Redox reactions of iron(III)-polypyridyl complexes with thiodicarboxylic acids: A Kinetic study

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ABSTRACT

Oxidation of thiodicarboxylic acids with iron(III)-polypyridyl complexes depend on the nature of the carboxylic acids and ligands with the Iron complexes. Iron(III)-polypyridyl complexes were prepared and electron transfer reactions have been investigated spectrophotometrically. These complexes were used as oxidant with thiodipropionic acid and thiodiglycolic acid in aqueous acetonitrile medium under pseudo first order condition. Kinetic measurements were used to calculate first and second order rate constant for these reactions. Various reaction parameters, order, stoichiometry, activation parameters of the reactions were determined. The kinetic, spectral and reaction parameters are used to investigate the mechanism of the reaction. IR and NMR spectroscopy are used to confirm the product sulfoxide.

Keywords- Electron transfer reactions, Iron(III)-polypyridyl complexes, Kinetic study, Redox reactions, Thiodicarboxylic acids.

I.INTRODUCTION

In recent years, sulfur-cantered radicals and radical cations were given much attention due to the importance of this intermediate in organic synthesis, environmental and biological studies. Organo sulfur compounds are present in all living systems, foods, and acidic volcanoes and deep inside the ocean. It is considered as valued reagents and mainly used for synthesizing new compounds. One of the most important organo sulfur compound is thiodicarboxylic acids. It is used as intermediate in pharmacology and raw material in polymer industry, reducing agent, additive for electro plastics and analytical reagent. Oxidation of different organo sulfur compounds like organic sulfides [1, 2,3], sulfur containing amino acids [4, 5], sulfoxides [6,7] were already studied in the presence [1, 3] and absence of the catalyst [2, 6, 8, 9]. Photo-chemically assisted reactions were also reported [4, 5, 7].

Different varieties of oxidants are used for oxidation. But transition metal with different organic ligands plays a crucial role in the oxidation reaction [1-11]. Polypyridyl complexes with different metals like Fe [1-3, 6, 8, 9], Ru [4, 5, 7, 9], Ir [10], Au [12, 13], Rh [14,15] were already studied. Metal polypyridyl complexes were mainly used for electron transfer reactions [1-11] and biological studies [12-15]. Iron is an inexpensive and highly active metal among transition metals. Flora et al observed that tris(polypyridy1) complexes of Fe(III) showed ten times higher rate constant than Ir Complex [9]. Most of the kinetic studies explained the role of alkyl or aryl

substituent's on organic sulfide and sulfoxide [1-3,6,7]. Balakumar et al explained the effect of electron withdrawing and electron donating group present in the alkyl aryl organic sulfide with respect to rate constant [2]. Effect of substituents of the organic sulfide/sulfoxide and structure of polypyridyl ligand shows great influence on the rate constant [6]. Thiodicarboxylic acid derivatives were used for transesterification, esterification and oxidation reactions [16, 17]. To the best of our knowledge, a comparative study of number of alkyl group on thiodicarboxylic acid with rate constant is not yet studied.

Fe^{3+}/Fe^{2+} is responsible for vital biological reactions. For clear understanding of electron transfer reactions in biological system, iron(III)-polypyridyl complexes have been synthesized as model compounds and used as electron acceptors. Recently iron polypyridyl complexes have been identified as potential anticancer drug by inhibiting the cancer cell proliferation [2016].To understand the role of oxidation reduction properties of iron(III)-polypyridyl complexes, the kinetic study was done with two different thiodicarboxylic acids like thiodipropionic acid and thiodiglycolic acid. On the basis of various activation parameters and rate constants, a suitable mechanistic path is proposed.

II. EXPERIMENTAL

2.1. Materials

Analar grade ferrous ammonium sulfate, Ligands 2,2'- bipyridine and 1,10 phenanthroline, Thiodipropionic acid, Thiodiglycolic acid were purchased from Aldrich and used as such without further purification. Iron(III)-polypyridyl complexes were prepared by the standard protocol[6].

Iron(II)-polypyridyl complexes were prepared by mixing ferrous ammonium sulfate solution and the hot ligand solution (2,2'- bipyridine/ 1,10 phenanthroline)followed by the addition of sodium perchlorate solution. The reaction mixture is then digested for half an hour in water bath, cooled and filtered. Red coloured crystals of iron(II)-polypyridyl complexes were obtained and it dried in vacuum.

Iron(II)-polypyridyl complexes were converted into iron(III)-polypyridyl complexes by the addition of ammonium hexanitrato cerium(IV) in 40ml of 60% $HClO_4$ or PbO_2 solution in ice bath. Complete oxidation happened within half an hour and then sodium perchlorate solution is added. Blue precipitate of iron(III)-polypyridyl complexes were filtered and washed with ethanol and icecold water and dried in vacuum.

2.2. Kinetic Measurement

The absorption spectra of $[Fe(phen)_3]^{3+}$and $[Fe(bpy)_3]^{3+}$ complexes were obtained using a HP-diode array UV Visible spectrophotometer. The reaction between the iron(III)- polypyridyl complexes and thiodicarboxylic acids was monitored by following the increase in absorbance of $[Fe(phen)_3]^{2+}$ at 510 nm and $[Fe(bpy)_3]^{2+}$ at 522 nm at definite time intervals at 303 K. Fe(III)-poypyridyl complexes are transparent at these wavelength regions and Fe(II)-polypyridyl complexes have high molar extinction coefficients of the order $1 \times 10^4 M^{-1}cm^{-1}$ [6].Thiodicarboxylic acid and iron(III)-polypyridyl complex was taken in 10:1 ratio in aqueous acetonitrile under pseudo first order conditions. Initially in the absence of oxidant, the substrates with all additives were

taken in a required constant temperature bath. Calculated volume of $[Fe(NN)_3]^{3+}$ complexes were transferred to the reaction mixture, shaken well and absorbance was measured.

First and second order rate constants were calculated using the corresponding rate equations.

$$k_1 = \frac{2.303}{t} \log \frac{a_\infty - a_t}{a_\infty - a_0}$$

$$k_1 = 2.303 \times \text{slope} \quad (5)$$

$$k_2 = \frac{k_1}{[\text{sub}]} \quad \quad \quad \quad (6)$$

where k_1 is pseudo first order rate constant and t is the time in seconds, a_0, a_t, a_∞ denote the absorbance at time zero, t and absorption maximum respectively. The plot of log $(a_\infty - a_t)$ vs time gave a linear line and first order rate constant k_1 was calculated by least square method. Second order rate constant k_2 was calculated using equation (6).

Activation parameters were calculated from Eyring's equation (7),

$$k = \frac{k_B T}{H} e^{-\Delta H^{\neq}/RT} e^{\Delta S^{\neq}/RT} \quad (7)$$

$$\log \left(\frac{k}{T} \right) = 10.319 + \Delta S^{\neq}/4.576) - (\Delta H^{\neq}/4.576T) \quad (8)$$

Where k_B is the Boltzman constant, h is Plank's constant, T is temperature, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are enthalpy and entropy of activation respectively. Plot of log k/T vs 1/T of the logarithmic form of Eyring's equation, gave linear line. $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were evaluated by the least square method.

III. RESULTS AND DISCUSSION

Two different iron(III)-polypyridyl complexes were prepared and used to oxidize two different thiocarboxylic acids, whose structure and abbreviations were given in Chart I.

The prepared iron(III)-poypyridyl complexes (oxidants) dissolved in 1M $HClO_4$, showed an absorption maximum at 600 and 618 nm for $[Fe(phen)_3]^{3+}$ and $[Fe(bpy)_3]^{3+}$ respectively, which were well correlated with the previous results [1, 2, 6].

$[Fe(phen)_3]^{3+}$

I

$[Fe(bpy)_3]^{3+}$
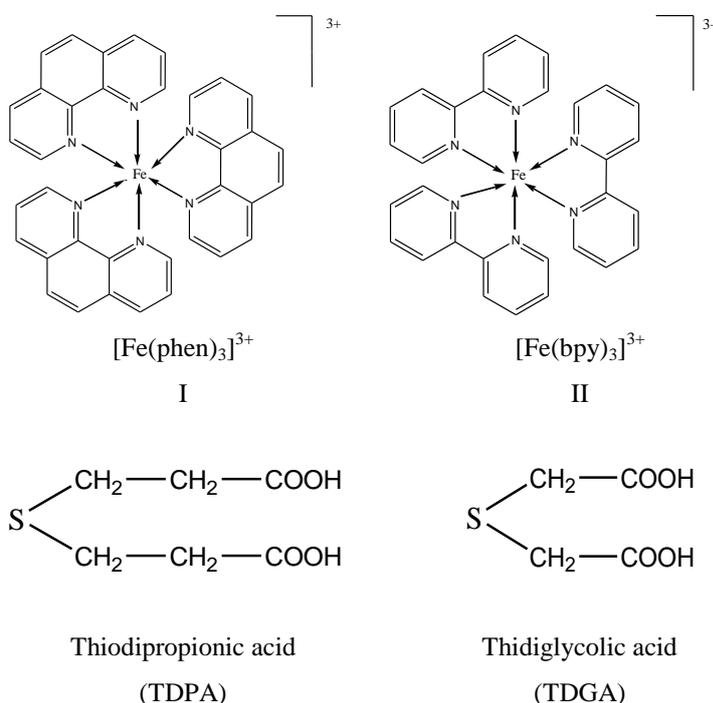
II

Thiodipropionic acid

(TDPA)

Thidiglycolic acid

(TDGA)

Chart I. Structure of iron(III)-polypyridyl complexes and thiodicarboxylic acids

During the kinetic run, $[Fe(phen)_3]^{2+}$ and $[Fe(bpy)_3]^{2+}$ complexes were studied spectrophotometrically by monitoring the increase in the absorption wavelength of Fe(II) complexes (Figure 1 and 2).
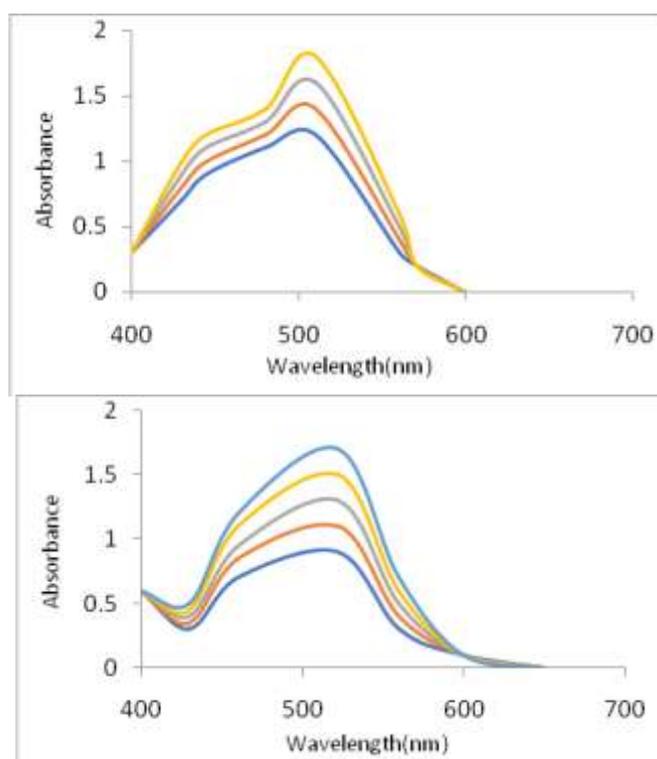
Figure 1. Increase of absorption of $[Fe(phen)_3]^{2+}$ in aqueousacetonitrile at 303K at a time interval of 60 s.

Figure 2. Increase of absorption of $[Fe(bpy)_3]^{2+}$ in   aqueous acetonitrile at 303K at a time interval of 60 s

First order and second order rate constants of these redox reactions were calculated using equation (5) and (6) at different substrate concentration and are shown in Fig. 3 and 4. Generally in all the four reactions, first order rate constant (k_1) increases with increasing substrate concentrations. Second order rate constant (k_2) remains constant with various substrate concentrations. This showed all the reactions were first order with respect to substrate. The first and second order rate constant for all the reactions were in the following order,
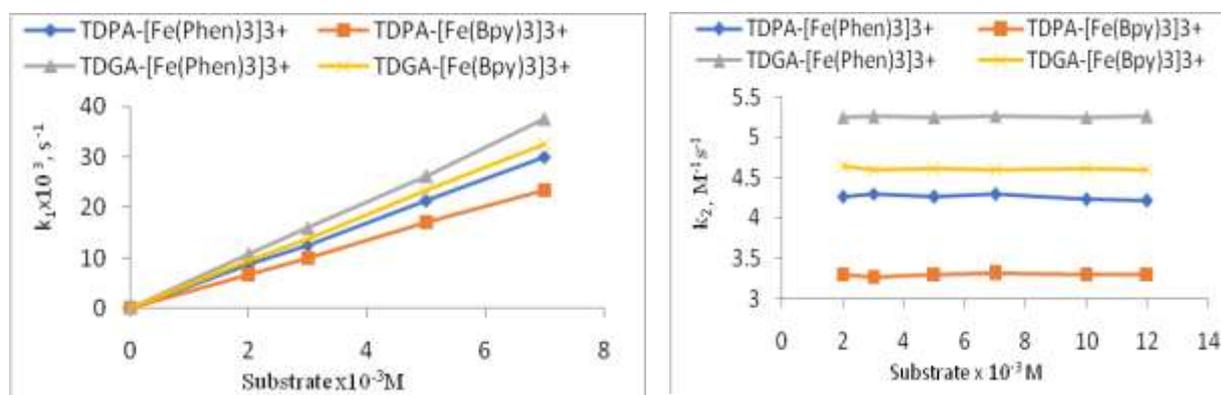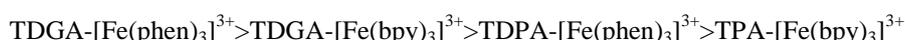
$$TDGA-[Fe(phen)_3]^{3+} > TDGA-[Fe(bpy)_3]^{3+} > TDPA-[Fe(phen)_3]^{3+} > TPA-[Fe(bpy)_3]^{3+}$$

Figure 3. Plot of k_1 vs [substrate] for the oxidation of TDPA/TDGA with $[Fe(phen)_3]^{2+}/[Fe(bpy)_3]^{3+}$ in aqueous acetonitrile (90:10v/v) at 303K.

Figure 4. Plot of k_2 vs [substrate] for the oxidation of TDPA/TDGA & $[Fe(phen)_3]^{2+}/[Fe(bpy)_3]^{3+}$ with acid$[H^+]=(0.6M)$ in aqueous acetonitrile (90:10v/v) at 303K.

Among all these reactions, thiodiglycolic acid showed higher rate than thiodipropionic acid. Dicarboxylic acids present in beta position to sulfur atom increases the rate of reaction than gamma position. Here number of alkyl groups between sulfur atom and carboxylic acids play a major role. Less number of alkyl group shows higher rate constant. As the number of alkyl group increases, rate constant decreases. It was observed that, electron with drawing groups like COOH substituted on alkyl aryl organic sulfide reduces the rate constant of the reaction [2].

At the same time, nature of ligand also gets important role in reaction rate. From the results, phenanthroline ligand complex shows higher rate than bipyridine ligand complex. This is because of the hydrophobic nature of phenanthroline ligand complex. Similar results were observed in oxidation of organic sulfides and sulfoxides [1-3, 6, 9]

Variation of oxidant concentration was studied with different volume of oxidant on the kinetics of these oxidation reactions. It was found that as the concentration of oxidant increases, the rate constant (k_1) remained constant for all the four reactions (Fig. 5). Plot of 2+ log (a_x-a_o) and time (t) give a linear plot (Fig. 6) which indicates that all the reactions were first order with respect to oxidant. Over all order of the reaction was found

to be two, while it is first order with respect to substrate and first order with respect to oxidant. In recent study, increase of oxidant concentration leads to decrease in rate of reaction due to the conversion of oxidant into oxo bridged diiron complex [8].
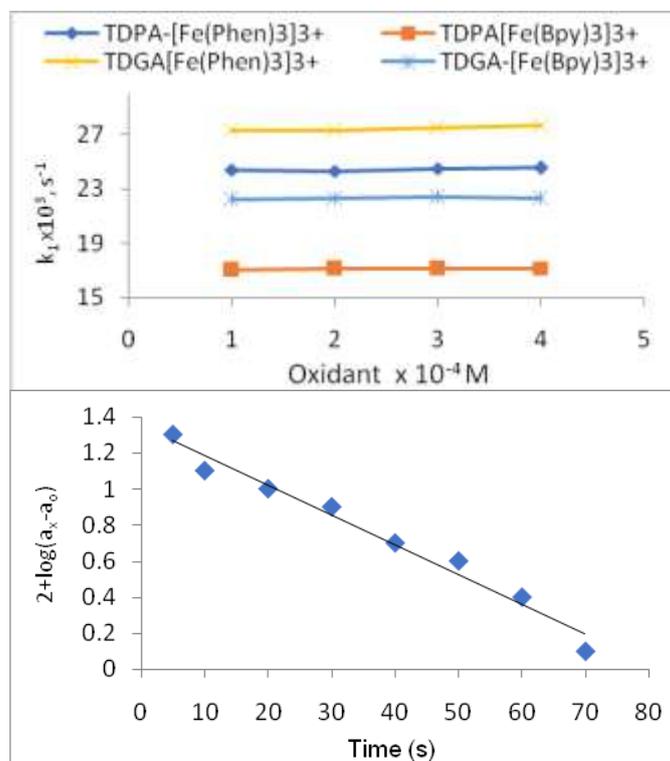

Figure 5. Variation of oxidant concentration with rate constant, TDPA and TDGA($5x10^{-3}$M) with acid$[H^+]=(0.6M)$ in aqueous acetonitrile (90:10v/v) at 303K.

Figure 6. Plot of $2+\log(a_x-a_o)$ vs Time for TDPA vs $Fe(bpy)_3]^{3+}$.

To study the influence of acidity on the reaction rate, different concentrations of $[H^+]$ ions were used in the kinetic study. The observed results are shown in Table 1. Less H^+ ionic environment favors the reactions while high H^+ ion concentration retarded first order rate constants, which is in agreement with already reported one [1, 6,7]. TDGA-$[Fe(phen)_3]^{3+}$ reaction shows higher rate constant in low $[H^+]$ concentration and TDGA-$[Fe(bpy)_3]^{3+}$ reaction shows the least value for the first order rate constant.

Table 1. Effect on first order rate constant with $[H^+]$ and solvent composition for the oxidation of TDPA/TDGA with $[Fe(phen)_3]^{3+}/[Fe(bpy)_3]^{3+}$ at 303K.

$[H^+]$ (M)	$k_1 \times 10^3$ (s^{-1})				CH$_3$CN (%)	$k_1 \times 10^3$ (s^{-1})			
	TDPA		TDGA			TDPA		TDGA	
	$[Fe(phen)_3]^{3+}$	$[Fe(bpy)_3]^{3+}$	$[Fe(phen)_3]^{3+}$	$[Fe(bpy)_3]^{3+}$		$[Fe(phen)_3]^{3+}$	$[Fe(bpy)_3]^{3+}$	$[Fe(phen)_3]^{3+}$	$[Fe(bpy)_3]^{3+}$
0.2	35.3±0.06	30.3±0.08	38.9±0.08	26.5±0.03	90	9.8±0.02	2.7±0.08	5.3±0.01	8.2±0.04
0.3	29.7±0.01	27.2±0.09	22.0±0.01	19.1±0.02	80	12.5±0.07	8.6±0.03	7.0±0.02	9.3±0.04

0.5	14.7±0.09	18.6±0.08	15.0±0.03	15.0±0.01	50	16.2±0.05	11.6±0.06	11.6±0.09	13.8±0.07
0.7	8.5±0.02	6.6±0.01	10.4±0.01	9.3±0.04	30	24.6±0.04	14.6±0.09	12.7±0.01	17.7±0.06
1.0	7.5±0.01	5.6±0.01	9.7±0.01	8.3±0.03	20	27.30.01	8.1±0.04	16.3±0.09	21.9±0.03
1.2	6.8±0.01	3.6±0.09	6.90.02	7.8±0.09	10	9.1±04	6.6±0.01	10.7±0.06	9.3±0.02
					0	4.31	3.1±0.05	8.2±0.01	5.2±0.03

In order to understand the influence of solvent on the reaction rate, the kinetics of the reaction has been studied at different solvent composition and the results are tabulated in Table 1. Different ratios of acetonitrile and water were selected for performing the reaction. When the amount of acetonitrile decreases, the rate of the reaction increases up to 20% of acetonitrile –water mixture. This can be attributed to the charge development on the substrate in the transition state, because of the high - water content [7]. In 10% composition there is a decrease in the rate of the reaction. This can be due to the high dilution which separates the reactants and retards the reaction rate.

Temperature always induces the rate of the reaction and thus the rate constant k_1. The reaction was conducted at three different temperatures with a difference of 10 K and evaluated the rate constant (Fig. 7). Rate constant was maximum at 323 K compared to 303 K. Phenanthroline ligand complex with TDGA and TDPA showed higher rate constant than bipyridine ligand complex.
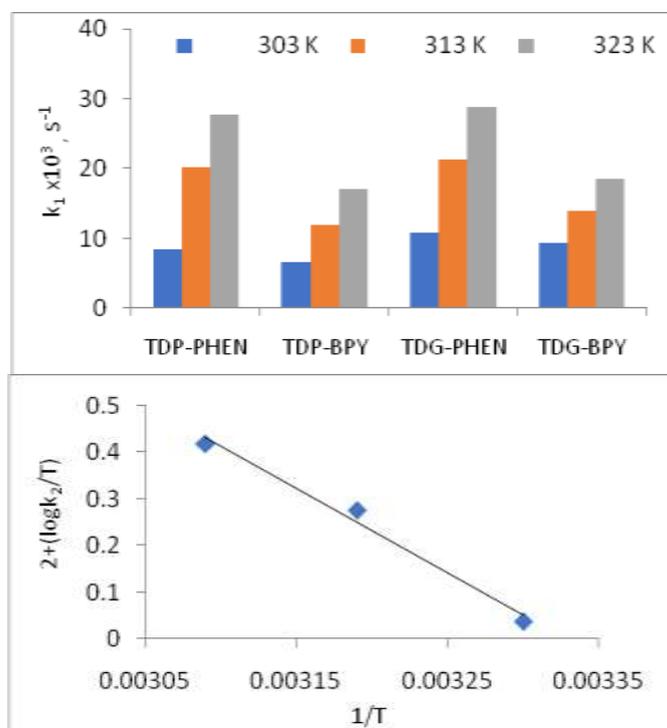

Figure 7. Rate constant at various temperature for theoxidation of TDPA/TDGA vs $[Fe(phen)_3]^{2+}/[Fe(bpy)_3]^{3+}$ with acid$[H^+]$=(0.6M) in aqueous acetonitrile (90:10 v/v)at 303K.
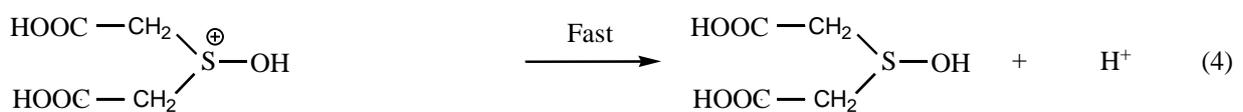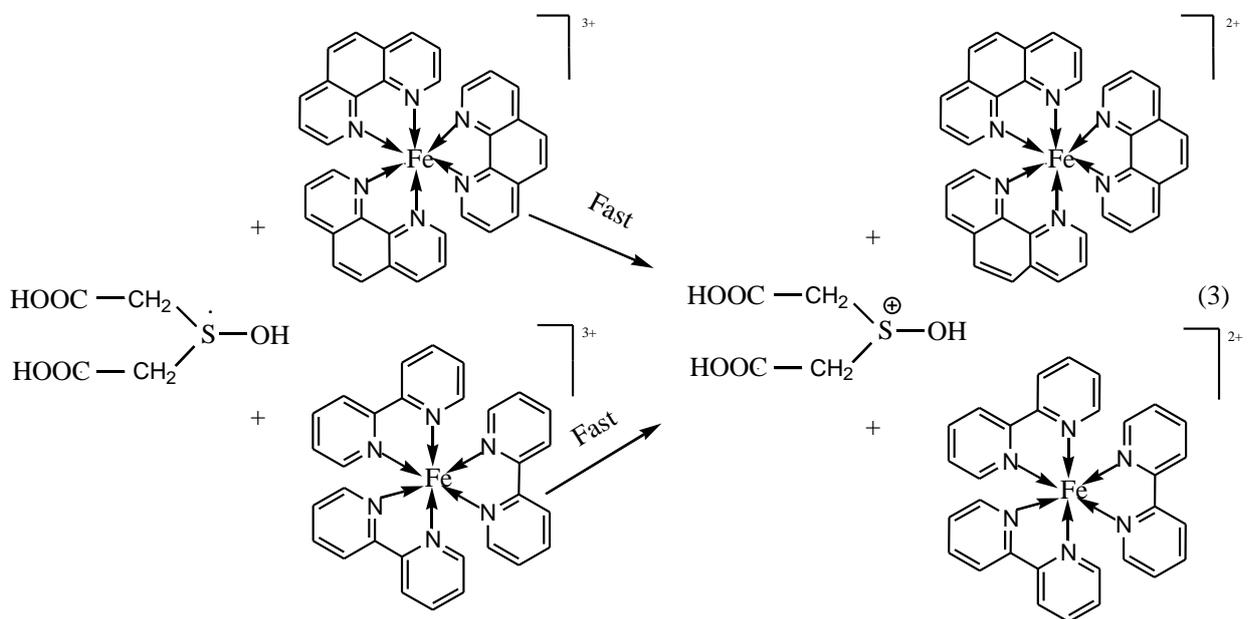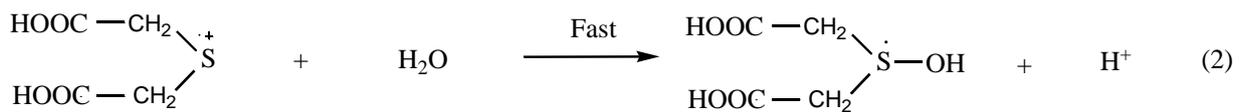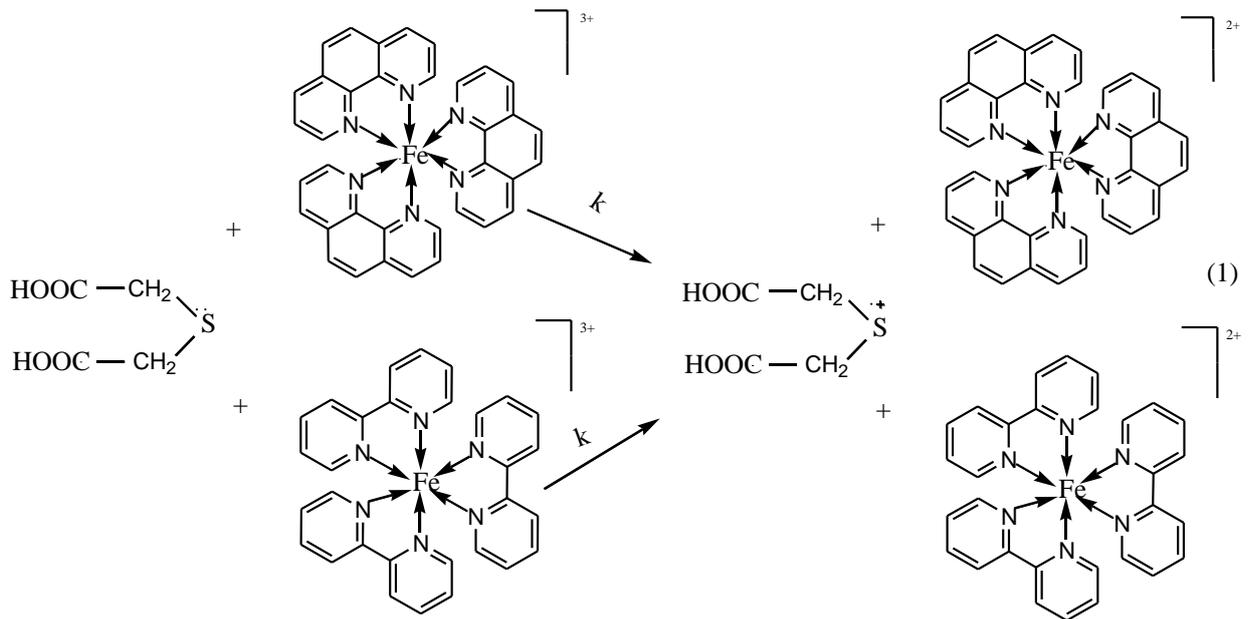
Figure 8. Eyring's plot for TDGA with $[Fe(phen)_3]^{3+}$.

Activation parameters were calculated for the redox reactions of TDPA and TDGA with iron(III)-polypyridyl complexes at three different temperatures (Table 2). Activation parameters such as $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were calculated from Eyring's plot, $2+\log k_2/T$ vs $1/T$ (Fig. 8). $\Delta G^{\neq}$ values were calculated from $\Delta H^{\neq}$ and $\Delta S^{\neq}$ and given in Table 2. The negative values of $\Delta S^{\neq}$ indicate the compactness of transition state [4] and suggest extensive solvation and disorder arrangement of products over reactants in the rate determining step [8]. Based on the structure of the thiodicarboxylic acid, there is a change in the $\Delta H^{\neq}$, i.e., the reaction was enthalpy controlled [7]. A constant $\Delta G^{\neq}$ values in these reactions indicates that they followed a similar electron transfer mechanism in which electron is transferred from reactant to oxidant [4].

Table 2. Values of $\Delta H^{\neq}$, $-\Delta S^{\neq}$, $\Delta G^{\neq}$ for the oxidation of TDPA/TDGA with $[Fe(phen)_3]^{2+}/[Fe(bpy)_3]^{3+}$ in aqueous acetonitrile (90:10v/v) at 303K, 313K and 323K.

REACTANTS	k_2, M^{-1} s^{-1}			$\Delta H^{\neq}$ k cal mol^{-1}	$-\Delta S^{\neq}$ cal K^{-1} mol^{-1}	$\Delta G^{\neq}$ k cal mol^{-1}
	303K	313K	323K			
TDP-PHEN	4.2±0.06	10.1±0.03	13.8±0.02	10.5±0.08	11.4±0.05	14.1±0.06
TDP-BPY	3.3±0.01	5.9±0.03	8.4±0.09	8.3±0.06	19.3±0.09	14.4±0.03
TDG-PHEN	5.3±0.08	10.6±0.08	14.4±0.02	8.7±0.06	17.0±0.04	14.0±0.09
TDG-BPY	4.6±0.07	6.9±0.08	9.2±0.03	5.8±0.07	26.9±0.05	14.3±0.01

The above kinetic study helps to investigate the mechanistic path way of redox reaction between iron(III)-bipyridyl complexes and thiodicarboxylic acids. The misobesticechanism of the redox reactions are shown in Equations. (1) - (4). Thiodiglycolic acid reacted with iron(III)-bipyridyl complexes, to give organic sulfur radical cation and iron(II)-bipyridyl complexes in the rate determining step (Equation 1). Formation of iron(II)-bipyridyl complexes were confirmed by spectral data (Fig. 1 and 2.). It also showed the isosbestic point at 580nm and 600nm. It revealed that, there is a direct single electron transfer from iron(III)-bipyridyl to iron(II)-bipyridyl complex and no intermediate formation [6].

Scheme 1. Mechanism for the reaction between thiodiglycolic acid and$[Fe(phen)_3]^{3+}/[Fe(bpy)_3]^{3+}$.

A mechanism similar to this has been proposed [1, 4] and confirmed the formation of sulfide radical cation ($S^{.+}$) as the transient for the reaction. Sulfur radical cation, further reacted with water from solvent and provided hydroxyl sulfuranyl radical (Eqs. 2). This was confirmed by the solvent variation study. The presence of aqueous solvent is essential for the reaction to proceed. In 100 % acetonitrile the reaction does not proceed. The observed results on water acetonitrile mixture also support the given mechanism.

This hydroxyl sulfuranyl radical reacted with second molecule of the oxidant and formed hydroxyl sulfuranyl cation (Eqs. 3). This was supported by stoichiometric study. In stoichiometric study substrate and oxidant ratio is 1:2. Liberation of H^+ gave sulfoxide as final product (Eqs. 4). The product sulfoxide was confirmed by NMR and IR spectral studies.

Thiodicarboxylic acids can undergo decarboxylation or back electron transfer reactions. When the reaction proceeds through $^{.+}S–(CH_2-CH_2-COOH)_2$, there is a chance for the decarboxylation reaction to form HOOC-$CH_2-CH_2-S-CH_2-CH_3$. Krzysztof Bobrowski and coworkers have shown that for $^{.+}S–(CH_2-COOH)_2$ decarboxylation is the major path at low acidic condition [17]. They also indicated that the radical cation is more stable at high $[H^+]$. The present work was carried out at high $[H^+]$, thus intermediate was stable. This helped to exclude the decarboxylation and reversible electron transfer reaction. Stable intermediate reacted with water to form sulfoxide as the major product.Generally, the outer sphere oxidants $[Fe(NN)_3]^{3+}$, undergo reaction with electron donors by second order kinetics and rate determining step is electron transfer from substrate to oxidant and formation of organic radical ions. This wasconfirmed by kinetic data.

Stoichiometry study of the reaction was determined by mixing the thiodicarboxylic acid with oxidant in three different ratios like 1:1, 2:1 and 1:2. Higher rate constant was shown by 2:1 ratio, which indicates that the reaction consumes two molecules of oxidant with one molecule of thiodicarboxylic acid.

$$HOOC-_n(H_2C) \diagdown S \diagup _n(H_2C)-COOH \; + \; 2Fe[(NN)_3]^{3+} \; + \; H_2O \longrightarrow HOOC-_n(H_2C) \diagdown S=O \diagup _n(H_2C)-COOH \; + \; 2Fe[(NN)_3]^{2+} \; + \; 2H^+$$

In product analysis, iron(III)-polypyridyl complexes and thiodicarboxylic acids were mixed under the experimental condition and kept for overnight. Inorganic products iron(II)- polypyridyl complexes were measured by spectrophotometrically. Organic product was separated by mixing with diethylether and treated with anhydrous sodium sulfate. Ether layer was evaporated to get the product. The product was confirmed by comparing its melting point of sulfoxide and NMR and IR spectra. In NMR Spectra, two peaks were observed at 2.566 and 2.685 ppm. In IR spectra a peak at 1049 cm^{-1} confirms the presence of corresponding sulfoxide.

IV.CONCLUSION

Kinetic study of the above redox reaction reveals the single electron transfer from thiodicarboxylic acid to iron(III)- polypyridyl complex. Spectrophotometric study shows all the four reactions were second order and the stoichiometry ratio of oxidant and reactant was 2:1. For all the reactions, first order rate constant (k_1) was high at higher substrate concentration, higher temperature and low $[H^+]$ in aqueous acetonitrile. Electron transfer from substrate to oxidant in all the reactions were proved by constant $\Delta G^{\neq}$ values.

V. ACKNOWLEDGEMENTS

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