 \times 10^{-4}$ M and pH = 2.50.

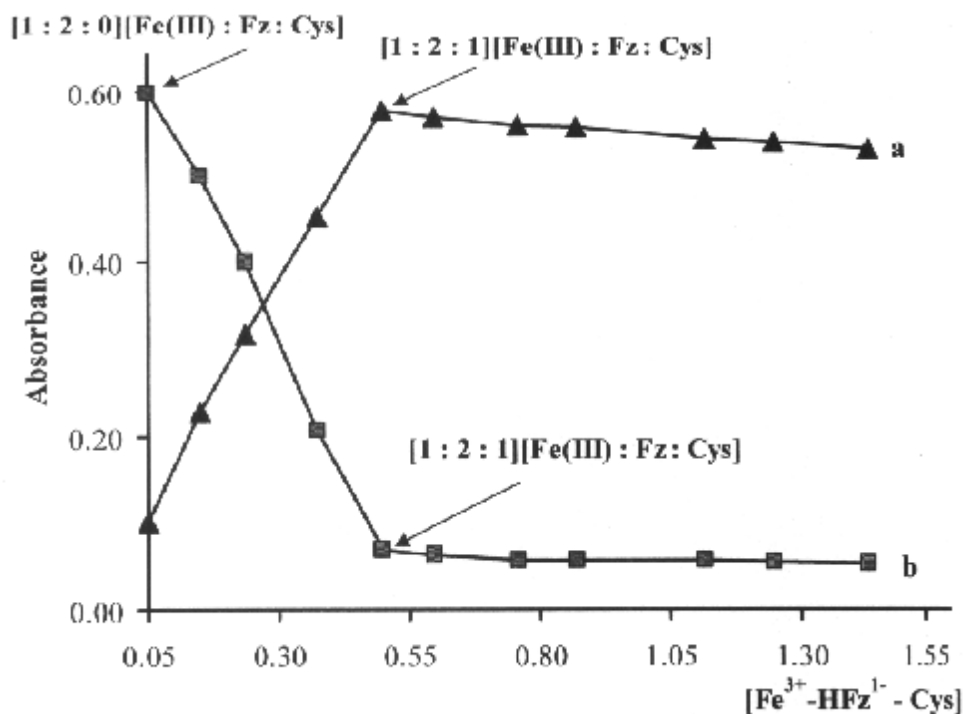


Figure 3: Job's plots to determine the molar ratios at $t = 28^\circ\text{C}$; a) Plot of absorbance vs. $[\text{Fe}^{3+}]$ at $\lambda_{\text{max}} = 562\text{nm}$, $\text{pH} = 2.50$, $[\text{HFz}^-] = 3 \times 10^{-4}\text{M}$, $[\text{Cysteine}] = 1.5 \times 10^{-4}\text{M}$, and $[\text{Fe}^{3+}] = 0.1 - 4.0 \times 10^{-4}\text{M}$; b) Plot of absorbance vs. $[\text{Cysteine}]$ at $\lambda_{\text{max}} = 344\text{nm}$ $\text{pH} = 2.50$, $[\text{HFz}^-] = 3 \times 10^{-4}\text{M}$, $[\text{Fe}^{3+}] = 1.5 \times 10^{-4}\text{M}$ and $[\text{Cysteine}] = 0.10 - 3.0 \times 10^{-4}\text{M}$.

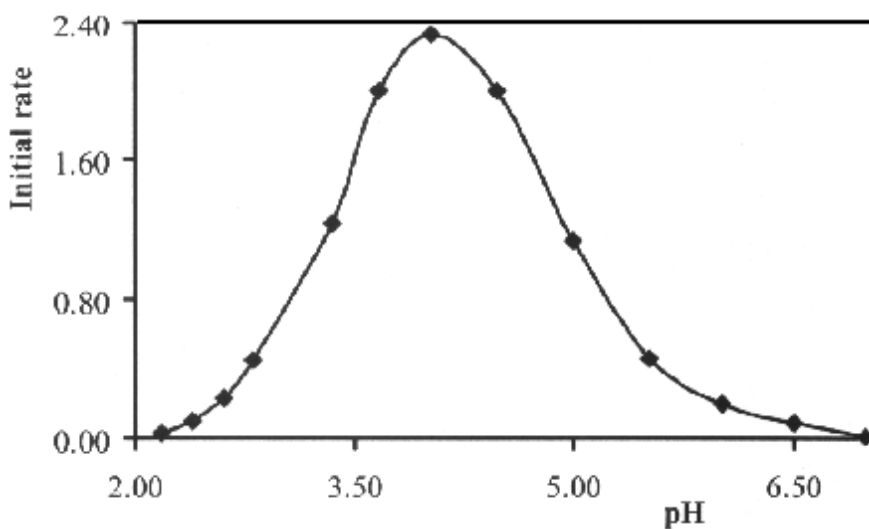


Figure 4: Influence of H^+ concentrations on the initial rate at $\lambda_{\text{max}} = 562\text{nm}$, $t = 28^\circ\text{C}$, $[\text{HFz}^-] = 3 \times 10^{-4}\text{M}$, $[\text{Fe}^{3+}] = 5 \times 10^{-5}\text{M}$ and $[\text{Cysteine}] = 1 \times 10^{-4}\text{M}$.

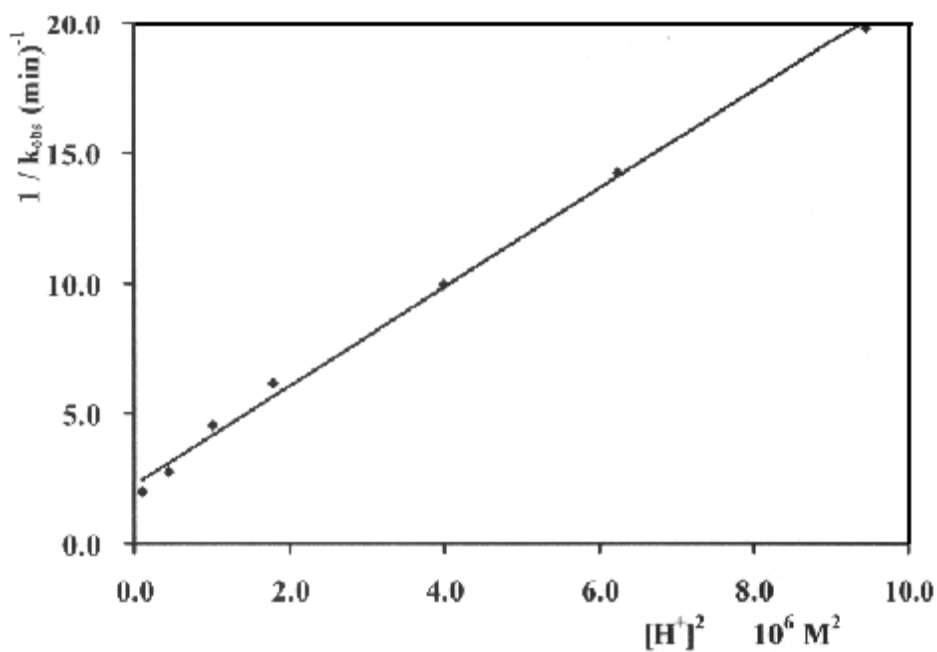


Figure 5: Plot of $1/k_{\text{obs}}$ vs. $[H^+]^2$ at $\lambda_{\text{max}} = 562 \text{ nm}$, $t = 28 \text{ }^\circ\text{C}$, $[\text{HFz}] = 3 \times 10^{-4} \text{ M}$, $[\text{Fe}^{3+}] = 5 \times 10^{-5} \text{ M}$, $[\text{Cysteine}] = 1 \times 10^{-4} \text{ M}$.

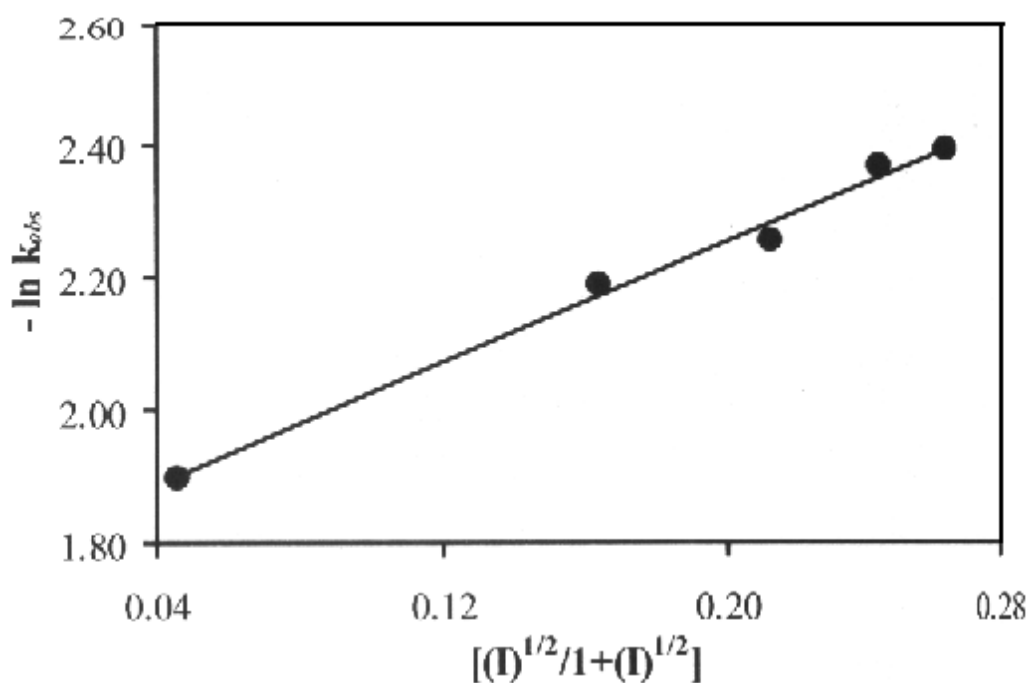


Figure 6: Plot of $-\ln k_{\text{obs}}$ vs. $[(I)^{1/2}/(1+(I)^{1/2})]$ at $\lambda_{\text{max}} = 562 \text{ nm}$, $t = 28 \text{ }^\circ\text{C}$, $[\text{HFz}] = 3 \times 10^{-4} \text{ M}$, $[\text{Fe}^{3+}] = 5 \times 10^{-5} \text{ M}$, $[\text{Cysteine}] = 1 \times 10^{-4} \text{ M}$ and $\text{pH} = 2.80$.

The dependence of the rate on the reagents concentrations:

Effect of Iron(III) concentration

At constant temperature 28 °C, and by fixing all the other reaction conditions, the rate increased by raising the concentration of Fe^{3+} . The plot of $1/k_{\text{obs}}$ vs. $1/[\text{Fe}^{3+}]$ revealed the best straight line (Figure 7).

Effect of ferrozine ligand concentration

The effect of HFz^- concentration on the rate of the reaction mixture was presented in Figure 8. A straight line was exhibited when $1/k_{\text{obs}}$ was plotted against $[\text{HFz}]^2$.

Effect of L-Cysteine concentration

Figure 9 showed an increase in the rate when L-cysteine concentration was increased; the plot of $1/k_{\text{obs}}$ vs. $1/[\text{Cysteine}]$ gave a straight line (Figure 9).

Table 1: The effect of ionic strength on the reaction at $\lambda_{\text{max}} = 562 \text{ nm}$, $t = 28 \text{ }^\circ\text{C}$, $[\text{HFz}] = 3 \times 10^{-4} \text{ M}$, $[\text{Fe}^{3+}] = 5 \times 10^{-5} \text{ M}$, $[\text{Cysteine}] = 1 \times 10^{-4} \text{ M}$ and $\text{pH} = 2.80$.

$[\text{NaClO}_4] / \text{M}$	I / M	$(I)^{1/2}$	$[(I)^{1/2}/(1+(I)^{1/2})]$	$k_{\text{obs}} (\text{min})^{-1}$	$-\ln k_{\text{obs}}$
0.125	0.127	0.347	0.261	0.087	2.442
0.100	0.103	0.319	0.242	0.092	2.386
0.070	0.073	0.269	0.212	0.105	2.254
0.037	0.039	0.197	0.164	0.112	2.189
0.000	0.002	0.047	0.046	0.156	1.898

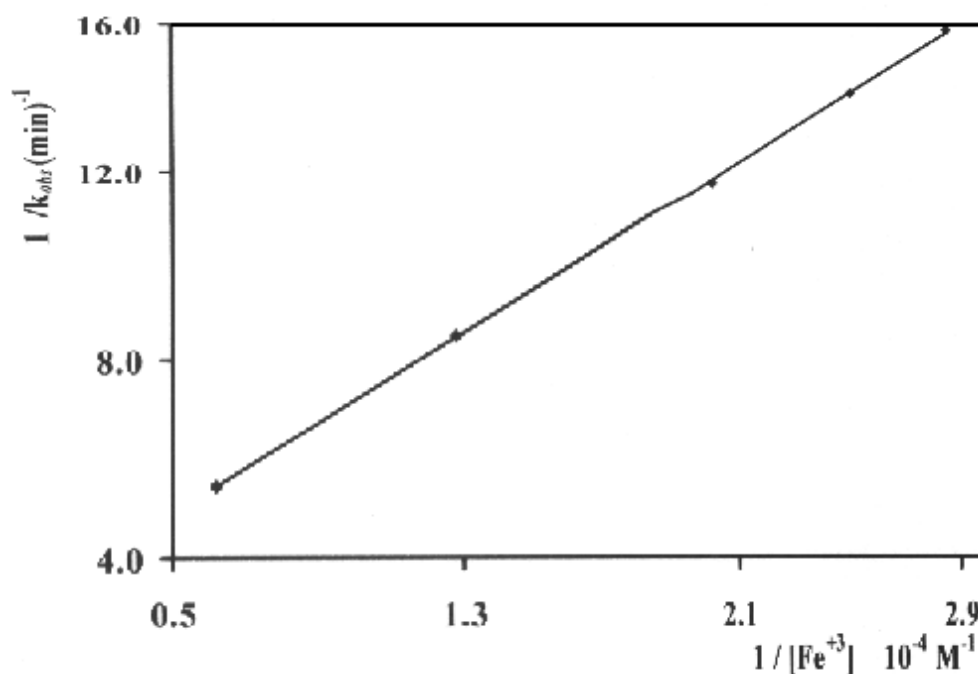


Figure 7: Plot of $1/k_{\text{obs}}$ vs. $1/[\text{Fe}^{3+}]$ at $\lambda_{\text{max}} = 562 \text{ nm}$, $[\text{HFz}] = 5 \times 10^{-4} \text{ M}$, $[\text{Cysteine}] = 1 \times 10^{-4} \text{ M}$, $t = 28 \text{ }^\circ\text{C}$ and $\text{pH} = 2.50$.

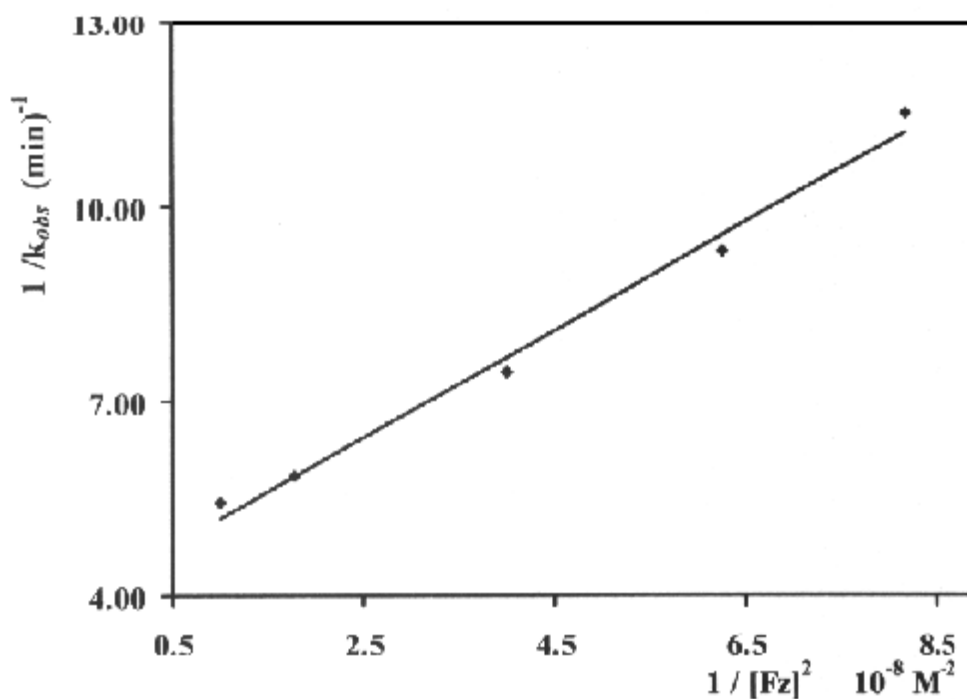


Figure 8: Plot of $1/k_{obs}$ vs. $1/[HFz]^{-2}$ at $\lambda_{max} = 562 \text{ nm}$, $[Fe^{3+}] = 1 \times 10^{-4} \text{ M}$, $[Cysteine] = 1 \times 10^{-4} \text{ M}$, $t = 28 \text{ }^\circ\text{C}$ and $\text{pH} = 2.70$.

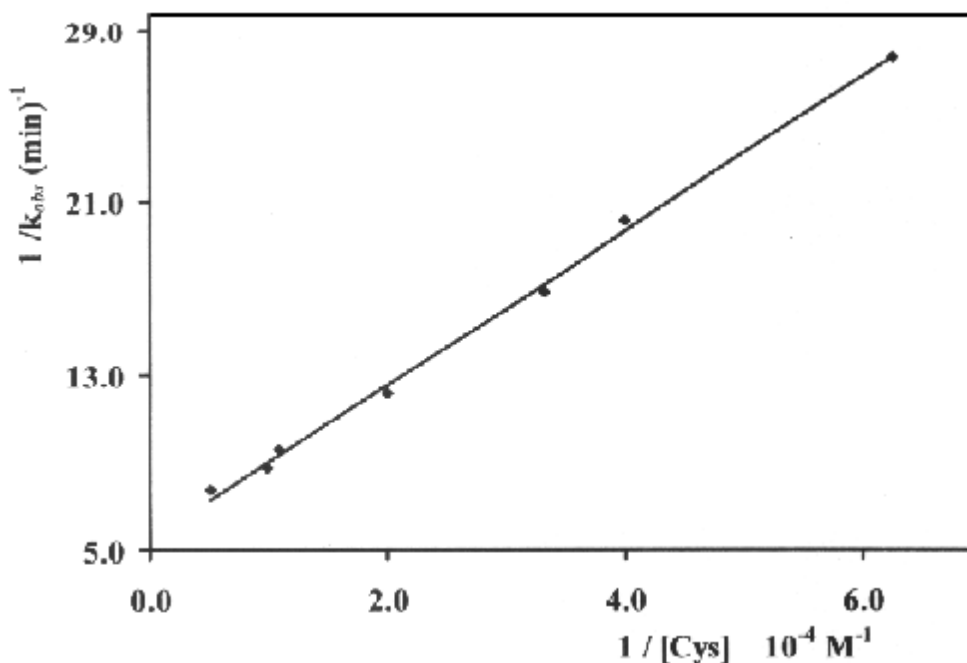


Figure 9: Plot of $1/k_{obs}$ vs. $1/[Cysteine]$ at $\lambda_{max} = 562 \text{ nm}$, $[HFz] = 3 \times 10^{-4} \text{ M}$, $[Fe^{3+}] = 1 \times 10^{-4} \text{ M}$, $t = 28 \text{ }^\circ\text{C}$ and $\text{pH} = 2.70$.

The Dependence of reaction rate on temperature:

The dependence of the reaction rate on temperature was investigated between 32 °C and 68 °C, to control the reaction rate at such high temperature in acidic medium (pH = 2.1). The

values of k_{obs} , were increased linearly by increasing temperature in the above temperature range (Table 2). The data fulfilled Arrhenius equation and allowed us to calculate the thermodynamic parameters (Table 3 and Figure 10).

Table 2: The effect of temperature on the rate of the reaction.

Temp. C°	Temp. K	$1 \times 10^{-3}/T$ (K ⁻¹)	k_{obs} (min) ⁻¹	$-\ln k_{obs}$
68	341	2.931	0.097	2.333
62	336	2.976	0.083	2.485
52	325	3.077	0.063	2.757
42	315	3.175	0.047	3.051
32	305	3.279	0.035	3.352

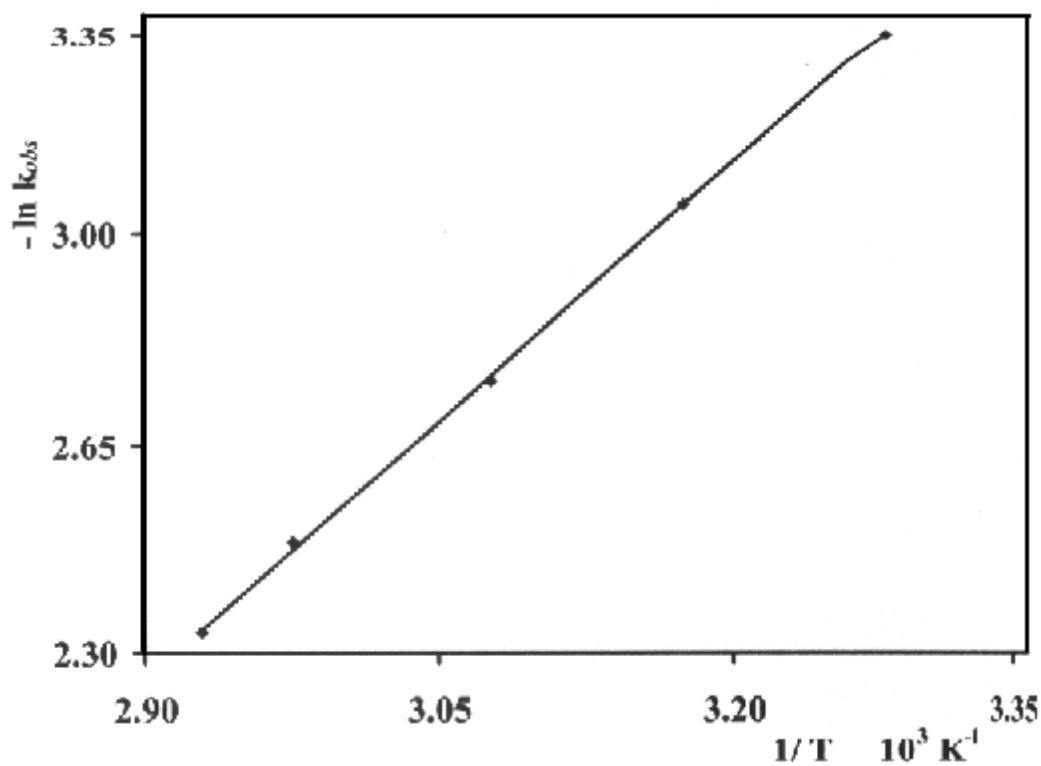


Figure 10: Plot of $-\ln k_{obs}$ vs. $1/T$ (K⁻¹) at $\lambda_{max} = 562$ nm, $[HFz] = 3 \times 10^{-4}$ M, $[Fe^{3+}] = 5 \times 10^{-5}$ M, $[Cysteine] = 1 \times 10^{-4}$ M, $I = 0.05$ M and pH = 2.05.

Table 3: Activation parameters of the rate-determining step calculated from Arrhenius equation by plotting of $-\ln k_{\text{obs}}$ vs. $1/T \text{ K}^{-1}$ at $\lambda_{\text{max}} = 562 \text{ nm}$, $[\text{HFz}^-] = 3 \times 10^{-4} \text{ M}$, $[\text{Fe}^{3+}] = 5 \times 10^{-5} \text{ M}$, $[\text{Cysteine}] = 1 \times 10^{-4} \text{ M}$, $\text{pH} = 2.05$ and Temperature range = $32\text{-}68 \text{ }^\circ\text{C}$.

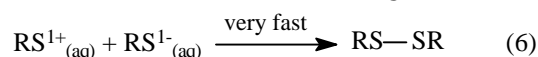
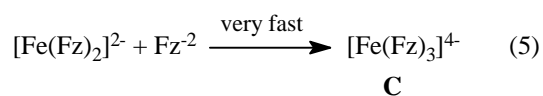
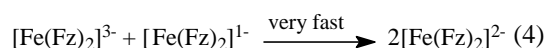
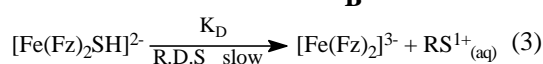
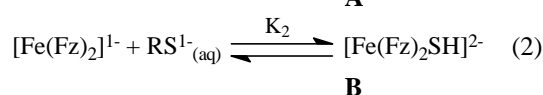
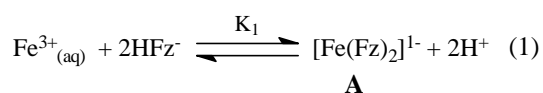
The Activation Parameters	Calculated value
Activation Energy (Ea.)*	24.03 KJ/mol
Entropy (ΔS)*	- 202.03 J/mol
Enthalpy (ΔH)*	21.55 KJ/mol
Gibbs Energy (ΔG)*	81.92 KJ/mol
The equilibrium (K)*	$4.38 \times 10^{-15} \text{ KJ/mol}$

Effect of acrylonitrile as free radical scavenger:

The addition of acrylonitrile to the reaction mixture at 36°C and 60°C did not alter the rate and there was absolutely no polymer detection, showing the absence of free radicals in the reaction mechanism.

The proposed mechanism:

We made every effort depending on the literature and the kinetic observed result to suggest steps illustrated in Scheme 4 formed the mechanism of this oxidation process.



Scheme 4: The proposed mechanism of L-cysteine oxidation processes by $[\text{Fe}^{3+}\text{-Fz}]$ A complex.

The first step is the formation of $[\text{Fe}(\text{Fz})_2]^{1-}$ (A) [1:2] complex between Fe^{3+} and HFz^- ligand. This step was proved stoichiometrically and has been confirmed by separation, solubility and extraction tests. The concentration of Fe^{3+} was low enough to prevent any dimers or hydroxyls

complexes formation. The second step involved the flash charge-transfer-complex $[\text{Fe}(\text{Fz})_2\text{SR}]^{2-}$ formation [1:2:1] B, between Fe^{3+} , Fz and Cysteine respectively. This step was proved also stoichiometrically and provided to be an intermediate. The intermediate B complex in step three decomposed slowly to give the RS^+ and complex product $[\text{Fe}(\text{Fz})_2]^{3-}$. It was suggested to be the rate-determining step [37]. Complex $[\text{Fe}(\text{Fz})_2]^{3-}$ reacted very fast in two more steps (fourth and sixth) to form the final $[\text{Fe}(\text{Fz})_3]^{4-}$ C complex. The charges transfer steps in this mechanism were provided by no free radical detections. The absorbance of C complex formation at $\lambda_{\text{max}} = 562 \text{ nm}$ by function of time has been followed spectrophotometrically in this study. Step six was very fast and provided the disulfide bridge formation (cystine).

Derivation of the rate law:

The following equations have been suggested to derive the rate law of this oxidation process.

$$K_1 = [\text{A}][\text{H}^+]^2 / [\text{Fe}^{3+}][\text{HFz}^-]^2 \quad (1)$$

$$[\text{A}] = K_1[\text{Fe}^{3+}][\text{HFz}^-]^2 / [\text{H}^+]^2$$

$$[\text{A}] = \text{Fe}_T - [\text{Fe}^{3+}] - [\text{B}] \quad (2)$$

$$[\text{B}] = K_2[\text{A}][\text{RS}^-]$$

$$[\text{A}] = \text{Fe}_T - [\text{A}][\text{H}^+]^2 / K_1[\text{HFz}^-]^2 - K_2[\text{A}][\text{RS}^-]$$

$$[\text{A}]K_1[\text{HFz}^-]^2 = \text{Fe}_T K_1[\text{HFz}^-]^2 - [\text{A}][\text{H}^+]^2 - K_2K_1[\text{HFz}^-]^2[\text{A}][\text{RS}^-] \quad (3)$$

$$[\text{A}] = \text{Fe}_T K_1[\text{HFz}^-]^2 / [\text{H}^+]^2 + K_1[\text{HFz}^-]^2 + K_1K_2[\text{HFz}^-]^2[\text{RS}^-] \quad (4)$$

$$\text{Rate} = k_{\text{obs}} [\text{Fe}^{3+}] \quad (5)$$

The rate of the reaction is the rate of the slowest step.

$$\text{Rate} = k_{\text{D}}[\text{B}] \quad (6)$$

$$\text{Rate} = k_{\text{D}}K_2[\text{A}][\text{RS}^-] \quad (7)$$

$$= k_{\text{D}} K_2 [\text{RS}^-] \text{Fe}_T K_1 [\text{HFz}^-]^2 / [\text{H}^+]^2 + K_1 [\text{HFz}^-]^2 + K_1 K_2 [\text{HFz}^-]^2 [\text{RS}^-] \quad (8)$$

$$k_{\text{obs}} = k_{\text{D}} K_2 [\text{RS}^-] K_1 [\text{HFz}^-]^1 / [\text{H}^+]^2 + K_1 [\text{HFz}^-]^2 + K_1 K_2 [\text{HFz}^-]^2 [\text{RS}^-] \quad (9)$$

$$\frac{1}{k_{\text{obs}}} = \left[\frac{1}{[\text{RS}^-] k_{\text{D}} K_1 K_2 [\text{HFz}^-]^2} + \frac{1}{k_{\text{D}} K_2} \frac{1}{[\text{RS}^-]} \right] + \frac{1}{k_{\text{D}}} \quad (10)$$

$$\frac{1}{k_{\text{obs}}} = \left[\frac{[\text{H}^+]^2}{k_{\text{D}} K_1 K_2 [\text{HFz}^-]^2} + \frac{1}{k_{\text{D}} K_2} \right] \frac{1}{[\text{RS}^-]} + \frac{1}{k_{\text{D}}} \quad (11)$$

$$\frac{1}{k_{\text{obs}}} = \left[\frac{[\text{H}^+]^2}{k_{\text{D}} K_1 K_2} \right] \frac{1}{[\text{HFz}^-]^2} + \left[\frac{1}{k_{\text{D}} K_2 [\text{RS}^-]} + \frac{1}{k_{\text{D}}} \right] \quad (12)$$

1) A plot of $1/k_{\text{obs}}$ vs. $1/[\text{RS}^-]$ as in equation (11) was linear with a slope $\{[\text{H}^+]^2 / k_{\text{D}} K_1 K_2 [\text{HFz}^-]^2 + 1/k_{\text{D}} K_2\}$ and an intercept = $1/k_{\text{D}}$. From Figure (9) k_{D} was calculated, it equal 0.024 (min)^{-1} .

2) A plot of $1/k_{\text{obs}}$ vs. $1/[\text{HFz}^-]^2$ as in equation (12) was linear with a slope $[\text{H}^+]^2 / k_{\text{D}} K_1 K_2 [\text{RS}^-]$ and an intercept = $\{1/k_{\text{D}} K_2 [\text{RS}^-]^2 + 1/k_{\text{D}}\}$. From Figure (8) K_2 and K_1 were calculated and it equal 140 and 14.80 respectively.

Conclusion:

Complex $[\text{Fe}(\text{Fz})_2]^{1-}$ has been used as an oxidizing agent in the kinetic oxidation of L-cysteine study in acidic medium under pseudo rate conditions. The molar ratios between iron(III), iron(II) and HFz^- complexes in absence and presence of L-cysteine were determined. The reaction was found to be first-order with respect to iron(III) and L-cysteine, second-order with respect to HFz^- ligand and negative second-order with respect to hydrogen ion concentration. The salts affected the reaction rate while no radical species have been detected when free radical detector was added. The rate-determining step was suggested and the activation parameters were calculated using Arrhenius equation. With a

pre-equilibrium of an adduct formation between L-cysteine and $[\text{Fe}^{3+}\text{-Fz}]$ complex a mechanism and rate law derivation were proposed.

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