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# Kinetic Study on Oxidation of Thiodipropionic Acid by Iron (III)-bipyridine Complex

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## Abstract

Iron(III)-bipyridine complex was prepared and characterized by UV-Visible spectrophotometer. Kinetic study was carried out by using this iron(III)-bipyridine with thiodipropionic acid in aqueous acetonitrile solution. The reaction was optimized by studying the effect on substrate, solvent, oxidant, acidity and temperature. First order, second order rate constants and activation parameters were calculated. The above reaction was found to be second order and proceeded through electron transfer from thiodipropionic acid to iron(III)-bipyridine complex. The product was characterized and confirmed by IR and NMR spectroscopy.

**Keywords**: Thiodipropionic acid, Iron(III)-bipyridine complex, kinetic study of Iron(III)-bipyridyl complexes.

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## 1. Introduction

Thiodipropionic acid plays a vital role in pharmaceutical, food, rubber, cosmetic and soap industry. It is also used as intermediate for the synthesis of organic compounds, colour stabilizer for polymers including poly olefins, preservative in food industry and medicine for hepatic coma and fatty liver diseases[1]. Many researchers have been studied about the oxidation of thiodipropionic acid and its applications. Bobrowski et al., studied oxidation of thiodipropionic acid by hydroxyl radicals [2]. Thiodipropionic acid was also used in Lipase-catalyzed esterification and transesterification reactions[3]. Polypyridyl ligand reacts with different metals (Ir, Ru, Cr, Fe) and forming a complex, which has redox properties[4-7]. Iron(III)-polypyridyl complexes are mild oxidising agents. It is used as oxidant in various organic sulphur compounds such as organic sulphides and organic sulphoxides[7-12]. John Adaikalasamy and co-workers proved that, organic sulphides have higher rate than organic sulphoxides [3]. Substitution of different electron withdrawing /electron donating group on organic sulphides changes the rate of reaction [7]. This creates curiosity to study the kinetics of organic sulphide substituted with two carboxylic acids.

The goal of this work was to prepare Iron(III)-bipyridine complex and study the kinetics of oxidation of thiodipropionic acid . Five different parameters such as effect of substrate, solvent, acidity, oxidant and temperature on its reaction rate were also studied. The spectral studies were used to confirm the products and to propose a possible mechanism for the reaction.

## 2. Experimental

The ligand 2,2′- bipyridine was purchased from Aldrich and used as such without further purification. Iron(II)-bipyridine complex ($[Fe(bpy)_3]^{2+}$) was prepared by following the procedure in the literature [11] and oxidized to Iron(III)-bipyridine ($[Fe(bpy)_3]^{3+}$) by using ammonium hexa nitrato cerium(IV) complex.

### 2.1 Preparation of $[Fe(bpy)_3]^{3+}$ complexes:

Preparation of $[Fe(bpy)_3]^{2+}$ was done as follows: Analar grade ferrous ammonium sulfate (1g, 2.5mM) dissolved in 20ml of water containing 1ml of 0.01N $H_2SO_4$. 2,2′- bipyridine (1.2g, 7.5mM) dissolved in 50ml of hot water and to this 2ml of 1M $HClO_4$is added. To the hot bipyridyl solution, ferrous ammonium sulfate solution was added slowly with stirring followed by sodium perchlorate solution. The reaction mixture was then digested for half an hour in water bath, cooled and filtered. Red coloured crystals of tris (2,2′-bipyridine) iron(II) perchlorate was dried in vacuum. The absorption of the complex in 1M $HClO_4$was measured using HP-diode array UV Visible spectrophotometer and it showed a maximum at 522 nm.

Conversion of $[Fe(bpy)_3]^{2+}$ to $[Fe(bpy)_3]^{3+}$ was done in the following way: Ammonium hexanitrato cerium(IV) (2.8g Analar grade) dissolved in 40 ml of 60% $HClO_4$. It was added to the already prepared tris(2,2′-bipyridine) iron(II) perchlorate kept in ice. Oxidation takes place and the solution turned dark blue. It was kept aside for half an hour to ensure complete oxidation and then sodium perchlorate solution was added. Blue precipitate of tris(2,2′-bipyridine) iron(III) perchlorate was formed. It is filtered and washed with ethanol and ice cold water and dried in vacuum. The absorption of the complex in 1M $HClO_4$ was measured using HP-diode array UV Visible spectrophotometer and it showed a maximum at 618nm.

### 2.2 Kinetic study

The kinetic studies were carried out under pseudo first order conditions with substrate (thiodipropionic acid), $[Fe(bpy)_3]^{3+}$ complex ratio was 10:1. The substrate with all additives except the oxidant was allowed to attain the experimental temperature by keeping them separately in the constant temperature bath. A known volume of $[Fe(bpy)_3]^{3+}$ complex was then transferred to the reaction mixture at zero time and mixed well. The rate of formation of $[Fe(bpy)_3]^{2+}$ complex was followed using the HP-diode array UV-Visible spectrophotometer by measuring the change in the absorbance wavelength 522nm corresponding to $[Fe(bpy)_3]^{2+}$. The

$[Fe(bpy)_3]^{2+}$ complex had molar extinction coefficient of the order of $1\times10^4 M^{-1}cm^{-1}$ in the observed region while the corresponding iron(III)-complex was practically transparent at this wavelength region.

The reaction mixture was kept overnight for product analysis. Then it was mixed with diethylether, the ether layer separated and was treated with anhydrous sodium sulphate. The filtered ether solution was evaporated to get the product. The product was characterized by IR and NMR.

### 2.3 Evaluation of Rate constants:

The pseudo first order rate constant for each run was evaluated from the slopes of linear plots of $\log(a_\infty - a_t)$ versus time according to first order rate equation by method of least squares[13]. The linearity of each fit was confirmed in terms of the values of correlation coefficient and standard deviation.

$$k_1=(2.303/t)\log[(a_\infty-a_0)/ (a_\infty-a_t)]$$

$$k_1=2.303 \times \text{slope (expressed in } s^{-1})$$

Where $k_1$ is pseudo first order rate constant and'$t$' is the time in seconds, $a_0$, $a_t$, $a_\infty$ denote the absorbance at zero time , time t and absorption maximum respectively. The second order rate constant is evaluated from the relation:

$$k_2= k_1/[sub] \text{ in } M^{-1}s^{-1}.$$

## 3. Results and Discussion

Iron(III) bipyridine complex was prepared and used to carry out oxidation reaction. HP-diode array UV –Visible spectrophotometer was employed to record the absorption spectra of Iron(II) and Iron (III)-bipyridine complexes. Absorption maximum($\lambda_{max}$) of $[Fe(bpy)_3]^{3+}$ and $[Fe(bpy)_3]^{2+}$ were 618 nm and 522 nm. These values are well co-ordinated with previous works [10] and [11].

Oxidation reaction was carried out by changing different parameters like substrate, oxidant, acidity, solvent and temperature.

### 3.1 Effect of Substrate Variation

Different concentration of thio dipropionic acid was treated with Iron(III)-bipyridine complex and oxidant($1\times10^{-4}$ M) under the experimental condition of $[H^+]=0.6M$ with suitable solvent ratio ($CH_3CN$=10%; $H_2O$=90%) at 303K. First order and second order rate constants were calculated and given in table1.

Table1: Effect of substrate on first order and second order rate constants

| Substrate Conc ($10^{-3}$ M) | $k_1 \times 10^3$ ($s^{-1}$) | $k_2$ ( $M^{-1}s^{-1}$) |
|---|---|---|
| 2 | 6.60 | 3.30 |
| 3 | 9.80 | 3.27 |
| 5 | 17.9 | 3.40 |
| 7 | 24.60 | 3.32 |
| 10 | 33.67 | 3.30 |
| 12 | 39.96 | 3.33 |

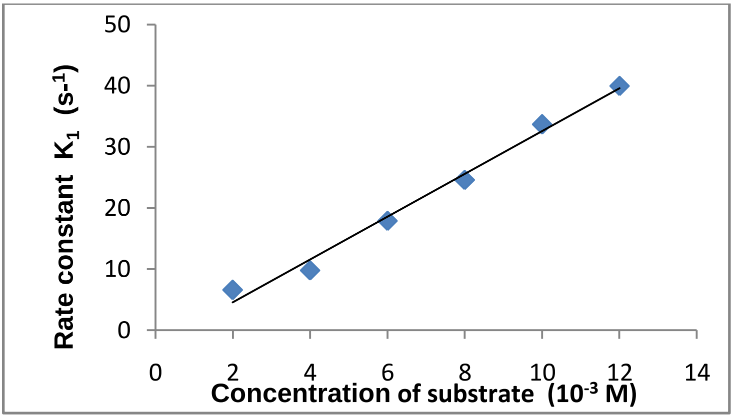

Fig 1 First order dependency with respect to substrate

When concentration of substrate increases, first order rate constant ($k_1$) values increases and second order rate constant ($k_2$) values were constant. First order dependence of substrate was proved by linear plot of $k_1$ versus [substrate] which is given in figure1. This indicates that the reaction was first order with respect to substrate.

### 3.2 Effect of Oxidant Variation

During the variation of oxidant (Iron(III) bipyridine) concentration with specific experimental condition ([Sub]=$5\times10^{-3}$M;$[H^+]$=0.6M; $CH_3CN$:$H_2O$=10:90; Temp=303K)and the results were tabulated in table2. Here, first order rate constant remained constant with different concentrations of the oxidant. From figure 2, plot of time versus 2+log ($a_\alpha$-$a_t$) was found to be linear. These results revealed that, the reaction was first order with respect to oxidant.

Table 2: Effect of oxidant on rate constant(k1)

| Oxidant Conc ($10^{-4}$M) | $k_1 \times 10^3$ ( $s^{-1}$) |
|---|---|
| 1 | 17.000 |
| 2 | 17.100 |
| 3 | 17.102 |
| 4 | 17.170 |

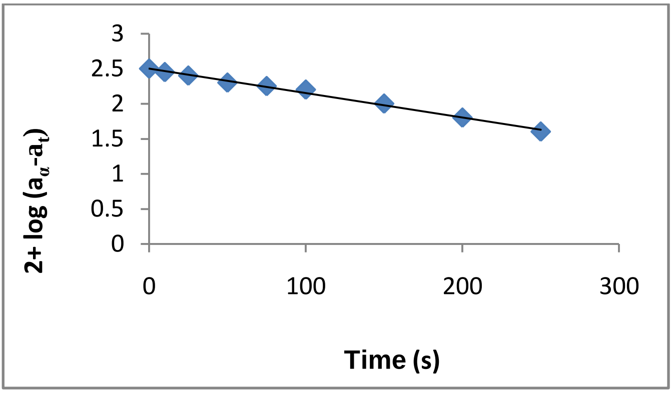

Fig 2 First order dependency with respect to oxidant

Thus oxidation reaction of thiodipropionic acid with iron (III)-bipyridine complex was first order with respect to substrate and first order with respect to oxidant. Thus the order of the reaction was second order.

### 3.3 Effect of Acid Variation

Oxidation reactions were carried out under different concentration of acid under the experimental condition of ([Oxi]=$1\times10^{-4}$M; [Sub]=$2\times10^{-3}$M concentrations; with suitable solvent ratio($CH_3CN$

=10; $H_2O$=90) at 303K and calculated first order rate constant (table 3). Increase in acid concentration, retards the reaction rate.

Table 3: Effect of Acidity on first order rate constants

| $[H^+]$ in M | $k_1 \times 10^3$ ( $s^{-1}$) |
|---|---|
| 0.2 | 30.38 |
| 0.3 | 27.29 |
| 0.5 | 18.68 |
| 0.7 | 6.60 |
| 1.0 | 5.60 |
| 1.2 | 3.69 |

### 3.4 Effect of Solvent Variation

Acetonitrile and water were taken in different ratios with reaction mixture and experiments performed at 303K. Solvent variations increased the rate constant $k_1$ of the reaction, with increase in water content of solvent upto 80%. But further increase in water content from 80% to 100% resulted in decreasing the rate constant due to solvent effect.

Table 4: Effect of acetonitrile to water ratio on rate constant ($k_1$)

| $CH_3CN$ (%) | $H_2O$ (%) | $k_1 \times 10^3$ ($s^{-1}$) |
|---|---|---|
| 90 | 10 | 2.7787 |
| 80 | 20 | 8.6315 |
| 50 | 50 | 11.6610 |
| 30 | 70 | 14.6930 |
| 20 | 80 | 18.1353 |
| 10 | 90 | 6.6000 |
| 0 | 100 | 3.1549 |

### 3.5 Effect of Temperature

Oxidation reaction carried out under different temperatures(303K, 313K, 323K) with specific experimental condition([Sub]=$2\times10^{-3}$M;[Oxi]=$1\times10^{-4}$M;$[H^+]$=0.6M; $CH_3CN:H_2O$=10:90) were studied. It was seen that, first order rate constant increases with increasing temperature.

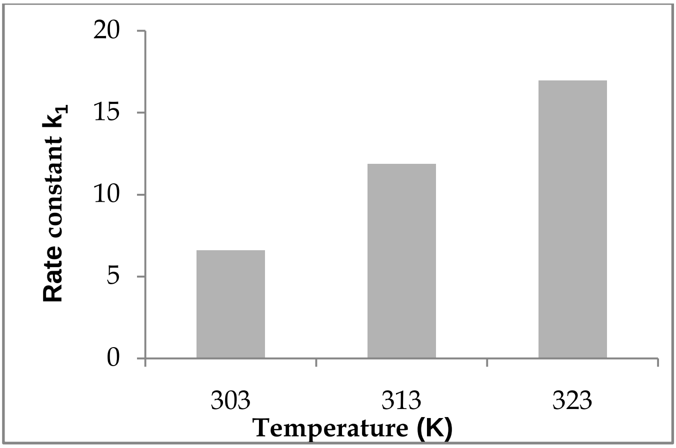

Fig: Effect of temperature on rate constant

### 3.6 Evaluation of Activation Parameters

According to Eyring's equation [13] of transition states the rate constant k of the reaction is given by the equation:

$$k=(k_BT/h)\ e^{-\Delta H^{\neq}}/RTe^{\Delta S^{\neq}}/RT$$

Where $k_B$ is the Boltzmann constant, h is Plank's constant, T is temperature, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are enthalpy and entropy of activation respectively. The activation parameters are calculated by plot of logk/T versus 1/T of the logarithmic form of Eyring's equation,

$$\mathrm{Log}(k/T)= 10.319+(\Delta S^{\neq}/4.576)-(\Delta H^{\neq}/4.576T)$$

$\Delta H^{\neq}$ and $\Delta S^{\neq}$ are calculated from the slope and intercept of the plot respectively. Thus,

$$\Delta H^{\neq} =-4.576 \text{ x slope}$$

$$\Delta S^{\neq} = 4.576 \text{ (intercept-10.319)}$$

Table 5: Enthalpy,Entropy and activation parameters of the reaction

| Second order rate constant $k_2$, $M^{-1} S^{-1}$ | | | $\Delta H^{\neq}$ KCal mol$^{-1}$ | $\Delta S^{\neq}$ Cal k$^{-1}$ mol$^{-1}$ | $\Delta G^{\neq}$ KCal mol$^{-1}$ |
|---|---|---|---|---|---|
| 303 K | 313 K | 323 K | | | |
| 3.30 | 5.93 | 8.49 | 8.3604 | -19.3922 | 14.4333 |

$\Delta H^{\neq}$,-$\Delta S^{\neq}$ and $\Delta G^{\neq}$ values were calculated for that reaction. In Table:6, $\Delta S^{\neq}$ values were negative, which shows the compactness of transition state[5]. The structure change of the substrate depended on $\Delta H^{\neq}$ and $\Delta S^{\neq}$ value. While comparing, $\Delta H^{\neq}$ value was higher than $\Delta S^{\neq}$. These results showed that, the reaction was enthalpy controlled [5]. $\Delta G^{\neq}$ values supported the electron transfer mechanism.

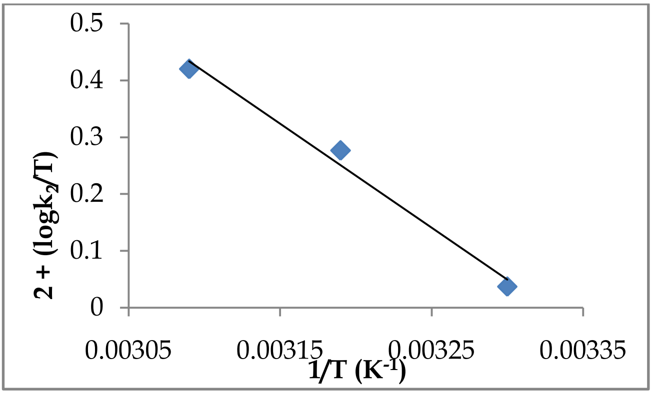

Fig 4: Eyring's Plot

### 3.7 Product Analysis

The product was analyzed by IR and NMR spectra.

In NMR spectra the reactant $S(CH_2\text{-}CH_2\text{-}COOH)_2$ (thiodipropionic acid), showed peak at 2.6 ppm due to proton present in third and fourth carbon and proton present in second and fifth carbon showed peak at 2.5ppm. But in the product, $O{=}S(CH_2\text{-}CH_2COOH)_2$ (sulfoxide) third and fourth carbon showed a small shift in the peak at 2.7 ppm due to the presence of oxygen.

In IR spectra a peak at 1049cm$^{-1}$ confirmed the presence of corresponding sulfoxide.

### 3.8 Mechanism

Based on the kinetic and spectral data, oxidation reaction of thiodipropioic acid with Iron(III)-bipyridine complex, a suitable mechanism was proposed. The formation of isobestic point at 580 nm indicated that, the reaction follows simple kinetics and it did not support any complex mechanism. A mechanism involving single electrontransfer in the rate determining step can be proposed.

$\cdot\cdot S - (CH_2\text{-} CH_2\text{-}COOH)_2 + [Fe(bpy)_3]^{3+} \rightarrow \cdot^{+}S - (CH_2\text{-} CH_2\text{-}COOH)_2$

$+ [Fe(bpy)_3]^{2+}$

$\cdot^{+}S-(CH_2\text{-} CH_2\text{-}COOH)_2 + H_2O \rightarrow \cdot S(OH)-(CH_2\text{-} CH_2\text{-}COOH)_2 + H^+$

$\cdot S(OH)-(CH_2\text{-}CH_2\text{-}COOH)_2 + [Fe(bpy)_3]^{3+} \rightarrow$

$^{+}S(OH)-(CH_2\text{-}CH_2\text{-}COOH)_2 + [Fe(bpy)_3]^{2+}$

$^{+}S(OH)-(CH_2\text{-}CH_2\text{-}COOH)_2 \rightarrow (O)S - (CH_2\text{-} CH_2\text{-}COOH)_2 + H^+$

A mechanism similar to this, has been proposed by Balakumar et al., and confirmed the formation of sulfide radical cation ($S^{\cdot +}$) as the transient for the reaction [10]. Thus our proposal for the formation of $\cdot^{+}S-(CH_2\text{-}CH_2\text{-}COOH)_2$ as the transient of the reaction got support from the experimental observation of similar species using $[Ru(NN)_3]^{3+}$ as the oxidant [5]. Generally the outer sphere oxidants $[Fe(NN)_3]^{3+}$, undergo reaction with electron donors by second order kinetics using rate limiting electron transfer to generate organic radical ions. This second order reaction was also proved by kinetic data.

The formation of sulfoxide as the major product leads us to conclude that the major of sulfide cation radicals are consumed by solvent water. Though decarboxylation and back electron transfer may be competing reactions. When the reaction proceeds through $\cdot^{+}S - (CH_2\text{-}CH_2\text{-}COOH)_2$, there is a chance for the decarboxylation reaction to form $HOOC\text{-}CH_2\text{-}CH_2\text{-}S\text{-}CH_2\text{-}CH_2$. Bobrowski and coworkers have shown that for $\cdot^{+}S - (CH_2\text{-}COOH)_2$ decarboxylation is the major path at low acidic condition[2]. In the same article, they indicated that the radical cation is more stable at high $[H^+]$.

The present work carried out at high $[H^+]$, intermediate was stable. This helped us to exclude the decarboxylation reaction and reversible reaction. Stable intermediate reacted with water to form sulfoxide as the major product. It is pertinent to point out that in the photosensitized $[Cr(NN)_3]^{3+}$ oxidation of $PhSCH_2COOH$ and $PhSCH_2COO^-$ leads to formation of $PhS(O)CH_2COOH$ and $PhSCH_3$ as the products[6]. As the present reaction has been carried out at appreciable [$H^+$], so Sulfide radical cation formed is stabilized at high [$H^+$]. Further the presence of protic solvent is essential for the reaction. In hundred percent acetonitrile the reaction does not proceed. The observed results on solvent effect also support the given mechanism.

## 4. Conclusion

Kinetic study was successfully carried out by thiodipropionic acid with Iron(III)-bipyridine complex(oxidant) in aqueous acetonitrile solution at 303K. When increasing the concentration of the substrate, first order rate constant increased continuously and second order rate constant remained constant. In solvent variation, 80:20 ratio of water and acetonitrile mixture showed maximum rate of reaction. There was no change of rate constant on oxidation variation, but increasing acidity decreased the rate constant. Conversion of product was high at high temperature(323K). Spectral, kinetic and mechanistic study confirmed the electron transfer from thiodipropionic acid to iron(III)bipyridine(oxidant).

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