

Role of Iron(III)-salen Chloride as Oxidizing Agent with Thiodiglycolic Acid: The Effect of Axial Ligands

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Abstract. The sulfoxidation of thiodiglycolic acid with iron(III)-salen chloride, which acts as an oxidizing agent without any terminal oxidant, in 50% aqueous acetonitrile medium has been studied. A substantial red shift in the λ_{max} value of Fe^{III}-salen was observed in aqueous medium. The spectrophotometric kinetic study indicates that [Fe^{III}(salen)]⁺ is the active oxidizing species and the reaction follows Michaelis-Menten kinetics with respect to the substrate. The rate of the reaction is highly sensitive to the medium. A reaction mechanism involving electron transfer from sulfur atom of thiodiglycolic acid to the central iron atom of [Fe^{III}(salen)]⁺ is proposed. The presence of nitrogenous bases like pyridine, imidazole and 1-methylimidazole shows a retarding effect on the reaction rate. This can be explained on the basis of binding of these ligands to the coordination sphere of [Fe^{III}(salen)]⁺ prior to the reaction with the substrate. The observed order of reactivity, pyridine > 1-methylimidazole > imidazole, is in accordance with the inverse of π -donating ability of nitrogen bases.

Key words: Thiodiglycolic acid, Iron(III)-salen, Nitrogenous bases, Michaelis-Menten kinetics, Sulfoxidation.

Resumen. En este trabajo se estudia la sulfoxidación del ácido tiodiglicólico con cloruro de Fe(III)-salen, que actúa como agente oxidante en un medio 50% acetonitrilo-agua. Se observa un desplazamiento importante hacia el rojo del valor del λ_{max} del Fe(III)-salen en medio acuoso. El estudio cinético espectrofotométrico indica que el [Fe(III)(salen)]⁺ es la especie oxidante activa y que se sigue una cinética Michaelis-Menten, con respecto al sustrato. La velocidad de reacción es altamente sensible a la composición del medio de reacción. Se propone un mecanismo de reacción que considera la transferencia de un electrón del átomo de azufre del ácido tiodiglicólico al átomo de hierro central del [Fe(III)(salen)]⁺. La presencia de bases nitrogenadas como piridina, imidazol y 1-metil-imidazol provocan una disminución de la velocidad de reacción. Este efecto puede ser explicado por la entrada de estas bases a la esfera de coordinación del [Fe(III)(salen)]⁺, previo a la reacción con el sustrato. El orden de reactividad observado, piridina > 1-metil-imidazol > imidazol es inverso al efecto donador- π de las bases nitrogenadas.

Key words: Ácido tiodiglicólico, Fe(III)-salen, bases nitrogenadas, cinética de Michaelis-Menten, sulfoxidación.

Introduction

Salen complexes are a versatile and standard system and are generally used as effective catalysts with terminal oxidants such as iodosylarenes, H₂O₂, NaOCl, NaIO₄ and peracids [1-5] and in a variety of oxotransfer reactions like enantioselective epoxidation of non-functionalized alkenes [6-9], sulfoxidation [10-16], oxidative polymerization [17], oxygenation reactions of hydrocarbons [18-20], oxidation of several other substrates and other processes [21-28]. In these reactions a high degree of stereoselectivity was achieved by the introduction of proper chiral ligands in the complex. Rajagopal and co-workers [29, 30] have studied the detailed mechanism of oxygenation of organic sulfides and sulfoxides with Fe^{III}-salen complexes as catalyst in H₂O₂ oxidation. Fe^{III}-salen complexes were developed as group transfer catalysts in cyclization and oxidation reactions [31].

The catalytic activity of Fe^{III}-salen complexes was enhanced significantly when they were encapsulated with molecular sieves [32] and zeolites [33-35], anchored with clay [36], covalently supported with polymer matrix [37-39] and intercalated into host molecules [40]. Poly(iron-salens) exhibit electrocatalytic properties [41-43] in the reduction of oxygen and hydrogen peroxide.

Besides their catalytic activity, Fe^{III}-salen derivatives act as

potential anti-tumour agents that affect cell viability and induce strong apoptotic activity [44]. Hilt et al. [45] have shown that Fe^{III}-salen complexes minimize the formation of polymerization side products in the ring expansion reactions of epoxides. An electroactive bromide-PVC - iron(III)-salen membrane is found to possess sensor activity [46]. Wang and co-workers have developed bio sensing electrodes for glucose and uric acid on the basis of interaction between Fe(salen)⁺ and glucose oxidase, uricase respectively [47-50].

Although iron(III)-salen complexes were used as versatile catalysts in many type of reactions with terminal oxidizing agents no work has been reported in the literature in which iron(III)-salen complex itself acts as an oxidizing agent. However, the kinetics of oxidation of L-cysteine by iron(III), cobalt(III) and chromium(VI) complexes of salicylaldiminato ligands in aqueous medium have been reported recently by Hamzeh et al. [40]. In the preliminary work it was interesting to find that iron(III)-salen reacts itself with thiodiglycolic acid even in the absence of any terminal oxidizing agents. Hence, a systematic study on the oxidation of thiodiglycolic acid (TDGA) by iron(III)-salen chloride as oxidant in the absence of other terminal oxidants was undertaken in aqueous acetonitrile medium. The effects of ligand bases like pyridine, imidazole and 1-methylimidazole on the oxidation are also examined and are reported herein.

Results

The overlay spectrum of the decrease in absorbance of iron(III)-salen at different time intervals for a reaction mixture containing TDGA ($5 \times 10^{-2} \text{ mol dm}^{-3}$) and $2 \times 10^{-4} \text{ mol dm}^{-3}$ of iron(III)-salen chloride is shown in Fig. 1. Since the reaction is carried out under pseudo first-order condition with large excess of TDGA, the observed excellent linear plots ($r > 0.998$) of $\log(\text{OD})$ at λ_{max} 498 nm versus time with negative slopes indicate that the reaction is first order in iron(III)-salen. As only one species of iron(III)-salen is involved in aqueous solution and is characterised by its absorbance band at 498 nm, the rate constant values calculated by using decrease in OD at 498 nm vs time correspond to the reaction between TDGA and iron(III)-salen only. It is pertinent to mention here that the rate constant calculated using decrease in OD at λ_{max} of 242 nm which is another characteristic peak of Fe(III)-salen is also found to be of the same rate constant value. However, the observed pseudo first-order rate constants decrease with increase in the concentration of Fe(III)-salen (Supporting information Table S1). The source for this retardation lies with the decrease in concentration of the active species, as the concentration of Fe(III)-salen increases.

The oxidation was studied in different reaction mixtures by varying the ratio of acetonitrile and water. Perusal of rate constants (Supporting information Table S2) shows that the rate of the reaction decreases as the percentage of acetonitrile increases from 20% to 80%. Experiments conducted in the presence of radical scavenger, acrylamide ruled out the participation of any free radical in the reaction. Addition of Cl^- at different concentrations indicates rather an insignificant effect at low $[\text{Cl}^-]$ region while positive effect is observed at higher Cl^- concentrations (Supporting information Table S2).

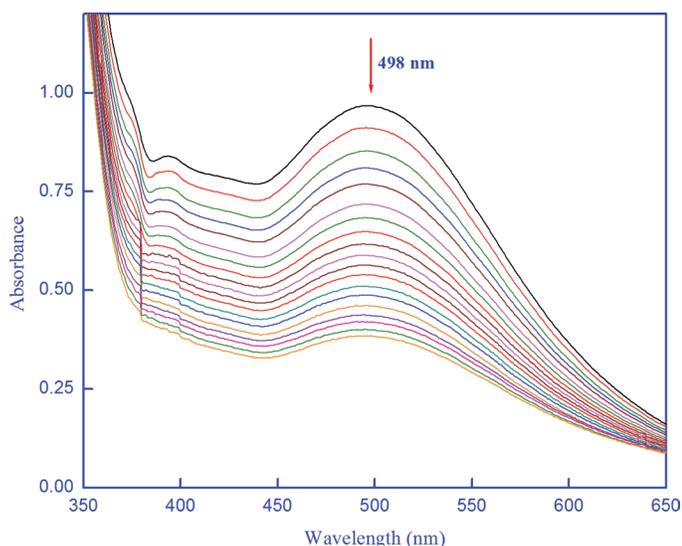
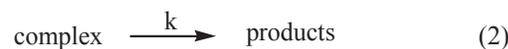


Fig. 1. Absorption spectral changes in the reaction of iron(III)-salen complex ($2 \times 10^{-4} \text{ mol dm}^{-3}$) with TDGA ($5 \times 10^{-2} \text{ mol dm}^{-3}$) in 50% aqueous acetonitrile medium at 30 °C. The spectra were recorded for 900 sec (every 45 sec) after mixing.

The reaction kinetics was carried out at five different temperatures ranging from 20 °C to 40 °C. All the kinetic runs at different temperatures were conducted in 50% CH_3CN -50% H_2O medium under pseudo first-order conditions by maintaining the concentration of TDGA and iron(III)-salen as $5 \times 10^{-2} \text{ mol dm}^{-3}$ and $2 \times 10^{-4} \text{ mol dm}^{-3}$ respectively. The activation parameters, ΔH^\ddagger and ΔS^\ddagger computed from the slope and intercept respectively of the linear Eyring's plot, indicate that the reaction is characterised by a low enthalpy and considerable negative entropy of activation ($\Delta H^\ddagger = 41.2 \pm 1.37 \text{ kJ mol}^{-1}$; $\Delta S^\ddagger = -130 \pm 4.83 \text{ J K}^{-1} \text{ mol}^{-1}$).

Michaelis-Menten kinetics. The observed pseudo first-order rate constants (k_1) depend on TDGA concentration and increase with the increase of $[\text{TDGA}]$ (Supporting information Table S1). The fractional order dependence on $[\text{TDGA}]$ is confirmed from the excellent linear plot of $\log k_1$ vs $\log [\text{TDGA}]$ with a fractional slope. The plot of $1/k_1$ vs $1/[\text{TDGA}]$ at constant $[\text{Fe(III)-salen}]$ is linear having a positive slope and definite intercept, and not passing through the origin (Supporting information Fig. S1). Such a plot is indicative of Michaelis-Menten kinetics [51] which gives a direct kinetic proof for complex formation. On this basis an initial complex formation between TDGA and the oxidant, Fe(III)-salen is proposed prior to the rate controlling step. This leads to Equations (1) and (2). Similar type of Michaelis-Menten mechanism was proposed in many sulfoxidation reactions using different oxidants [29, 30, 52, 53].



Active species. The λ_{max} value for the characteristic peak of iron(III)-salen complex in 100% acetonitrile was influenced by the addition of water. An obvious red shift in wavelength from 471 nm to 498 nm and a significant decrease in absorbance were detected when water was added to Fe(III)-salen in acetonitrile. These results indicate the interaction of the complex and water. However, with successive addition of water though the absorbance values decreased slowly, the λ_{max} value did not change (Fig. 2). The same λ_{max} value at different percentage of H_2O is an indication of existence of the same oxidizing species at all conditions.

Recently Liou and Wang [50] reported the existence of $[\text{Fe}^{\text{III}}(\text{salen})]^+$ species in $\text{DMSO-H}_2\text{O}$ (4:1 v/v) solvent system and characterised its absorbance at 490 nm to be corresponding to the charge transfer between Fe(III) and the ligand. Further, they pointed out that $[\text{Fe}^{\text{III}}(\text{salen})]^+$ is more stable than $\text{Fe}(\text{salen})$ in aqueous medium on the basis of their stability constants. Lloret *et al.* [54] and Liou *et al.* [50] respectively reported the stability constants of $[\text{Fe}^{\text{III}}(\text{salen})]^+$ and $\text{Fe}(\text{salen})$ as $7.1 \times 10^{25} \text{ dm}^3 \text{ mol}^{-1}$ and $3 \times 10^{17} \text{ dm}^3 \text{ mol}^{-1}$. The involvement of oxidizing species, $[\text{Fe}^{\text{III}}(\text{salen})\text{H}_2\text{O}]^+$ formed by the replacement of Cl^- ligand with H_2O can be ruled out on the basis of the following: X-ray crystallographic analysis revealed a drastic structural change from square pyramidal to distorted trigonal bipyramidal

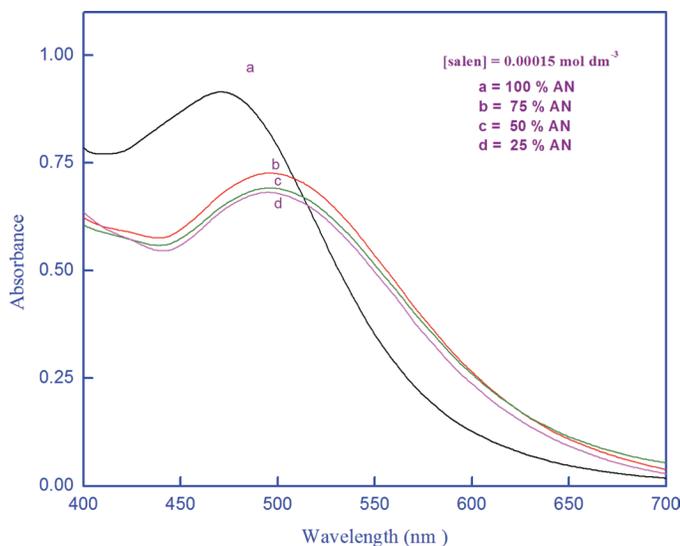
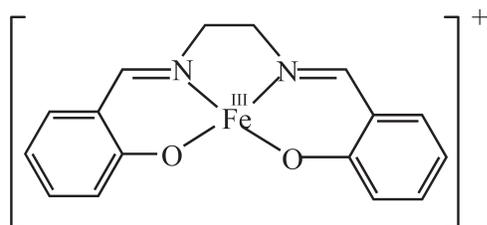


Fig. 2. Overlay spectrum of iron(III)-salen complex in different solvent mixtures.

iron(III) centre upon exchange of fifth ligand from Cl^- to OH_2 [55]. EPR measurements indicated that such a structural difference is seemingly retained in solution also [56] and found that H_2O coordinated complex has a more rhombic iron centre than Cl coordinated complex. Connelly et al. [57] have also shown that in salen complexes coordinated H_2O ligand is easily replaced with Cl^- ion [56]. Further, the ESI mass spectrum of H_2O coordinated iron salen perchlorate in solution gives a single signal which corresponds to $[\text{Fe}^{\text{III}}(\text{salen})]^+$ with loss of H_2O and ClO_4^- [56].

Thus, based on UV-visible absorption and other earlier studies, it has been concluded that the active species in the present aqueous medium is $[\text{Fe}^{\text{III}}(\text{salen})]^+$ (Structure 1), which is formed by the removal of the chloride ion from the coordination sphere of the Fe^{III} -salen. The formation of this oxidative species was inferred by the change in colour of iron(III)-salen from dark brown in non-aqueous medium to pink colour by the addition of water. The absence of any reaction between $\text{Fe}(\text{III})$ -salen and TDGA in 100% acetonitrile medium not only rules out the possibility of $\text{Fe}(\text{III})$ -salen acting as an oxidizing agent as such but also eliminates the existence of $[\text{Fe}^{\text{III}}(\text{salen})]^+$ species in non-aqueous medium. The increase in rate with increase



Structure 1.

in water content of the medium can be explained on the basis of easy formation of oxidative species (Structure 1) in highly aqueous medium.

Liou and Wang [50] have found that $[\text{Fe}^{\text{III}}(\text{salen})]^+$ gets transformed into a dimer, $[\text{Fe}^{\text{III}}(\text{salen})_2]\text{O}$ in the presence of water. In the present reaction the decrease in reaction rate with increase in concentration of $\text{Fe}(\text{III})$ -salen may be attributed to the transformation of $[\text{Fe}^{\text{III}}(\text{salen})]^+$ to its dimer in a parallel reaction followed by decrease in concentration of the active species, $[\text{Fe}^{\text{III}}(\text{salen})]^+$. This parallel reaction is supported by the absence of any isobestic point in the overlay spectrum of the reaction mixture at different times. In addition to this, it has been reported that $\text{Fe}(\text{III})$ -salen chloride also leads to the formation of the dimer, $[\text{Fe}^{\text{III}}(\text{salen})\text{Cl}]_2$, in an equilibrium step [58-61] which has no oxidizing property. The inability of the $[\text{Fe}^{\text{III}}(\text{salen})\text{Cl}]_2$ species to form the active species, $[\text{Fe}^{\text{III}}(\text{salen})]^+$, may be the other reason for the retardation of reaction rate with increase in $[\text{Fe}^{\text{III}}(\text{salen})]$. In many salen catalyzed reactions [62-67] diminished reactivity has been observed due to the formation of μ -oxo dimers which act as a sink for oxosalen complexes.

Discussion

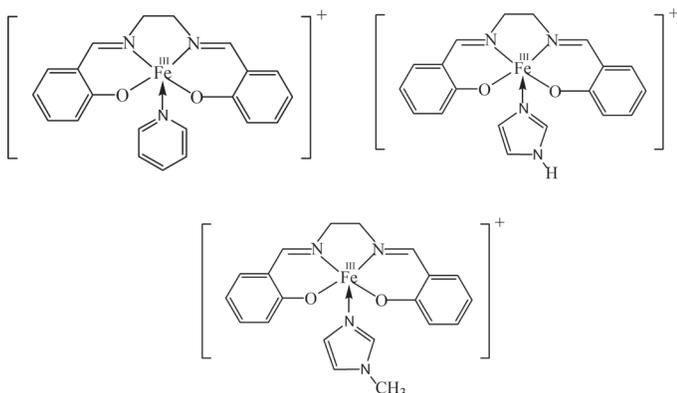
The kinetic and spectral evidences presented above can be interpreted on the basis of the Michaelis-Menten mechanism [51] shown in Scheme 1. The insignificant effect of added Cl^- at its low concentrations clearly points out that the formation of the active species, $[\text{Fe}^{\text{III}}(\text{salen})]^+$, from salen complex (Eqn. 3) in a non-equilibrium step. Similar to Michaelis-Menten model it has been proposed that the first step of the mechanism involves an initial binding of TDGA with the active species of the salen in an equilibrium step (Eqn. 4) to form an intermediate (**II**).

Such type of binding between TDGA and $\text{Fe}(\text{III})$ -salen is confirmed by the Michaelis-Menten kinetics observed with TDGA and decrease in the absorbance of salen complex with increase in concentration of TDGA (Supporting information Fig. S2). Similar type of binding of organic sulfides and sulf-oxides with iron(III)-oxosalen complex [29, 30] have been proposed as a necessary condition for the reaction to occur. The non-saturation kinetics observed in the plot of k_1 vs $[\text{TDGA}]$ and relatively large K_m value obtained in the present study can be taken as evidence for weak binding of TDGA with the oxidant. The intermediate (**II**) then undergoes single electron transfer from sulfur atom of TDGA to the iron atom of salen within the complex in a slow step to yield sulphur cation radical. Thus $\text{Fe}(\text{III})$ is reduced to $\text{Fe}(\text{II})$ in the reaction. However, the spectrum of the reduced form could not be detected as that observed in majority of cases. This suggests that the reduced species is not stable in this medium. Indeed, the reduced species, $\text{Fe}(\text{II})\text{salen}$, is extremely sensitive to oxygen and moisture and easily undergoes dimerization in aqueous medium [50, 68, 69].

The saturation kinetics along with the decrease in absorbance indicate strong ability of these ligands to coordinate with the central metal of the salen. Thus $[\text{Fe}^{\text{III}}(\text{salen})]^+$ coordinates with pyridine, imidazole and 1-methylimidazole leading to the formation of 1:1 adduct (intermediate **III**, Structure 2) in a parallel reaction to the formation of intermediate **II** (Eqn. 4; Scheme 1).

It is pertinent to mention that Kochi [76-78], Rajagopal [79] and their co-workers have proved that one molecule of added ligand enters the coordination sphere of oxo(salen)chromium(V) ion prior to the reaction with the substrate. The binding of ligands with $[\text{Fe}^{\text{III}}(\text{salen})]^+$ restricts the free coordination sites that would be required for binding of TDGA for the reaction to take place. The increase in concentration of added ligand bases favour the formation of intermediate (III) with simultaneous retardation of binding of TDGA with $[\text{Fe}^{\text{III}}(\text{salen})]^+$. Thus the observed decrease in reaction rate with increase in nitrogen base concentration can be explained on the basis of prevention at binding of TDGA with $[\text{Fe}^{\text{III}}(\text{salen})]^+$ by nitrogen bases. Siv-subramanian et al. [29] explained the absence of oxygenation reaction between methyl phenyl sulfide and oxo(salen) iron complex in the presence of imidazole due to the binding of imidazole with the reactive site of the complex. Bagherzadeh et al. [80] have explained the decrease in catalytic activity of MoO_2^- (2-salicylideneamine)phenolate-EtOH in t-butylhydro peroxide oxidation on the addition of ligands like imidazole, 1-methylimidazole and triethylamine on the basis of binding of ligands to central metal atom.

Among the three nitrogenous bases investigated, imidazole with a strong π -donating ability [81-83] showed the highest retarding effect on rate. The reaction shows highest reactivity in the presence of pyridine which has the least π -donating ability [84, 85]. Thus, imidazole binds stronger than the other two bases with the iron atom of the salen complex. This decreases the binding of the substrate to the active species followed by high retardation in rate. The higher reactivity in the presence of 1-methylimidazole to that in the presence of imidazole is due to the presence of the methyl substituent that may considerably prevent the binding to the oxidant. Thus, in the present reaction



Structure 2. Adduct formed between $[\text{Fe}^{\text{III}}(\text{salen})]^+$ and pyridine bases.

the observed order of reactivity among the basic ligands i.e., pyridine > 1-methylimidazole > imidazole, is inversely related to π -donating ability of these nitrogenous donors [81-85].

The results obtained in the oxidation with the axial ligands are contradictory to other oxidation and epoxidation reactions involving salen as catalyst [86-88], where rate enhancement is observed. In such cases, the rate enhancement is explained on the basis of easy transfer of oxygen atom from oxo-salen intermediates to the substrate which is facilitated by the binding of donor ligands to salen.

Conclusion

Iron(III)-salen chloride acts itself as an oxidizing agent in the reaction with thiodiglycolic acid. $[\text{Fe}^{\text{III}}(\text{salen})]^+$ has been identified as the active oxidizing species in the present experimental conditions. The addition of nitrogenous bases like pyridine, imidazole and 1-methylimidazole to the reaction mixture decreased the rate of sulfoxidation reaction. The maximum decrease in the rate constant was observed with imidazole. The binding of nitrogenous bases with the active oxidizing species is attributed to the variation of rate of sulfoxidation.

Experimental

Thiodiglycolic acid was prepared by the method of Barkenbus and Landis [89]. Iron(III)-salen chloride was synthesised by complexation of ferric chloride with stoichiometric amount of salen, N,N' -ethylene-bis(salicylideneimine) ligand in absolute ethanol medium [90,91]. The complex, $[\text{Fe}^{\text{III}}(\text{salen})]$ chloride was characterized by UV-visible and IR (Supporting information Fig. S3) spectral studies and also by elemental analysis. Colour: dark brown; Mol. wt.: 322; UV-vis (in CH_3CN , nm): 260, ($\pi - \pi^*$); 303, ($n - \pi^*$); 471 (d - d); (in 50% CH_3CN -50% H_2O , nm): 292, 351, 495; Selected FT-IR bands (KBr, cm^{-1}): 2924, $\nu_{\text{ali C-H}}$; 1628, $\nu_{\text{C=N}}$; 1543, $\nu_{\text{C=C}}$; 1445, $\nu_{\text{C-N}}$; 1302, $\nu_{\text{C-O}}$; 762, $\nu_{\text{Fe-O}}$; 424, $\nu_{\text{Fe-N}}$. Elemental analysis (%): calculated: C, 53.74; H, 3.95; N, 7.84; Cl, 9.91; Found: C, 53.68; H, 3.90; N, 7.89; Cl, 9.86; $E_{1/2}$ V (SCE): -0.28.

All the other chemicals used for the kinetic study, viz., acrylamide, potassium chloride, imidazole, 1-methylimidazole (Merck, GR) and pyridine (Rankem, AR) were used as such without further purification. The solvent, acetonitrile (Merck, HPLC grade) was used as received.

Kinetic measurements. The kinetic study was carried out in 50% acetonitrile - 50% water (v/v) under pseudo first-order conditions with large excess of substrate. The reaction was initiated by injecting thermally equilibrated solution of iron(III)-salen into the reaction mixture. The course of the reaction was monitored by measuring the decrease in the absorbance of iron(III)-salen ($\lambda_{\text{max}} = 498$ nm) at definite time intervals. UV-vis double beam spectrophotometer (ELICO BL 222) was employed to record the absorption spectra and to follow the kinetics of the reaction. The pseudo first-order rate constant (k_1)

for each kinetic run was evaluated from the slope of the linear plot of $\log [\text{OD}]$ versus time, using Microcal-Origin ver.6.0. The linearity of each fit is confirmed from the values of correlation co-efficient and standard deviation.

The stoichiometry of the reaction was determined by allowing known amounts of TDGA to react with a known excess of iron(III)-salen. Estimation of unreacted iron(III)-salen in the reaction mixtures after completion of the reaction showed that two moles of iron(III)-salen were consumed for one mole of thiodiglycolic acid. A solution containing TDGA and iron(III)-salen chloride in 1:2 ratio in 50% CH_3CN -50% H_2O medium was kept aside for completion of the reaction. After completion of reaction the solvent was removed under reduced pressure and the organic product was extracted with chloroform. It was dried over sodium sulphate and evaporated. The residual mass is subjected to IR and mass spectral studies. The product showed a strong IR absorption peak at 1075 cm^{-1} corresponding to the S=O stretching and a parent peak at $m/z = 166$ in GC-MS (Supporting information Fig. S4). On these bases, the product was identified as sulfinyldiacetic acid.

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