CHAPTER - I

INTRODUCTION

Chemical kinetics is concerned with the dynamics of chemical reactions. In particular, it deals with the rates of chemical reactions and how these rates can be explained in terms of a reaction mechanism. Ideally, a complete reaction mechanism would involve a knowledge of all the molecular details of the reaction, including the energetics and stereochemistry, for example, interatomic distances and angles throughout the course of the reaction, of the individual molecular steps involved in the mechanism. In practice, experiments involve the determination of an average rate of reaction of a large number of molecules; therefore proposed mechanisms usually present a sequence of steps in which the molecules are presumed to be in some sort of average energy and stereochemical state. Throughout its historical development, however, chemical kinetics has become increasingly concerned with presenting a more detailed molecular picture, although the ultimate goal has not been achieved even for relatively simple reactions.

Thermodynamics gives little information about the mechanism of chemical reactions, but chemical kinetics provides an approach for obtaining a reaction mechanism. In principle, kinetic properties should be predictable from quantum and statistical mechanics and kinetic theory; however, the difficulty of treating time-dependent problems, in general, and of knowing the non-equilibrium energy distributions has made it extremely difficult to develop a rigorous and a generally usable theory of chemical kinetics. Several useful approximate theories have been developed, but the elucidation of reaction mechanisms proceeds almost exclusively through experimental work at the present time.

Cane sugar dissolved in water may be kept almost indefinitely at room temperatures. In the presence of decinormal acid, however, the sugar is converted at a measurable velocity into glucose and fructose, and the chemical change is virtually complete at the end of one day. These well-known facts raise two questions. Why does the reaction not take place in the absence of acid ? Why does the reaction in presence of acid end in a day rather than in a second or a century ? The science of chemical kinetics sets out to answer these and similar questions by a formal treatment of all the factors which may determine or influence the velocity of chemical change. In the development of the subject, the inversion of cane sugar occupies a prominent position as the first chemical change to be timed[1] and one of the first reactions in the study of which the importance of temperature was realized.[2] This reaction has attracted hundreds of investigators and over a thousand publications have appeared in many journals.

Berthelot[3] and St.Gilles made a careful study of equilibrium between acetic acid,ethanol,ethyl acetate and water.

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

They were able to show that, in this reversible reaction, the rate of forward reaction was proportional to the concentration of ethanol multiplied by the concentration of acetic acid.

The idea that the rate of a chemical reaction at a given temperature depends upon the concentration was generalized by Guldberg[4] and Waage who, in 1863 stated the law of mass action. In modern terms this law states that, the rate of a chemical reaction is proportional to the concentration of each reactant. This law provides a quantitative basis of kinetic investigation.

The oxidation processes like rusting of iron, burning of wood, fermentation of sugars are known since many years and these processes are of considerable importance not only in the field of inorganic and organic chemistry but have vast implications in biochemistry to understand the nature of life.

In oxidation reactions, the common oxidising agents used are nitric acid, potassium dichromate, potassium permanganate, chlorine , bromine, ceric sulphate, potassium periodate. These oxidising agents are sufficiently strong and oxidation is rather fast. As such, it is very difficult to separate and identify intermediate products of oxidation.

The use of peroxydisulphate ion is comparatively recent. It is a mild oxidising agent. Although the standard redox potential of the system

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

is 2.01 volts (Latimer[5]). The oxidation by peroxydisulphate ion, generally takes place slowly.[6] Because of this fact peroxydisulphate ion has been largely used for kinetic study of the oxidation of various class of compounds, and with this oxidant it is very often possible to isolate and identify the intermediate 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. Polymerisation reactions and
4. Reactions with organic substances.

Since the mechanism of oxidation of 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 House[7] and Wilmarth[8] and Haim. The first studies on the self decomposition of peroxydisulphate ion were made by Elbs[9] and schonherr and

and by Caro[10], followed by the kinetic studies of Levi and Migliarini[11], Green and Masson[12] and of Kalian and Olbrich.[13] The results of these studies may be summarised as under:

1. Decomposition of potassium and sodium peroxydisulphate follow first order kinetics but not that of ammonium salt.
2. The reaction is catalysed by H^+, OH^-, platinum black, lead and other metals.
3. In strongly acid solution, permonosulphuric acid is formed, while in aqueous solution, acid sulphate is formed with the evolution of oxygen according to the equation,

$$S_2O_8^{2-} + H_2O \longrightarrow 2\,HSO_4^- + \tfrac{1}{2}\,O_2$$

4. The specific rate is a 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 substrate, i.e. alcohols was studied by Bartlett[14] and Cotman, who found that this decomposition process is greatly enhanced by the presence of organic substances and suggested that the primary process is the decomposition of $S_2O_8^{2-}$ into two radical ions viz.

$$S_2O_8^{2-} \longrightarrow 2\,SO_4^{\dot{-}}$$

Rius and Zuleta[15] studied the decomposition of $(NH_4)_2S_2O_8$ while, Kolthoff[16] and **Miller** in their study of the thermal decomposition of aqueous $K_2S_2O_8$ solution concluded that the decomposition occurs by means of two reactions, both of which occur simultaneously, and are independent.

1. An uncatalysed reaction in which there is a symmetrical rupture of the 0-0 bond to form two sulphate radical ions (SO_4^-) which are removed by the reaction with water, liberating O_2.

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

$$2\ SO_4^{\dot{-}} + 2H_2O \longrightarrow 2HSO_4^- + 2\ OH$$

$$2\ OH \longrightarrow H_2O + \tfrac{1}{2}\ O_2$$

2. An acid catalysed reaction in which there is an unsymmetrical rupture of the 0-0 bond of the $HS_2O_8^-$ ion, yielding sulphate radical and HSO_4^-, i. e.

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

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

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

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

While in strongly acid medium the $SO_4^{\dot{-}}$ radical hydrolyses to form Caro's acid according to the following reaction :

$$\dot{SO}_4 + H_2O \longrightarrow H_2SO_5$$

Several workers[17-20] studied the kinetics of the decomposition of peroxydisulphate ion from different pointsof 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 (SO_4^-).

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 reactions are generally of the first order with respect to $S_2O_8^{2-}$ and Ag^+ . The nature of the Silver intermediate formed in the process is uncertain. Bawn[17] and Margerison suggested the primary step in the Ag^+ catalysed decomposition of $S_2O_8^{2-}$ as :

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

where, Yost[21] and co-workers 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[22] on the basis of his study of the determination of isotopic composition of oxygen formed, condluded that, SO_4^- radical ion is formed in the decomposition of $S_2O_8^{2-}$ ion and that its formation is catalysed by Ag^+ ion.

In the field of inorganic chemistry the kinetics of oxidation of a number of compounds by $S_2O_8^{2-}$ ion has been studied. Uncatalysed oxidation of iodide ion have been most extensively studied and work upto 1954 has been reviewed by Morgan[23] and Meretoja[24]. This reaction has been generally found to be bimolecular[25-28] in nature since this reaction is between ions of like charges, so it has been investigated by many workers[29-34], to test the predictions of Bronsted[35] theory of kinetic salt effects and the Debye Huckel limiting law. Later work however, indicates that the salt effect depends more on the concentration and nature of the cation than on the ionic strength.[36-41]

Lyubimova[42] studied this reaction catalysed by Cu^{2+} ion and showed that it follows complex kinetics.

Uncatalysed rapid oxidation of Fe^{2+} by $S_2O_8^{2-}$ ion, was studied by Kolthoff[43] and co-workers and was found to obey second order kinetics.

Gupta and Srivastava, studied the uncatalysed oxidation of mercurous nitrate[44] and Stannous ion[45] by $S_2O_8^{2-}$ ion in aqueous medium and found the order of the reaction to be one and two respectively. Stehlik[46] and Nedbalkova, studied the kinetics of oxidation of silver(I) with $S_2O_8^{2-}$ forming silver(III) oxide and suggested the first step to be the oxidation of Ag^+ to Ag^{2+} ion.

Most of the work done on the kinetics of oxidation of peroxydisulphate ion was with the aim of studying the catalytic role of Ag^+ ion. Thus Yost[47] and Co-workers studied the silver-catalysed oxidation of chromic salt and ammonia[47], vanadyl ion [48] and manganous ion[49] by $S_2O_8^{2-}$ ion and came to the following conclusions :

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 characterized by a negative exponential salt effect.

The above observations were explained by Yost and Co-workers[48,49] by postulating the formation of tervalent silver ion as a primary step in all the silver-catalysed oxidations, ie.

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

This reaction was taken as the rate determining step which was followed by the rapid oxidation of the reducing substance by the tervalent 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[50-52] does not fall in line with the view of Higginson[53] and Marshall, according to whom, one electron transfer is more likely in reaction involving ions of transition metals.

Beckier[54] and Kijowski found the Ag^+ catalysed oxidation of Mn^{2+} by $S_2O_8^{2-}$ to be the first order with respect to the catalyst as well as with respect to $S_2O_8^{2-}$.

King studied Ag^+ catalysed oxidation of ammonia and ammonium ion[55] and found that the reactions obeys the first order kinetics, but the oxidation of ammonium ion was slightly autocatalytic. This was accounted for by supposing the occurrence of the following fast reaction also,

$$4Ag^{3+} + NH_4^+ + 3H_2O \longrightarrow 4Ag^+ + NO_3^- + 10\ H^+$$

Srivastava[56] and Ghosh in their study of Ag^+ catalysed decomposition of hydrogen peroxide by $S_2O_8^{2-}$ proposed the formation of Ag^{2+} in the rate determining step

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

Mushran and Co-workers studied the uncatalysed[57] as well as Ag^+ catalysed oxidation of Thallium (I) and also the Ag^+ catalysed oxidation of Tellurium[58,59] (IV) and selenium (IV) by $S_2O_8^{2-}$ ion and found the reaction to be of the first order in $S_2O_8^{2-}$ and Ag^+ and zero order in the reductants. They proposed the formation of Ag^{2+} and $SO_4^{\dot{-}}$ as reactive species in the initial step.

Kinetic studies involving peroxydisulphate ion have lately been of great interest for the chemists, because of the fact that the peroxydisulphate ion acts as a catalyst, in the polymerisation processes.

Eager[60] and Winkler studied the kinetics of oxidation of mercaptans by peroxydisulphate in acetic acid. Like most of the reactions of peroxydisulphate the rate was found to be the first order in peroxydisulphate ion and independent of the mercaptan concentration. They proposed that the rate determining process is the dissociation of peroxydisulphate ion into two sulphate radical ions (SO_4^-) with an activation energy of the order of 26 K.Cals.mole^{-1}. The reaction was reinvestigated by Kolthoff[61] and Miller from emulsion polymerisation point of view. Quite similar results have also been reported in the peroxydisulphate oxidation of organic sulphides[62] and sulphoxides. Levitt[63] proposed a new mechanism for such reactions according to which the first stage in the heterocylic dissociation of $S_2O_8^{2-}$ into sulphate radical (SO_4^-) and sulphate ion (SO_4^{2-}) and the sulphate radical then attacks the organic substrate. Emulsion polymerisation studies of allyl acetate, by Nozaki and Bartlett[64], initiated by peroxydisulphate also showed that the decomposition of potassium peroxydisulphate is a first order reaction. In the earlier studies, Evans[65] and others had also suggested that, in the polymerisation processes in aqueous solution and in emulsion polymerisation initiated by peroxydisulphate ion, the initial step was the decomposition of $S_2O_8^{2-}$ into two sulphate radical ions. Thus Smith[66] and Campbell using $K_2S_2O_8$ containing radioactive S^{35} established the presence of fragments of the peroxydisulphate on the polymer chain emulsion polymerised styrene and Bartlett[64] and Nozaki showed the presence of terminal sulphate groups on 75% of the molecule formed in the emulsion polymerised polly--allyl acetate.

Recently Riggs and Rodriguez[67] studied the peroxydisulphate initiated polymerisation of acrylamide using dialatometric technique and found that the reaction follows an expression :

$$\frac{d}{dt}\left[M_1\right] = k_{1.25}\left[K_2S_2O_8\right]^{0.5} \quad M_1^{\ \ 1.25}$$

Where M_1 represents the initial monomer concentration.

From the results of analysis of the kinetics and energatics of the polymerisation process, they favour a Cage effect theory rather than a Complex formation theory to explain the order with respect to monomer.

The kinetics of oxidation of aldehydes and ketones by peroxydisulphate, both catalysed and uncatalysed, was studied by many workers.[68-70] Thus Subraman and Santappa[68] studied the mechanism of uncatalysed oxidation of formaldehyde and acetaldehyde and silver catalysed oxidation of acetone and cyclohexanone, and observed a similarity in behaviour with those of aliphatic alcohols. They proposed a similar mechanism to that suggested by Khulbe and Srivastava[69,70] involving Ag^{2+} and SO_4^{2-} as reactive species.

Bacon[71] and Co-workers carried out Ag^{+}-catalysed oxidation of primary and secondary amines and α -amino acids by peroxydisulphate. Srivastava and Chandra studied the oxidation of glycine[72] and alanine[73] and found that the reactions followed the general character of redox-reactions of peroxydisulphate. Beileryan[74] and Chaltykiyan 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.

A kinetic study of the reaction between aromatic amines and peroxydisulphate ion in aqueous base, called Boyland-Sims[75-78] oxidation, was made by Behrman[79]. The reaction was found to be first order in neutral amine and initially first order in peroxydisulphate ion. Ortho-aminoaryl sulphate, ammonia and humic acid were found to be the products of the reaction. Behrman proposed a mechanism involving a neucleophilic displacement by the amine nitrogen on the peroxide oxygen to yield the corresponding aryl- hydroxylamine-O-sulphonate. The effect of substituents on this reaction was recently investigated by Venkatsubramanian[80] and Sabesan who found that the reaction is accelerated by electron releasing substituents and retarded by eledtron withdrawing substituents pointing to an electrophilic attack of $S_2O_8^{2-}$ ion. Srivastava[81-83] and Gupta carried out a kinetic study of the oxidation of aromatic amines in acetic acid medium. They found that the reaction is of second order and first order with respect to each reactant leading to the formation of N-phenyl-P-Benzoquinone-di-imine or its substituted compounds. Kinetics of oxidation study of di-isopropylamine was made by Babu.J.Shreekanta[84] and Co-workers. They have shown that the reaction is of second order-first order in oxidant and reductant.

Silver (I)-catalysed oxidation of some aminoacids by peroxydisulphate ion was studied by Reddy[85] and Co-workers. 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+}, $SO_4^{\bar{}}$ 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(1^+) + Copper(2^+) catalysed oxidation of glycine by peroxydisulphate in aqueous medium was studied by Reddy[86] and Co-workers. The oxidation was first order in $S_2O_8^{2-}$ and $\frac{1}{2}$ order in Ag^+ in the presence of Ag^{2+} Cu^{2+} mixtures.

Peroxydisulphate oxidation (of amino acid-glutamic) acid) study was made by Srivastava[87] and Co-workers. They have shown that the reaction is first order in $S_2O_8^{2-}$ and Ag^{2+} and zero order in glutamic acid. A radical mechanism was proposed.

Kinetics of oxidation of alcohols by peroxydisulphate ion has been a subject of study by a number of workers during recent years. The kinetics of oxidation of alcohols by $S_2O_8^{2-}$ has been studied by Bartlett[14] and Cotman and they found 3/2 order for the uncatalysed oxidation of methanol by $S_2O_8^{2-}$. On the other hand, Levitt[88] and Malinowski, in the uncatalysed oxidation of 2-propanol showed that at higher concentration of alcohol the order with respect to alcohol is zero while at low concentration it is unity.

Subraman and Santappa[89,90] and others[91-94] studied the Ag^+ catalysed oxidation of methanol and ethanol by peroxydisulphate and found the order as 3/2 and 1/2 respectively. Bisht and Srivastava[95] studied the Ag^+ catalysed oxidation of aliphatic alcohols and they have shown that the reaction follows first order behaviour with respect to peroxydisulphate and zero order with respect to alcohol. They have also suggested that the fractional order reported by earlier workers is due to the variation on ionic strength and faulty kinetic experimentation further, Khulbe[96] and Srivastava studied Ag^+ catalysed oxidation of n-propanol and found that the rate constant increases with an increase in alcohol concentration. Stehlik[97] and Faila showed that the following rate expressions are obeyed for the Ag^+ catalysed oxidation of CH_3OH and C_2H_5OH .

$$-\frac{d}{dt}\left[S_2O_8^{2-}\right] = 2.9 \pm 0.1 \left[S_2O_8^{2-}\right] \; Ag^+ \; / \left[CH_3OH\right]^{1/2}$$

and

$$-\frac{d}{dt}\left[S_2O_8^{2-}\right] = 7.8 \pm 0.1 \left[S_2O_8^{2-}\right] \; Ag^+$$

Edward[98] and Co-workers studied the kinetics of methanol and ethanol spectrophotometrically. They have reported 3/2 order in $S_2O_8^{2-}$ and zero order in alcohol. Thus the results are contradictory regarding the order of reaction.

Kinetic studies on the oxidation of butane 1,3-diol[99], propane 1,2-diol[100], ethylene glycol[101] and pinacol[102] by peroxydisulphate ion have recently been carried out. Khan and Srivastava[101] , in their Ag^+ catalysed oxidation of ethylene glycol and Bakore[102] and Menghani, in the oxidation of pinacol observed a first order behaviour in $S_2O_8^{2-}$ and zero order in reductant. Bakore[102] and Menghani postulated bivalent silver ion (Ag^{2+}) formed by the interaction of $S_2O_8^{2-}$ and Ag^+ playing an important role in the oxidation of pinacol. Mishra[103] and Ghosh in the silver-catalysed oxidation of glycerol found that the order with respect to glycerol was slightly negative but the order tends to approach zero as the temperature increases.

Ag^+ catalysed oxidation of benzyl alcohol by peroxydisulphate ion was studied by Srivastava[104] and Co-workers. They have shown that the order with respect to benzyl alcohol was zero and order with respect to peroxydisulphate and Ag^+ was first one. Kinetics of silver catalysed oxidation of isoamyl alcohol by peroxydisulphate was carried out by Singh[105] and Co-workers. They have shown that the order with respect to $S_2O_8^{2-}$ was first one and the reaction was zero order with respect to iso-amyl alcohol. A possible mechanism involving Ag^{2+} is suggested.

Silver(I) catalysed oxidation of 1-3 propanediol by peroxydisulphate was studied by Srivastava[106] and Co-workers (re-investigation). A mechanism different from that reported by Bakore[107] and Menghani was proposed on the basis of the oxidation products.

Kinetics of silver(I) ion catalysed oxidation of tert-alcohol by peroxydisulphate was studied by Singh[108]. He suggested that the reaction was first order in $S_2O_8^{2-}$ and Ag^+ while the reaction was zero order in alcohol.

Ag^+(I) catalysed oxidation of iso-amyl alcohol, crotyl alcohol by peroxydisulphate ion was studied by Gupta[109] and Co-workers. They have proposed a free radical mechanism of this reaction.

Silver(I) catalysed oxidation of alicyclic alcohols by peroxydisulphate was studied by Srivastava[110] and Co-workers. They have shown that the oxidation of cyclopentanol, cyclohexanol and cycloheptanol by peroxydisulphate in aqueous medium is first order in $S_2O_8^{2-}$ and Ag(I) and zero order in alcohols. A radical mechanism is proposed and the corresponding rate expression derived.

Silver(I) catalysed oxidation of hexane-1,6 diol by peroxydisulphate ion was studied by Srivastava[111] and Co-workers. They have shown that unlike other reactions of this class, it does not follow simple first order kinetics and is attenuated with nearly half order inhibition by the product of oxidation in the later stages of reaction. The specific rate is a function of the initial concentration of substrate and $S_2O_8^{2-}$. The product of oxidation was 6-hydroxyhexanol. A radical mechanism is discussed.

Laxmi Dutta and Srivastava[112,113] carried out the kinetic study of Ag^+ catalysed oxidation of phenol, O-cresol in acetone medium and found that the reaction is first order in acidic and neutral medium but in alkaline medium the reaction is of second order as studied by Behrman[114] and Walker and Bacon[115] and Munro.

The oxidation of phenols by peroxydisulphate ion in alkanine medium has been studied previously by a number of workers[116-120] and has been reviewed by Sethana[121].

Oxidation of phenols by peroxydisulphate ion in aqueous ethanol, tert-butanol, acetonitrile and acetone was studied by Panigrahi[122] and Co-workers. The reaction was first order in both oxidant and substrate. The order with respect to alkali was 0.5. A mechanism consistent with the 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.

Uncatalysed oxidation of formic[123] acid and formate ion was studied by Srivastava and Ghosh and they found the reaction to be first order in peroxydisulphate and zero order in organic substrates while Kappana[124] reported the oxidation of formate ion by peroxydisulphate to be a second order reaction. Gupta[125] and Nigam after studying the Ag^+ catalysed reaction supported the view point of Srivastava and Ghosh that the reaction is first order in $S_2O_8^{2-}$ and zero order in formate ion. Chaltykyn[126] and Co-workers while studying the Cu^{2+} catalysed oxidation of formate ion and formic acid found that the oxidation of 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.

Oxidation of malic acid was studied by Kumar and Saxena[127]. They have shown that the increase in temperature was found to bring about a variation of order , the reaction progressing to bimolecularity in the beginning and unimolecularity to completion. In oxidation of tartaric acid Saxena[128] and Singhal has reported a dependence of order on temperature and its variation with time. Vasudeva and Srivastava[129] have reported a first order behaviour independent of temperature for the uncatalysed oxidation of citric acid.

Silver catalysed oxidation of lactic acid was investigated by Mishra[130] and Ghosh. 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 $AgNO_3$ was increased. Bakore[131] 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[132] and Sabesan reported a strong dependence of first order rate constant on lactic acid concentration, a result quite different to that of Mishra[130] and Ghosh and Bakore[131] and Joshi.

Mhala[133] 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 recently studied by Anderson[134] 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.

In the kinetic study of dicarboxylic acids, the catalysed[135-138] and uncatalysed[55,139,140] 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[136] the Cu^{2+} catalysed reaction is first order in catalyst and zero order with substrate as well as in peroxydisulphate . Bhakuni[137] and Srivastava reported first order with respect to the catalyst and peroxydisulphate. Kemp[141] and King[55] observed that the kinetic results were not reproducible where as Srivastava[140] and Ghosh reported that, when proper precautions of purity of reactants and medium were taken, then the results are reproducible and the reaction is autocatalytic.

King[55] observed that Cu^{2+} has great catalytic activity for oxalate oxidation while Bhakuni[137] and Srivastava reported the existence of autocatalysis followed by auto-inhibition for both Ag^+ as well as Cu^{2+} catalysed oxidation of oxalic acid. Allen[136] 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 obstained by Bhakuni[137] and Srivastava.

Allen[142] and Benzvi reinvestigated this reaction and found it to be of first order in $S_2O_8^{2-}$ and half order in catalyst. Allen[142] 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[143] and Singhal.

Recently Allen[144] and Kalb studied the Ag^+ catalysed oxidation of oxalate by $S_2O_8^{2-}$ ion in 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[145] and Co-workers. The reaction exhibits 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[146] and co-workers. 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[147] and Co-workers 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) ion catalysed oxidation of propionic acid by peroxydisulphate ion was investigated by Malhotra[148] 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 Vasudava[149] and Co-workers. 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[150] and Co-workers. They have shown that the reaction was first order in peroxydisulphate and zero order in glyoxylic acid. A radical mechanism was suggested.

Similarly, a kinetic study of the reaction of fumaric acid with peroxydisulphate was carried out by Vasudeva[151] and Co-workers. They have shown that the reaction was first order in peroxydisulphate and zero order in fumaric acid. A radical mechanism was proposed.

Uncatalysed oxidation study of p-bromomandelic acid was carried out by Hambir[152] Singh and Co-workers. 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[153] and Co-workers. The rate showed first order dependence on $S_2O_8^{2-}$ concentration, independence of malic acid concentration and linear dependence on Copper(II). Similarly Copper(II) catalysed oxidation study was carried out by Agrawal[154] and Co-workers. The rate for this reaction was shown to be first order in peroxydisulphate, independent of succinic acid and half order in catalyst. A nine step radical chain mechanism involving a Cu(II)-succinate intermediate is proposed.

Difference in rates of silver(I) and copper(II) in the catalysed oxidation of organic acid (glycolic, malic, lactic, tartaric, succinic) by peroxydisulphate ion was studied by Agarawal[155] and Co-workers. They have shown that Ag(I) initiates the chain reaction by direct interaction with the oxidant, whereas Cu(II) does not participate in chain initiation. It was further shown that the rate determining step in the two cases is different.

Oxidation of lactic acid catalysed by Copper(II) by peroxydisulphate was studied by Agrawal[156] and Co-workers. A reaction mechanism involving reactions of Cu-lactate complexes was proposed.

Silver catalysed oxidation of di-atrolactic acid by peroxydisulphate was studied by Hambir[157] Singh and Co-workers. They have shown that the reaction was first order in $S_2O_8^{2-}$ and Ag^+. The mechanism of the reaction and its inhibition was discussed.

Kinetics and mechanism of Copper(II) catalysed oxidation of malic acid by peroxydisulphate ion was re-investigated by Meyerstein[158]. He suggested that the mechanism proposed by Agrawal and Co-workers [J-Inorg.Nucl.Chem., 41(6), 899 (1979)] 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 envisage how oxidation of a carboxylate will result in carbon dioxide formation. An alternative mechanism is proposed based on the known properties of copper complexes.

A kinetic study of the oxidation of succinic acid by peroxydisulphate was carried out by Vasudeva[159] and Co-workers. This uncatalysed reaction was studied at 60°C.

to 80 °C. The reaction is first order in $S_2O_8^{2-}$ and zero order in succinic acid. A free radical chain mechanism is proposed which agrees with the results of an ESR study of the reactions and explains the products formed.

Kinetics of the silver catalysed oxidation of p-fluoromandelic acid by peroxydisulphate ion was studied by Hambir[160] Singh and Co-workers. They have shown that the reaction was first order in $S_2O_8^{2-}$ and Ag^+ and zero order with respect to substrate. The reaction products were p-fluorobenzaldehyde and carbon dioxide. A radical mechanism was proposed.

Kinetics and mechanism of the Silver ion catalysed oxidation of dicarboxylic acids (malanic, succinic and adipic acids) was studied by Srivastava[161] and Co-workers. The reaction was shown to be first order in $S_2O_8^{2-}$ and in the catalyst Ag^+ and zero order in substrate. A radical chain mechanism was proposed.

Silver ion-catalysed oxidation of some aromatic azo-compounds by peroxydisulphate was studied by Murty[162] and Co-workers. The reaction was shown to be the first order in $S_2O_8^{2-}$ and in the catalyst Ag^+ and zero order in azo compound. A radical chain mechanism was suggested for this reaction.

Oxidation of aryl methyl sulfides by peroxydisulphate was studiedby Arumugam[163] and Co-workers. 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 proposed.

Substituent and steric effects in the oxidation of alkyl aryl sulfides by peroxydisulphate was studied by Srinivasan[164] and Co-workers. The oxidation of p- and m-substituted methyl sulfides with $S_2O_8^{2-}$ in aqueous alcohol is accelerated by electron releasing and retarded by electron withdrawing substituents, indicating rate determining attack by $S_2O_8^{2-}$ at $\overset{\text{atom}}{\text{S}}$. A good correlation exists between the rate constants and Hammet σ^+/σ^- constants.

Silver(I) catalysed oxidation of chromium(III) by peroxydisulphate ion was studied by Aditya[165] and Co-workers. The oxidation of Cr(III) to Cr(IV) by $S_2O_8^{2-}$ in one molar H_2SO_4 is first order reaction in $[Ag(I)]$, zero order in $[Cr(III)]$ and fractional order in $[S_2O_8^{2-}]$. There is a temperature dependent induction period. The retardation in the rate with H_2SO_4 and HSO_4^- is interpreted in terms of decreasing reactivity of the free radicals $\bar{O}H > HS\bar{O}_4 > SO_4^-$.

Silver catalysed oxidation of methyl, ethyl and n-propyl acetates by peroxydisulphate in aqueous medium was studied by Reddy[166] and Co-workers. The reaction was shown to be first order in catalyst Ag^+ and oxidant $S_2O_8^{2-}$ and fractional order in ACOR (R = Me, Et, Pr). The products are

CO_2, HCHO and aldehydes from the alcohol moiety of the ester. A reaction scheme is presented in which Ag(I)-ACOR adduct reacts with $S_2O_8^{2-}$ in a rate determining step to yield Ag(II)-ACOR adduct.

Silver(I) catalysed oxidation of sulfanilamide by peroxydisulphate was studied by Srivastava[167] and Co-workers. The peroxydisulphate ion oxidation of sulfanilamide follows 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 possible radical mechanism is suggested and a rate law is derived therefrom.

Silver(I) catalysed oxidation of phthalimide by peroxydisulphate was studied by Kadam[168] and Co-workers. It was shown that the reaction was first order in $S_2O_8^{2-}$, 0.5 order in Ag^+ and zero order in phthalimide. A free radical mechanism was proposed.

Silver catalysed oxidation of N-methylacetamide by peroxydisulphate was studied by Hambir[169] Singh and Co-workers. The reaction was first order in $S_2O_8^{2-}$ and in Ag^+ and zero order with substrate. A radical mechanism was proposed.

Silver catalysed oxidation of Thiourea by peroxydisulphate was studied by Anees[170] Qaiser and Nand.

The oxidation showed first order kinetics with respect to $K_2S_2O_8$ and Ag^+. The rate was independent of the thiourea concentration. A mechanism involving free radicals was proposed.

Mushran[171] and Agrawal studied the Ag^+ catalysed oxidation of acetamide and observed it to be first order in peroxydisulphate and zero order in acetamide. They have suggested the following mechanism ;

$$S_2O_8^{2-} + Ag^+ \longrightarrow 2\,SO_4^{2-} + Ag^{3+} \quad \text{(slow)}$$

$$Ag^{3+} + H_2O + S \longrightarrow \text{Product} + 2H^+ + Ag^+ \text{(fast)}$$

Where S represents the substrate. The mode of attack of oxidation species on the amides was not considered, hence Srivastava[172, 173] and Singh in a latter systematic study of the oxidation of various amides, have proposed that amides undergo hydrolytic decomposition and the hydrolytic products are further oxidised by SO_4^- and Ag^{2+}. Srivastava[174] and Co-workers further studied the oxidation of formamide by peroxydisulphate. It was shown that the Ag^+ catalysed oxidation of formamide gave CO_2, H_2O and NH_4 as final products. On this basis they have proposed a free radical mechanism. Oxidation study of Acetamide was also reported by Vasudeva[175] and Co-workers. It was shown that the reaction was first order in $S_2O_8^{2-}$ and zero order in amides.

A literature survey shows that very little work has been reported (on oxidation of amides) by previous workers.[176-182]

Hence a systematic study of amides of amino acids were undertaken. On the basis of this kinetic study a free radical mechanism has been suggested.

Here it must be mentioned that silver catalysed self-decomposition of peroxydisulphate without the substrate was carried out throughout the present work and the rate constants obtained with the self-decomposition of peroxydisulphate were deducted from the rate constants obtained with substrate.

Self decomposition of peroxydisulphate was not taken into consideration 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 results of amino-acetamide and Acetalglycineamide are presented in different chapters and the probable reaction mechanism is suggested in the chapter of discussion.

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