

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 $[Fe^{III}(salen)]$ is the active oxidising 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 rate of reaction in the presence of nitrogenous bases, pyridine, imidazole and 1-methylimidazole, shows a retarding effect. 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: Medium, Spectrophotometry, Mechanism, Species

Introduction

As Stuart Baird in his fact sheet "biomass Energy", Biomass, defined as all land water based vegetation as well as organic waste is produced by green plants converting sunlight to plant material through photosynthesis. Virtually, all crops whether grown for food, animal feed, fiber or any other purpose, result in some form of organic residues after their primary use has been fulfilled. These organic residues as well as animal wastes can be used for energy production through direct combustion or biochemical conversion. Current worldwide production of crop residues is very large but an increased scale of use for fuel may have significant environmental impacts.

Salen complexes are a versatile and standard system and are generally used as effective catalysts with terminal oxidants such as iodosyl arenes, H_2O_2 , $NaOCl$, $NaIO_4$, peracids in a variety of oxotransfer reactions [1-5] viz., enantioselective epoxidation of

non-functionalized alkenes [6-9], sulfoxidation [10-16], oxidative polymerisation [17], oxygenation reactions of hydrocarbons [18-20], oxidation of several other substrates and other processes [21-28]. In these reactions, high degree of stereoselectivity was achieved by the introduction of proper chiral ligands in the complex. Rajagopal and co-workers have studied the detailed mechanism of oxygenation of organic sulfides and sulfoxides [29, 30] 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 have considerable potential as catalysts in many types of reactions, their role as oxidising agent has not been reported so far in the literature. 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]. Herein, we report a systematic study of the oxidation of thiodiglycolic acid (TDGA) by iron(III)-salen chloride as oxidant in the absence of other terminal oxidants in aqueous acetonitrile medium. The effects of ligand bases, pyridine, imidazole and 1-methyl imidazole on the oxidation are examined and are also reported.

Materials and Methods

Thiodiglycolic acid was prepared by the method of Barkenbus and Landis [51]. 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 [52, 53].

All the other chemicals used for the kinetic study, viz., acrylamide, potassium chloride, imidazole, methyl imidazole (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 decrease in the absorbance of iron(III)-salen ($\lambda_{\text{max}} = 498 \text{ nm}$) at definite time intervals. UV-Vis double beam spectrophotometer (ELICO BL222) 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. The IR spectrum of the product showed an absorption peak at 1075 cm^{-1} corresponding to the S=O stretching and did not contain any band corresponding to SO_2 . On this basis, the product was identified as sulfinyldiacetic acid.

Results

The decrease in absorbance of iron(III)-salen at different time intervals was found to be steady and the overlay spectrum is shown in Figure 1. The oxidation proceeds smoothly and the reaction is first-order in iron(III)-salen as evidenced by good linear plots ($r > 0.998$) of $\log[\text{OD}]$ versus time with negative slopes. However, the pseudo first-order rate constants decrease with increase in the concentration of Fe(III)-salen (see ESI, Table T1). 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 (see ESI, Table T2) 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 free radical in the reaction. The effect of added Cl^- , at different concentrations, on the kinetics indicates insignificant effect at low $[\text{Cl}^-]$ region while positive effect is observed at higher Cl^- concentrations (see ESI, Table T2).

The reaction kinetics was carried out at five different temperatures ranging from 20°C to 40°C . 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 ($\Delta H^\ddagger = 41.2 \pm 1.37 \text{ kJ mol}^{-1}$; $\Delta S^\ddagger = -130 \pm 4.83 \text{ J K}^{-1} \text{ mol}^{-1}$).

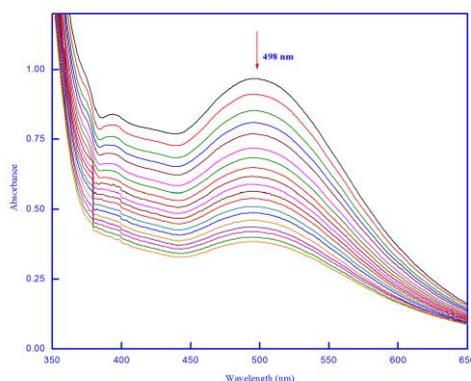
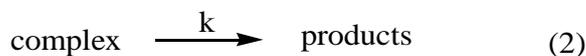


Fig.1 : Decay of absorbance of Fe(III)-salen complex with time

Michaelis-Menten kinetics

The observed pseudo first order rate constants (k_1) depend on TDGA concentration and increase with the increase of $[TDGA]$ (see ESI, Table T1). The fractional order dependence on $[TDGA]$ is confirmed from the excellent linear plot of $\log k_1$ vs $\log [TDGA]$ with a fractional slope. The Michaelis-Menten plot of $1/k_1$ vs $1/[TDGA]$ at constant $[Fe(III)\text{-salen}]$ is linear having a positive slope and definite intercept, and not passing through the origin (see ESI, Figure S1), clearly indicating that the TDGA binds to the oxidant, Fe(III)-salen before the rate controlling step. This leads to equation 1 and 2.



According to Michaelis-Menten kinetics, the pseudo first order rate constant is given by equation 3.

$$k_1 = k[TDGA] / (K_m + [TDGA]) \quad (3)$$

Where, K_m is the Michaelis-Menten constant and k is the rate constant for the formation of the product. The values of k and K_m evaluated from the slope and intercept values of the linear plot of $1/k_1$ against $1/[TDGA]$ are $1.13 \times 10^{-3} \text{ s}^{-1}$ and $1.14 \times 10^{-1} \text{ mol dm}^{-3}$ respectively.

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 (Figure 2).

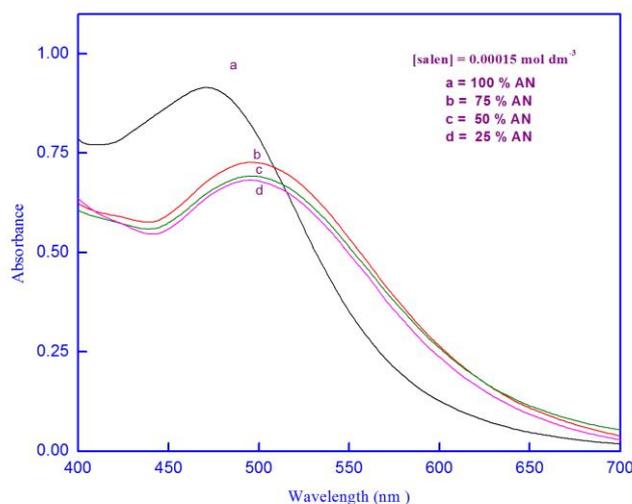
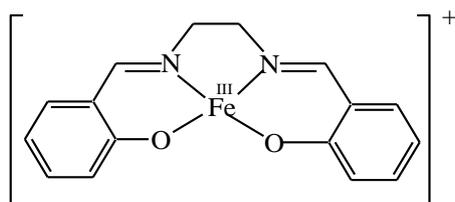


Fig. 2 : Overlay spectrum of iron(III)salen complex in different solvent mixtures

Recently Liou and Wang [50] reported the existence of $[\text{Fe}^{\text{III}}(\text{salen})]^+$ species in DMSO- H_2O (4:1 v/v) solvent system and characterised by its absorbance at 490 nm, 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 Fe(salen) in aqueous medium on the basis of their stability constants. The existence of this species has been already reported by Lloret et al [54]. Fujii and co-workers [55] have identified the oxidizing intermediate bearing H_2O molecule in the place of chlorine in the fifth coordination site from the sterically hindered iron-salen complexes only at a very low temperature of 203 K. Such type of active species formed by the replacement of Cl ligand with H_2O can be ruled out in the present case as the salen is not sterically hindered and the reaction temperature, 303 K is also moderately high.

Thus, based on UV-visible absorption and the 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 replacement of 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 Fe(III)-salen and TDGA in 100% acetonitrile medium not only rules out the possibility of Fe(III)-salen acting as an oxidising 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 in water content of the medium can be explained on the basis of easy formation of oxidative species (structure 1) in highly aqueous medium.

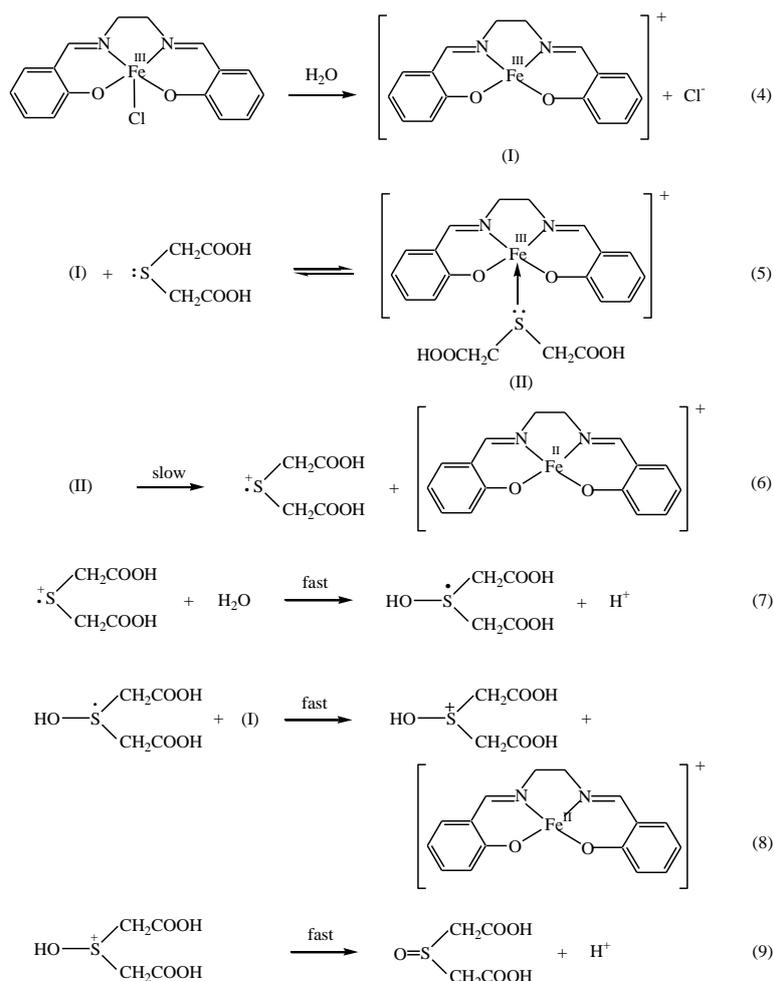


Structure 1

Liou and Wang [50] have found out 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. The decrease in reaction rate with increase in concentration of oxidant, Fe(III)-salen, in this case may be attributed to the decrease in concentration of $[\text{Fe}^{\text{III}}(\text{salen})]^+$. In addition to this, it has been reported that Fe(III)-salen chloride also leads to the formation of dimer, $[\text{Fe}^{\text{III}}(\text{salen})\text{Cl}]_2$, in an equilibrium step [56-59] 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 [60-65], 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 with the mechanism as shown in Scheme 1.



Scheme 1

The insignificant effect of added Cl^- at low concentrations clearly points out that the formation of active species, $[\text{Fe}^{\text{III}}(\text{salen})]^+$ from salen complex (Eqn. 4) is not an equilibrium step. The Michaelis-Menten kinetics observed with TDGA and the decrease in the absorbance with the increase in concentration of TDGA (see ESI, Figure S2) conclude that the reaction proceeds through an initial binding of TDGA with the active species of the salen to form an intermediate(II) in an equilibrium step. Such type of binding of organic sulfides and sulfoxides 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 sulfur cation radical. Thus Fe(III) is reduced to Fe(II) in the reaction. However, the spectrum of the reduced form could not be detected as observed in majority of cases. This suggests that the reduced species is not stable in this medium. Indeed, the reduced species, Fe(II)salen, is extremely sensitive to oxygen and moisture and easily undergoes dimerization in aqueous medium [50, 66, 67].

The increase in rate constant with increase in potassium chloride at higher concentrations may be due to primary salt effect which often affects the reactions involving ion-dipole molecules. Idris et al [68] have used acrylamide to detect the possibility of forming sulphide radicals in the oxidation of L-methionine by potassium bromate, while Henriquez et al [69] have used sulphide ions to terminate the polymerisation of acrylamide monomers. The absence of any effect when the reaction was performed in presence of acrylamide as a radical scavenger shows that the cation radical formed is highly reactive and it immediately undergoes further reaction. Rajagopal and co-workers have shown that the sulfide cation radical is formed as the transient intermediate in the oxidation of many organic sulfur compounds by Fe(III)-salen [30] and other oxidizing agents [70-73]. The sulfide cation radical formed may undergo degradation under different pathways, viz., fragmentation at C-S bond, oxidation, reaction with the solvent H_2O , dimerization etc., The formation of sulfoxide as the only product and water as the solvent for the reaction lead to the conclusion that the major portion of sulfide cation radical is consumed by water. Finally, the sulfide cation radical is converted into the product in several fast steps with a molecule of H_2O and iron(III)-salen. The above proposed mechanism is also in accordance with the observed stoichiometry of 1:2 between TDGA and iron (III)-salen complex.

Effect of axial ligands

In order to find out the role of axial ligands in the salen oxidation, the reaction was performed in the presence of nitrogenous bases, pyridine, imidazole and 1-methylimidazole. Table 1 shows the rate constants obtained for the oxidation reaction in the presence of various nitrogenous donors. It is found that the pseudo first order rate constant decreases with the addition of these ligands to the medium and reaches saturation at higher concentrations for imidazole and methylimidazole. The non-saturated kinetics observed with pyridine indicates weak binding. Above this pyridine concentration the reaction could not be conducted as self-decomposition of salen take place. It is presumed that at high pyridine concentrations, the oxidation of pyridine by the oxidant is also possible. Further,

the absorbance values at 498 nm decrease considerably by the addition of nitrogen ligands. From the change of absorbance with the change of [axial ligand], the binding constant values are estimated using Benesi-Hilde brand method. The calculated binding constant values for imidazole, methylimidazole and pyridine are 2.45×10^4 , 4.53×10^3 and 5.89×10^1 respectively.

The saturation kinetics along with the decrease in absorbance indicates strong ability of these ligands to coordinate with the central metal of the salen. Bagherzadeh et al [74] have explained the decrease in catalytic activity of MoO_2 -(2-salicylideneamine) phenolate-EtOH with the addition of ligands like imidazole, 1-methylimidazole and triethylamine on the basis of binding of ligands to central metal. Thus 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. It is pertinent to mention that Kochi [75-77], Rajagopal [78] 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.

Table 1: The rate dependence on added ligand bases

$$[\text{TDGA}] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$$

$$[\text{salen}] = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$$

$$\text{Solvent} = 50 \% \text{ CH}_3\text{CN} - 50 \% \text{ H}_2\text{O (v/v)}$$

$$\text{Temp.} = 30 \text{ }^\circ\text{C}$$

$10^4 [\text{ligand}]$ mol dm ⁻³	$10^4 k_1$ (s ⁻¹)		
	pyridine	methyl imidazole	imidazole
0	9.11 ± 0.13	9.11 ± 0.13	9.11 ± 0.13
0.01		8.48 ± 0.16	
0.05			7.63 ± 0.16
0.1	8.35 ± 0.10	7.42 ± 0.17	6.48 ± 0.12
0.5		6.45 ± 0.11	5.74 ± 0.09
1.0	7.62 ± 0.09	6.37 ± 0.08	5.59 ± 0.11
5.0		6.87 ± 0.13	5.64 ± 0.14
10.0	6.82 ± 0.13	6.82 ± 0.12	5.56 ± 0.12
20.0	5.31 ± 0.09		
50.0	4.50 ± 0.08		
100	4.18 ± 0.07		

Among the three nitrogenous bases investigated, imidazole, with a strong π donating ability [79-81] showed the highest retarding effect on rate. The reaction shows highest reactivity in the presence of pyridine which has the least π donating ability [82, 83]. 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 than imidazole is due to the presence of methyl substituent that may considerably prevents the binding to the oxidant. Thus due to the methyl substituent, 1-methylimidazole has less proximal effect than imidazole. The observed order of reactivity among the basic ligand is, pyridine > 1-methylimidazole > imidazole. This seems to be inversely related to π -donating ability of these nitrogen donors.

The results obtained in the oxidation with the axial ligands are contradictory with other oxidation and epoxidation reactions involving salen as catalyst [84-86], 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

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

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