CHAPTER I

CHAPTER - 1

- INTRODUCTION -

Chemical reactions do not occur instantanously. If some of them , because of their rapidity, appear to do so, for example, the neutralization of an acid by a base,others take a longer time, as in the case of the appearence of Sulphur precipitate resulting from the action of hydorchloric acid on a hyposulphite solution.

It is evident in fact that even the fastest reactions occur during an interval of time,in the combustion of a mixture of air and gas at the tip of a bunsen burner, it will be the time necessary for the fresh gas to appear, otherwise the flame would not be stationary.

It is easy to generlise; all chemical reactions are functions of time, all occur at a finite rate.

These facts have been known for a long time, but Wenzel (1740-1793) working on the corrosion of metals by acids (1777) was the first to introduce the idea of a relationship between the acid concentration and the rate of attack of the metal or the weight dissolved in unit time.

It was not until 1850 that Wilhelmy[1], using the inversion of Sugar Cane by acids, showed the proportionality of the reaction rate with the concentration of the reagents.This became the first experimental fact in kinetics, although at the time it passed almost unnoticed.

Chemical kinetics did not come into its own, however until 1884 with Van't Hoff[2] (1852 - 1911) & his classic work; " A study of Chemical dynamics." His experimental work marks the true beginning of chemical kinetics. Thus Van't Haff and before him Wilhelmy, can both be considered the true founders of this branch of chemistry.

Thermodynamics , was the science, which developed long before chemical kinetics , can predict whether a reaction will proceed under a given set of conditions of temperature anc pressure. It can also predict the direction in which the equilibrium will be shifted in response to a variation in these parameters. However, it cannot tell us the rate of the reaction. It cannot inform us about the nature of the chemical process by which the reaction proceeds.

Chemical kinetics can hence be regarded as the only approach to the study of chemical reactions. It is not surprising therefore, that its progress as a science was delayed since it depended for its advance on the developments in atomic stucture and bonding.

In every branch of chemistry, the study of Kinetics is important, for example it is certainly vital for the organic chemist to know whether he has to wait months or only several hours for the completion of a synthesis, or for an Engineer to anticipate the violence of an exothermic reaction.

It is therefore surprising that, until recently kinetics was considered of minor importance in the traditional teaching of chemistry, at best offering practical examples of first order differential equations treated in mathematics courses .

For oxidation reactions,the common oxidising agents used are Potassium dichromate, Chlorine, Bromine, Ceric sulphate, Potassium bromate,Potassium permanganate. These oxidising agents are strong and the oxidation is rather fast. It is very difficult to separate and identify intermediate products of oxidation.

The use of potassium persulphate is comparatively recent. It is a mild oxidising agent, although the standard redox potential of the system,

$$S_2O_8^{2-} + 2e^- \longrightarrow 2SO_4^{2-}$$

is 2.01 Volts (Latimer[3]). The oxidation by peroxydisulphate ion,generally takes place slowly (Marshall[4]). Because of this fact, peroxydisulphate ion, has been largly used for kinetic study of oxdition of various class of compounds,and with this oxidant,it is always possible to isolate and identify the intermidiate products formed during the course of the reaction.

Kinetic studies involving the use of peroxydisulphate ion may be categorized as follows :

1] Self decomposition of peroxydisulphate ion.

2] Reactions with inorganic reductants.

3] Polymerization reactions.

4] Reactions with organic substrates.

Since the mechanism of oxidation by peroxydisulphate ion is closely connected with the hydrolytic decomposition (oxidation of water) of peroxydisulphate ion, a brief review of the work done to investigate the mechanism of this decomposition is necessary. It may be mentioned that the work on the kinetic studies involving peroxydisulphate ion upto 1961 has been reviewed by D.A House[5] and Wilmarth[6] and Haim.

The first study of the self decomposition of peroxydisulphate ion was made by Elbs[7] and coworkers and by Caro[8].Similarly the furher study was made by Green[9] and Masson and by Kailan and Olbrich[10]. The results of their study are summarised as follows :

1] Decomposition of potassium & sodium peroxydisulphate follows first order kinetics but not that of ammonium salt.

2] The reaction is catalysed by H^+,OH^-,lead, platinum black and certain other metals.

3] In strongly acid solution permonosulpuric acid is formed while in aqueous solution acid sulphate is formed with evaluation of oxygen.

4] The specific rate is function of peroxydisulphate concentration which was explained as due to the specific inhibitory effect of K^+ ions.

The kinetics of decomposition of peroxydisulphate ion in presence of organic substrates , for example alcohols was made by Bartlett[11] and Cotman, who found that this decomposition process is greatly enhanced by the presence of organic substrate and suggested that the primary process is the decomposition of $S_2O_8^{2-}$ into two $\overline{SO_4}$ radical ions.

$$S_2O_8^{2-} \longrightarrow 2\overline{SO_4}$$

Rius and Zuleta[12] studied the decomposition of $(NH_4)_2S_2O_8$ while Kolthoff[13] and Miller in their study of the thermal decomposition of aqueous peroxydisulphate solution concluded that the decomposition occurs by means of two reactions, both of which occur simultaneously and are independent

a)An uncatalyested reaction in which there is a symmetrical rupture of the O-O bond to form two sulphate radical ions which are removed by the reaction with water.

$$S_2O_8^{2-} \longrightarrow 2\overset{\bullet}{S}\bar{O}_4$$

$$2S\bar{O}_4 + 2H_2O \longrightarrow 2HSO_4^- + 2\dot{O}H$$

$$2\dot{O}H \longrightarrow 2H_2O + 1/2O_2$$

b>An acid catalysed reaction in which there is unsymmetrical rupture of the O-O bond of the $HS_2O_8^-$ ion, yielding sulphate radical and HSO_4^-, i.e.

$$S_2O_8^{2-} + H^+ \longrightarrow HS_2O_8^-$$

$$HS_2O_8^- \longrightarrow \dot{S}O_4 + HSO_4^-$$

$$\dot{S}O_4 \longrightarrow \dot{S}O_3 + 1/2\ O_2$$

$$\dot{S}O_3 + H_2O \longrightarrow H_2SO_4$$

While in strongly acidic medium, the $S\dot{O}_4$ radical hydrolyses to form caro's acid according to the following reaction:

$$\dot{S}O_4 + H_2O \longrightarrow H_2SO_5$$

Serveral workers[14-17] studied the kinetics of decomposition of peroxydisulphate ion from different point of view and from all these studies it can be concluded that the primary process involved in the uncatalysed decomposition of peroxydisulphate ion is the breaking of $S_2O_8^{2-}$ into two sulphate radical ions.

Silver ions (Ag^+) has been found to be the most effective catalyst than any other metal ion. Silver catalysed decomposition has received much attention. Such reaction are generally of first order with respect to $S_2O_8^{2-}$ and Ag^+. The nature of the silver intermediate formed in the process is uncertain.It was suggested that the primary step in Ag^+ catalysed decomposition of $S_2O_8^{2-}$ as:

$Ag^+ + S_2O_8^{2-} \longrightarrow Ag^{2+} + \overset{\overset{\cdot}{-}}{SO}_4 + SO_4^{2-}$

Where as Yost and Coworkers[18] were of the view that the primary step is the formation of Ag^{3+} ion.

$Ag^+ + S_2O_8^{2-} \longrightarrow Ag^{3+} + 2SO_4^{2-}$

Recently, Franchuk,[19] on the basis of his study of the determination of isotopic composition of O_2 formed, concluded that $\overset{\overset{\cdot}{-}}{SO}_4$ radical ion is formed in the decomposition of $S_2O_8^{2-}$ ion and its formation is catalysed by Ag^+ ion.

In the field of Inorganic Chemistry,the kinetics of oxidation of a number of compounds by peroxydisulphate ion has been stucied .Uncatalysed oxidation of iodide ion has been studied and work upto 1954 has been reviewed by Morgan[20] and Meeratoja.[21] This reaction generally found to be bimolecular in nature[22-25]. Since this reaction is between ions of like charges , so it has been investigated by many workers[26-31] to test the predictions of Bronsted[32] theory of Kinetic salt effects and the Debye-Huckel limiting law . Later work indicates that the salt effect depends more on the concentration and nature of cation than on the ionic strength.[33-38]

Uncatalysed oxidation of Fe^{2+} ion by $S_2O_8^{2-}$ ion was studied by Kolthoff and cowrkers[39] was found to obey second order kinetics.

Gupta and srivastava[40,41] studied the uncatalysed oxidation of mercurous nitrate and stannous ion by $S_2O_8^{2-}$ ion in aqueous medium and found the order of reaction to be one and two respectively. Stehlik[42] and Nedbalkova studied the kinetics of oxidation of Silver(I) with $S_2O_8^{2-}$ forming Silver (III) oxide ard suggested the first step to be oxidation of Ag^+ and Ag^{2+} ions. Thus Yost[43,44] and coworkers studied the silver catalysed oxidation of chromic salt, ammonia , vanadyl ion and manganous ion by $S_2O_8^{2-}$ ion and come to following conclusion:

1] These reactions are first order in peroxydisulphate ion.

2] Reaction rate is independent of the reductant concentration.

3] Silver ion is an efficient catalyst for these reactions.

4] All these reactions are characterised by negative salt effect.

The above observations were explained by Yost[43-44] and coworkers by postulating the formation of tervalent silver ion as a primary step in all silver catalysed oxidations.

$$Ag^+ + S_2O_8^{2-} \text{ ---> } Ag^{3+} + 2SO_4^{2-}$$

This reaction was taken as the rate determining step which was followed by the rapid oxidation of the reducing substrate by the tervalant silver ion formed in the first process with the reproduction of silver ion (Ag^+). The formation of Ag^{3+} ion although supported by many other workers[45-47] does not fall in a line with the view of Higginson[48] and Marshall according to whom, one electron transfer is more likely in reactions involving ions of transition metals.

Beckier[49] and Kijowski found the Ag^+ catalysed oxidation of Mn^{2+} by $S_2O_8^{2-}$ to be first order with respect to catalyst as well as with respect to peroxydisulphate.

King[50,51] studied the Ag^+ catalysed oxidation of ammonium and ammonium ion and found that the reaction obey first order kinetic but the oxidation of ammonia ion was slightly autocatalytic.

Srivasgtava[52] and Ghosh in their study of Ag^+ catalysed decomposition of H_2O_2 by $S_2O_8^{2-}$ proposed the formation of Ag^{2+} in the rate determining step.

$$\mathbf{Ag^{+} + S_2O_8^{2-} \longrightarrow Ag^{2+} + \overset{\dot{-}}{SO_4} + SO_4^{2-}}$$

Mushran[53-55] and coworkers studied the uncatalysed as well as Ag^+ catalysed oxidation of Thallium (I), Tellurium (IV) and Selenium (IV) by peroxydisuphate ion and found that the reaction to be of the first order in peroxydisulphate and Ag^+ and zero order in the reductants.

Kinetic studies involving peroxydisulphate ion have been of great interest for the chemist because of the fact that the peroxydisulphate ion acts as a catalyst in the polymerisation process. Eagar[56] and Winkler studied the kinetics of oxidation of mercaptans by peroxydisulphate in concentrated acetic acid. Like most of the reactions of peroxydisulphate and independent of the mercaptan concentration. They proposed that the rate determining process is the dissociation of peroxydisulphate ion into two sulphate radical ions.Emulsion polymerisation studies of allyl acetate by Nozaki[57] and Bartlett initiated by peroxydisulphate showed that the decomposition of peroxydisulphate is a first order reaction. In the earlier studies, Evans[58] and coworkers had also suggested that in the polymerisation processes in aqueous solution and in the emulsion polymerisation initiated by peroxydisulphate ion, the initial step was the decomposition of $S_2O_8^{2-}$ into two sulphate radical ions.

Recently Riggs[59] and Rodriguez studied the peroxydisulphate initiated polymerisation of acrylamide using ditatometric technique and found that the reaction follows the expression:

$$d/dt\ [M_1] = k_{1.25}\ [K_2S_2O_8]^{0.5}\ [M_1]^{1.25}$$

Where M_1 represents the initial monomer concentration.

From the results of analysis of the kinetics and energetics of the polymerisation process they favour a cage effect theory rather than the complex formation theory to explain the order with respect to monomer.

The kinetics of oxiation of aldehyde and ketones, both uncatalysed as well as Ag^+ catalysed by peroxydisulphate was studied by many workers.[60-62].Thus Subraman[60] and Santappa studied the mechanism of uncatalysed oxidation of formaldehyde and acetaldehyde and Ag^+ catalysed oxidation of acetone and cyclohexanone and observed a similarity in behaviour with those of aliphatic alcohols. They proposed a mechanism involving Ag^{2+} and SO_4^{2-} as the reactive species.

The Ag^+ catalysed oxidation of benzaldehyde by peroxydisulphate in sulphuric acid medium was also studied by Srivastava[63] and coworkers. The reaction was found to be first order in $S_2O_8^{2-}$ and zero order in benzaldehyde.

The kinetics of reaction between ammonia and potassium peroxydisulphate with formaldehyde in aqueous medium was studied by Nikolaev[64] and Kochetkova. They have shown that the reaction was second order with respect to persulphate and zero order with respect to formaldehyde. They have suggested a free radical mechanism for this reaction. The oxidation resulted in the formation of CO_2.

The kinetics of reaction between peroxydisulphate (in presence of Ag^+) with porphyrin at 35°C was studied by

Okoh[65] Joseph and Krishnamurthy. They have shown that the reaction was first order in porphyrin.

Bacon[66] and coworkers studied the Ag^+ catalysed oxidation of primary and secondary amines and α-amino acids by peroxydisulphate. Srivastava and Chandra studied the oxidation of glycine[67] and alanine[68] and found that the reactions followed the general character of redox reactions of $S_2O_8^{2-}$. Silver (I) catalysed oxidation of some amino acids by $S_2O_8^{2-}$ ion was studied by Reddy[69] and coworkers. They have shown that the reaction is first order with respect to peroxydisulphate and Ag^+ and zero order with respect to amino acid. The rate law is explained by assuming Ag^{2+}, $\overset{\cdot -}{SO_4}$ and amino acid radicals as intermediates. The rates of these reactions were shown to be higher when Cu^{2+} is added to a system under similar conditions. Silver (I) and Copper (II) catalysed oxidation of glycine by peroxydisulphate in aqueous medium was studied by Reddy[70] and coworkers. The oxidation was first order in $S_2O_8^{2-}$ and 1/2 order in Ag^+, in the presence of Ag^{2+}, Cu^{2+} mixtures. Oxidation study of glutamic acid was made by Srivastava[71] and Mathur. They have shown that the reaction is first order in $S_2O_8^{2-}$ and Ag^{2+} and zero order in glutamic acid. A free radical mechanism was proposed.

Subraman[72-73] and Santappa and others[74-77] studied the Ag^+ catalysed oxidation of methanol and ethanol by $S_2O_8^{2-}$

ion and found the order as 3/2 and 1/2 respectively. Bisht[78] and Srivastava studied the Ag^+ catalysed oxidation of alcohols. They have observed that the reaction was first order with respect to $S_2O_8^{2-}$ and zero order with respect to alcohol. They have also suggested that the fractional orders reported by earlier workers was due to the variation in ionic strength and faulty kinetic experimentation. Khulbe[79] and Srivastava studied the Ag^+ catalysed oxidation of n-propanol and found that the rate constant increases with an increase in alcohol concentration. Srivastava[80] and Gupta studied the oxidation of acyclic alcohols by peroxydisulphate in the presence of Ag(I) as a catalyst. They have shown that the reaction was first order with respect to $S_2O_8^{2-}$ and Ag^+ and zero order in alcohol. A free radical mechanism was suggested. Kinetics of oxidation of both aliphatic[81-83] and aromatic alcohols have also been reported by many workers.[84-85]

Edward[86] and coworkers following the kinetics of methanol,ethanol,spectrophotometrically reported 3/2 order in $S_2O_8^{2-}$ and zero order in alcohol. Thus the results are contradictory regarding the order of the reaction.

Kinetic study on the oxidation of 1,3 -diol, propane 1,2 -diol and pinacol by $S_2O_8^{2-}$ ion have been studied by Bakore[87-89] and Menghani, Khan[90] and Srivastava, in their Ag^+ catalysed oxidation of ethylene glycol and Bakore and Menghani[89] in the oxidation of pinacol observed a first order behaviour in $S_2O_8^{2-}$ and zero order in reductant. Bakore and Menghani[89] postulated bivalent silver ion (Ag^{2+}) formed by the interaction of $S_2O_8^{2-}$ and Ag^+ playing an important role in oxidation of pinacol. Mishra[91] and Ghosh in the silver catalysed oxidation of glycerol found that the order of the reaction with respect to glycerol was slightly negative (-0.06 for glycerol concentration from 0.8 to 0.1 M) but the order tends to approach zero as the temperature increases.

Silver (I) catalysed oxidation of 1-3 propanediol by peroxydisulphate was studied by Srivastava[92] and coworkers. (re-investigation). A mechanism different from that reported by Bakore[93] and Menghani was proposed on the basis of the oxidation products.

Kinetic and mechanism of oxidation of 2,3-Dimethylindole by potassium peroxydisulphate was studied by Almeida[94] and Munoz Perez. They have shown that the formation of the intermediate is first order in both 2,3 dimethylindole and peroxydisulphate. Whereas its decomposition is independent of oxidant concentration and acid-catalysed.

Ag^+ catalysed oxidation of benzyl alcohol by peroxydisulphate was studied by Srivastava[95] and coworkers. They found that the order with respect to $S_2O_8^{2-}$ and Ag^+ was one and order with respect to benzyl alcohol was zero.

Silver (I) catalysed oxidation of isoamyl alcohol by peroxydisulphate was studied by Singh[96] and coworkers. They found that the order with respect to $S_2O_8^{2-}$, was first one and the reaction was zero order with respect to isoamyl alcohol. A free radical mechanism involving Ag^{2+} was proposed.

Ag(I) catalysed oxidation of iso-amyl alcohol, crotyl alcohol by peroxydisulphate was studied by Srivastava[97] and coworkers. They have proposed a free radical mechanism for this reaction.

Ag(I) catalysed oxidation of tert-alcohol by paroxydisulphate was studied by Singh[98] He suggested that the reaction was first order in $S_2O_8^{2-}$ and Ag^+ and zero order in alcohol.

The oxidation of phenols by peroxydisulphate ion in alkaline medium has been studied by many workers[99-103] and has been reviewed by Sethna.[104].

Oxidation of phenols by $S_2O_8^{2-}$ ion in aqueous ethanol, tert-butanol, acetonitrile and acetone was studied by Panigrahi[105] and coworkers. They found that the reaction was first order in $S_2O_8^{2-}$ and reductant and the order with respect to alkali was 0.5. A mechanism consistent with electrophilic attack of $S_2O_8^{2-}$ at the oxygen atom of the phenoxide ion and the neutral phenol rather than at the carbon atom was discussed.

Kinetic study on the oxidation of hexane - 1,6-diol by peroxydisulphate (in presence of Ag^+ as a catalyst) was studied by Srivastava[106] and coworkers. They have proposed that, unlike other reactions of this class, it does not follow simple first order kinetics, and is attenuated with near half order inhibition by the product of oxidation in the later stages of reaction.The product of oxidation was 6-hydroxyhexanol. A free radical mechanism was suggested.

Ag(I) catalysed oxidation of phenol, O - Cresol in acetone medium was studied by Srivastava[107-108] and coworkers. They have shown that the reaction was first order in acidic and neutral medium but in alkaline medium the reaction is of second order as studied by Behrman[109] and Walker and Bacon[110] and Munro.

Kinetic study of oxidation of mucic and benzilic acid by $S_2O_8^{2-}$ ion in presence of Ag(I) as a catalyst was studied by Gupta[111] and Saksena. They have studied the reaction in dioxane conductivity system using the same concentration of dioxan in each kinetic run. In both the cases the reaction was first order in $S_2O_8^{2-}$ and Ag^+ and zero order in substrate. A radical mechanism was proposed for this reaction.

Ag(I) catalysed oxidation of acrylic acid by $S_2O_8^{2-}$ ion was studied by Agrawal[112] . He found that the reaction was first order in $S_2O_8^{2-}$ and zero order in substrate. A radical mechanism was proposed by him for this reaction.

The kinetic study of the reaction between aromatic amines and peroxydisulphate ion in aqueous base, called Boyland[113-116] Sims oxidation was made by Behrman.[117] The reaction was found to be first order in neutral amine and initially first order in peroxydisulphate ion. Orthoaminoaryl sulphate , ammonia and humic acid were found to be the products of the reaction. Behrman proposed a mechanism involving a nucleophilic displacement by the amine nitrogen on the peroxide oxygen to yield the corresponding arylhydroxylamine -O- sulphonate. The effect of substituents on this reaction was recently investigated by Venkatsubramanian[118] and Sabesan who found that the reaction is accelerated by electron releasing substituents and retarded by electron withdrawing substituents pointing to an electrophilic attack of $S_2O_8^{2-}$ ion. Srivastava[119-121] studied the oxidation of aromatic amines by peroxydisulphate in acetic acid medium and found that the reaction is of second order - first order with respect to each reactant. Babu J. Shreekanta[122] and coworkers studied the oxidation of di-isopropylamine by peroxydisulphate. They have shown that the reaction is of second order - first order in oxidant and reductant. Beilerian[123] and Chaltykyan studied the kinetics of oxidation of aliphatic amines in aqueous medium. They observed that $(CH_3)_2NH$, $(C_2H_5)_2NH$, $C_2H_5NH_2$ follow the second order kinetics, while the amines $(CH_3)_3N$, $(C_2H_5)_3N$ gave fractional orders.

Kinetics of oxidation of ethylene-diamine tetraceto cobaltate(II) complexes by peroxydisulphate ion, induced by irradiation with visible light of aqueous solutions containing tris(2¹-2¹ bipyridine) rethenium(II) ion was studied by Nishida[124] Suzuko and coworkers. They have shown that the oxidation of ethylene-diamine tetraceto cobaltate (II)$[Co(Edta)^{2-}]$ by $S_2O_8^{2-}$ was greatly accelerated by irradiation with visible light of aqueous solution containing tris (2,2¹-bipyridine) rethenium (II) ion $[Ru(bpy)_3]^{2+}$. The overall reaction is,

$$2[CO(Edta)]^{2-} + S_2O_8^{2-} \longrightarrow 2\,[CO\,(Edta)]^{-} + 2SO_4^{2-}$$

The $[Ru(bpy)_3]^{2+}$ acts as a photosensitiser, and catalyst for this reaction and the mechanism consists of a chain reaction being initiated by the quenching of the photo-excited $[Ru(bpy)_3]^{2+}$ by $S_2O_8^{2-}$ ion and peroxydisulphate ion, induced by photo-excited tris (2,2¹ -bipyridine) ruthenium ion was studied by Nishida[125] Suzuka and Kimura Masura. They studied the reaction is

$$HCO_2^{-} + S_2O_8^{2-} \longrightarrow H^{+} + CO_2 + 2SO_4^{2-}$$

consistuting a chain reaction initiated by the reaction between $S_2O_8^{2-}$ and $[Ru(bpy)_3]^{2+}$. A reaction mechanism was also presented.

The Ag^+ catalysed oxidation of iso-nicotinic, nicotinic hydrazides by peroxydisulphate were studied by Hogale[126] and coworkers. They have shown that the reaction was first order in $[S_2O_8^{2-}]$ and $[Ag^+]$ and independent of substrate. The reaction was inhibited by allyl acetate and H^+. The salt effect was negative. A radical mechanism involving Ag(II) was proposed.

The oxidation of picolinic acid hydrazide by peroxydisulphate in presence of silver (I) catalyst was studied by Hogale[127] and coworkers. Picolinic acid hydrazide undergoes oxication by peroxydisulphate to picolinoyl di-imide which is further oxidised to picolinic acid and nitrogen. Swains treatment has been utilized to separate the rate constants for the first and the second step of the reaction.

The kinetics of oxidation of some orthosubstituted N-N Dimethyl anilines by peroxydisulphate was studied by Srinivasan[128] and coworkers in 50% (v/v) aqueous ethanol containing phosphate buffer. They have observed that the reaction was second order over all and first order in each reactant. They have further shown that the rate was not influenced by the presence of free radical inhibitor, allyl acetate.

Oxidations of thyamines and uracil with sodium peroxydisulphate was studied by Itahara[129] and coworkers.

They have shown that the oxidation of thiamines with $Na_2S_2O_3$ in hydrochloric acid gave 5-chloro, 6-hydroxy, 5,6-dihydrothiamines. The reactions of uracils also gave similar products together with 5-chloro uracils.

The kinetics of oxidation of pyrogallol red by peroxydisulphate, both uncatalysed as well as Ag^+ catalysed was studied by Sevillano[130] and coworkers. The reaction was studied in presence of 1,10-phenanthroline (Phen) as an activator. Rate equations for these reactions were derived from the minetic dependence on H^+ and reagent concentrations. The rate constants and the order of the reaction were also calculated. A kinetic model was also proposed.

Kinetics of a reaction between peroxydisulphate and iodide ions in aqueous medium was studied by Lai[131] Xinghua Wang and coworkers. The relation between reaction rate constant and temperature was also obtained. The values of transition state thermodynamic parameters were calculated at 298.2°K. The effect of ionic strength on this reaction was examined and the rate constant - temperature relation possesses a positive salt effect. The reaction mechanism was also disscussed.

Uncatalysed oxidation study of some organic acids (acrylic, cinnamic) was studied by Khan[132] and coworkers. They have shown that the reaction was first order in $S_2O_8^{2-}$ & zero order in the substrate. A radical mechanism was proposed.

Uncatalysed oxidation of formic acid and formate ion was studied by Srivastava[133] and Ghosh. They found that the reaction was first order in peroxydisulphate and zero order in organic substrate, while Kappana[134] reported the oxidation of formate ion by peroxydisulphate to be a second order reaction. Gupta[135] and Nigam after studing the Ag^+ catalysed reaction supported the view point of Srivastava[133] and Ghosh that the reaction is first order in $S_2O_8^{2-}$ and zero order in formate ion. Chaltykyan[136] and coworkers, while studing the Cu^{2+} catalysed oxidation of a formate ion and formic acid found that the oxidation of a formate ion is more rapid than that of formic acid. They also observed variation of the order with temperature. The reaction is second order upto 30°C while at 40-45°C the order decreases.

Mishra[137] and Ghosh studied the Ag(I) catalysed oxidation of lactic acid. They have reported a first order behaviour with respect to peroxydisulphate and a slight retarding effect due to H^+ ions, while the rate was found to increase linearly when the concentration of Ag^+ was increased. Bakore[138,139] and Joshi reported that first order rate constant is almost independent of peroxydisulphate concentration and lactic acid concentration. Rate was found to be unaffected by changes in pH. On the other hand, Venkatsubramanian[140] and Sabesan reported a strong dependence of first order constant on lactic acid concentration, a result quite different to that of Mishra, Ghosh, Bakore and Joshi

Oxidation of lactic acid catalysed by copper (II) by peroxydisulphate was also studied by Agrawal[141] & coworkers. A reaction mechanism involving reactions of copper-lactate complexes were proposed.

Silver catalysed oxidation of di-atrolactic acid by peroxydisulphate was studied by Hambir[142], Singh and coworkers. They have shown that the reaction was first order in $S_2O_8^{2-}$ and Ag^+. The mechanism of a reaction and its inhibition was discussed.

Oxidation of malic acid was studied by Kumar[143] and Saxena. They have shown that the increase in temperature was found to bring about a variation of order, the reaction progressing to bimolecularity in the begining and unimolecularity of completion. In oxidation of tartaric acid, Saxena[144] and Singhal has reported a dependence of order on temperature and its variation with time. Srivastava[145] and Vasudeva have reported a first order behaviour independent of temperature for the uncatalysed oxidation of citric acid.

Mhala[146] and Iyer studied the Ag^+ catalysed oxidation of citric acid and found first order behaviour with respect to peroxydisulphate and zero order with respect to organic substrate.

Decarboxylation of acids in presence of silver nitrate by peroxydisulphate ion in aqueous medium has been studied by Anderson[147] and Kochi. The rate of decarboxylation was found to be first order in $S_2O_8^{2-}$ and Ag^+ and zero order in carboxylic acid. The mechanism of decarboxylation proposed involves Ag^{2+} species formed as metastable intermediate and it plays an important role in the specific and efficient oxidation of the carboxylic acid.

The kinetic study of the dicarboxylic acids, the catalysed[148-151] and uncatalysed[152,153] oxidation of oxalic acid and oxalate ion have been studied by a number of workers. There is no general agreement about the exact mechanism of this reaction. According to Allen[149] the Cu^{2+} catalysed reaction is first order in catalyst and zero order with substrate as well as in peroxydisulphate. Bhakuni[150] and Srivastava reported first order with respect to the catalyst and peroxydisulphate. Kemp[154] observed that the kinetic results were not reproducible where as Srivastava[153] and Ghosh reported that, when proper precautions of purity of the reactants and medium were taken, then the results are reproducible and the reaction is autocatalytic. It was observed that Cu^{2+} has a great catalytic activity for oxalate oxidation while Bhakuni[150] and Srivastava reported the existance of autocatalysis followed by autoinhibition for both Ag^+ as well as Cu^{2+} catalysed oxidition of oxalic acid.

Allen[149] found that Cu^{2+} catalysed reaction is first order with respect to catalyst and zero order with respect to oxalate ion and $S_2O_8^{2-}$ which is contradictory to the results obtained by Bhakuni[152] and Srivastava. Allen[155] and Benzvi further observed that the reaction exhibits an induction period followed by auto-catalysis and then inhibition. This inhibition was also confirmed by Saxena[156] and Singhal. Recently, Allen[157] and Kalb studied the Ag^+ catalysed oxidation of oxalate by $S_2O_8^{2-}$ ion in the air free solution and found that the rate law varies with concentration of $S_2O_8^{2-}$ ion.

Oxidation reaction between peroxydisulphate and tartaric acid was studied by Agrawal[158] and coworkers. The reaction exhibiits a variation in order. The reaction starts as bimolecular and ends as monomolecular. H^+ and O_2 accelerate the reaction which is also dependent on the surface-volume ratio of the reaction vessel. The oxidation involves a radical chain mechanism.

Silver (I) catalysed oxidation of dicarboxylic acids by peroxydisulphate was carried out by Radhakrishnamurti[159] and coworkers. They have shown that the reaction was first order with respect to the oxidant and Ag^+ but shows zero order dependence on the substrate. A free radical mechanism was proposed.

Singh[160] and coworkers studied the silver catalysed oxidation of glyoxal and glyoxalic acid by peroxydisulphate. They have shown that the reaction was first order in $S_2O_8^{2-}$ and Ag^+ and zero order in substrate.

Silver (I) catalysed oxidation of propionic acid by peroxydisulphate ion was investigated by Malhotra[161] and Saxena. The reaction was first order in $S_2O_8^{2-}$ and Ag^+. Complex formation between Ag^+ and propionic acid was indicated.

Oxidation of glycolic acid by peroxydisulphate was studied by Vasudeva[162] and coworkers. They have shown that the reaction was first order in $S_2O_8^{2-}$ and zero order in glycolic acid. Glyoxylic acid and formaldehyde were the final products of oxidation. A free radical mechanism was proposed.

Uncatalysed oxidation of glyoxylic acid was studied by Vasudeva[163] and coworkers. They have shown that the reaction was first order in peroxydisulphate and zero order in glyoxylic acid. A free radical mechanism was suggested.

Vasudeva[164] and coworkers studied the oxidation of fumaric acid by peroxydisulphate. They have shown that the reaction was first order in $S_2O_8^{2-}$ and zero order in fumaric acid. A free radical mechanism was proposed.

Hambir[165], Singh and coworkers studied the uncatalysed oxidation of p-bromomandelic acid by peroxydisulphate. They have shown that the reaction was first order in $S_2O_8^{2-}$ ion and zero order in p-bromomandelic acid. The final oxidation product was p-BrC_6H_4CHO. A radical mechanism was proposed.

Copper (II) catalysed oxidation of malic acid by peroxydisulphate ion was studied by Agrawal[166] and coworkers. They have shown that the reaction was first order in $S_2O_8^{2-}$ and zero order in substrate. Copper (II) catalysed oxidation of succinic acid by peroxydisulphate was made by Agrawal[167] and coworkers. They have shown that the reaction was first order in $S_2O_8^{2-}$ and zero order in succinic acid and half order in catalyst. A nine step radical chain mechanism involvimg a Cu (II) succinate intermediate was proposed.

Silver (I) and Copper (II) catalysed oxidation of organic acids (glycolic, malic, lactic,tartaric and succinic) by peroxydisulphate was studied by Agrawal[168] and coworkers. They have shown that Ag (I) initiates the chain reaction by direct interaction with the oxidant, whereas Cu (II) does not precipitate in chain initiation. It was further shown that the rate determining step in the two cases is different.

Kinetics and mechanism of copper(II) catalysed oxidation of malic acid by peroxydisulphate ion was reinvestigated by Meyerstein[169]. He suggested that the mechanism proposed by Agrawal and coworkers in the oxidation study of copper (II) catalysed oxidation of malic acid by peroxydisulphate is a vague one. He further states that the mechanism suggested by Agrawal for this reaction is unreasonable, because no other decomposition reaction of a Cu (II) complex is known with simultaneous formation of three free radicals and it is difficult to state how oxidation of carboxylate will result in carbon dioxide formation. An alternative mechanism was proposed based on the known properties of copper complexes.

Silver ion catalysed oxidation of dicarboxylic acids (malonic, succinic, adipic acids) was studied by Srivastava[170] and coworkers. The reaction was shown to be first order in $S_2O_8^{2-}$ and Ag^+ and zero order in substrate. A radical mechanism was proposed.

Ag (I) catalysed oxidation of P-Phenyl propionic acid by peroxydisulphate in sulphuric acid medium was studied by Maheshwari[171] and coworkers. They have shown that the reaction was first order in $S_2O_8^{2-}$ and Ag^+ and zero order in substrate.

Silver catalysed oxidation of some aromatic compounds by peroxydisulphate was studied by Murty[172] and coworkers. They have shown that the reaction was first order in $S_2O_8^{2-}$ and in Ag^+ and zero order in azo compound. A radical mechanism was suggested for this reaction.

Arumugam[173] and coworkers studied oxidation of aryl methyl sulfides by peroxydisulphate. It was shown that the reaction was first order in each reactant. A polar mechanism involving $S_2O_8^{2-}$ ion acting on an electrophile is suggested

Srinivasan[174] and coworkers studied the substituent and steric effects in the oxidation of allyl aryl sulfides by peroxydisulphate. The oxidation of para and meta substituted methyl sulfides with $S_2O_8^{2-}$ in aqueous alcohol is accelerated by electron releasing and retarded by electron withdrawing substituents, indicating the rate determining attack by $S_2O_8^{2-}$ at sulphur atom.

Ag (I) catalysed oxidation of methyl, ethyl and n - propyl acetates by peroxydisulphate was studied by Reddy[175] and coworkers. They found that the reaction was first order in $S_2O_8^{2-}$ and Ag^+ and fractional order in substrate.

Ag(I) catalysed oxidation of phthalimide by peroxydisulphate was studied by Kadam[176] and coworkers. They have shown that the reaction was first order in $S_2O_8^{2-}$, 0.5 order in Ag^+ and zero order in substrate. A free radical mechanism was suggested.

Srivastava[177] and coworkers studied the Ag(I) catalysed oxidation of sulfanilamide by peroxydisulphate. The reaction follow second order kinetics, being first order in each of the reactants. However, the Ag^+ catalysed oxidation is composed of two simultaneous reactions, a first order Ag^+ catalysed reaction and a second order, uncatalysed reaction.A radical mechanism was suggested for this reaction.

Hambir[178] Singh and coworkers studied the Ag(I) catalysed oxidation of N - methylacetamide by $S_2O_8^{2-}$. They have shown that the reaction was first order in $S_2O_8^{2-}$ and Ag^+ and zero order in substrate. A radical mechanism was proposed .

Ag(I) catalysed oxidation of thiourea by peroxydisulphate was studied by Anees[179] Quaiser and Nand. The oxidation showed first order kinetics in $S_2O_8^{2-}$ and Ag^+ The rate was independent of the thiourea concentration. A mechanism involving free radicals was suggested.

Ag(I) catalysed oxidation of urea and acetamide by peroxydisulphate was studied by Agrawal[180,181] and coworkers. They found that the reaction was first order in $S_2O_8^{2-}$ and Ag^+ and zero order in substrate.

Srivastava[183,184] and Hambir Singh studied the Ag(I) catalysed oxidation of amides by peroxydisulphate. They have shown that the amides undergo hydrolytic decomposition and the hydrolytic products were further oxidised by $S_2O_8^{2-}$ and Ag^+.

Srivastava, Hambir Singh and Anil Kumar[185] studied the Ag(I) catalysed oxidation of forma-amide by peroxydisulphate CO_2 and NH_3 were the final products of oxidation. A free radical mechanism was proposed.

A literature survey shows that very little work on the oxidation of amides by peroxydisulphate has been reported by previous[186-188]workers.

Self decomposition of peroxydisulphate was not taken into considedration by many workers, a matter which did not receive much attention by many workers who are working in the field of peroxydisulphate oxidation study.

The kinetic study of Fumaramide and Azelaic-amide are presented in different chapters and the probable mechanism is suggested in the chapter of discussion.