CHAPTER–I

INTRODUCTION

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The subject of Chemical Kinetics is concerned with the quantitative study of the rates of chemical reactions and of the factors upon which they depend. Not much work was done in this field unitil comparatively recently. In a few investigations carried out at the beginning of the last century, rates of reactions were determined, but little attempt was made to interpret them in terms of exact laws.

From a scientific point of view there are two important things about a process of change. The first is the ultimate result of the change; the second is the time taken for this ultimate result to be attained. It is no consolation to the master of ship which has struck an iceberg, to be told that if only he had waited a few years for equilibrium to be reached, the iceberg would have melted and the ship would have been safe.

In chemical reactions, the problem of predicting the products when equilibrium is eventually reached is dealt with in termodynamics in which it is shown that the equilibrium constant can be predicted from free energies obtained from measurements made in a calorimeter. When equilibrium is achieved rapidly, it is possible to predict products of reaction in simple cases. Thermodynamics has, however, nothing to say about the rate at which a chemical reaction will occur. An analogy may be drawn with the case of a stone falling under gravity. Knowledge that its ultimate position will be on the ground (a thermodynamic result) enables no deductions to be made about the rate of fall.

The inadequacy of thermodynamics in explaning chemical processes is seen by considering the reaction of hydrogen and oxygen at one atmosphere pressure and room temperature. The reaction appears to occur instantaneously when the mixture is sparked. On the other hand, in the absence of the spark or a catalyst, no reaction is detectable after several years. Thermodynamic calculations show, however, that the reaction is accompanied by a large decrease in free energy, and so should be capable of occurring spontaneously with some vigour.

There are many examples of chemical reactions that occur at a measurable rate. It is worth noting that the process of life itself depends on the combined effect of many thousands of chemical reactions, each proceeding at a steady rate at body temperature. The dramatic effect of temperature on rate of reaction is illustrated by the fact that a 10°C rise in temperature of the human body invariably leads to death.

It is fairly easy to show experimentally that the rates of chemical reactions vary with time, but careful experiments are needed to show that this variation is regular and can be described by a mathematical equation.

The first accurate kinetic study of a chemical reaction was carried out in 1850 by Wilhelmy,[1] who measured the rate of conversion of an acidic solution of sucrose into glucose and fructose. This reaction was especially suitable for kinetic study as the amount of reaction could be found at any time by measuring the optical rotation of the solution in a polarimeter. Wilhelmy found that, at a given concentration of acid, the rate of reaction at any instant was proportional to the amount of sucrose remaining in solution.

In 1862, Berthelot[2] and St. Gilles made a careful study of the 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 the 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 on concentration was generalized by Gulberg[3] 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 for kinetic investigations.

Guldberg and Waage further showed that the position of chemical equilibrium can be explained quantitatively for a reversible reaction by assuming a dynamic rather than a static equilibrium, in which the rate of the forward reaction is equal to the rate of the reverse reaction.

In 1889 an important advance was made by Arrhenius[4] who explained the large increase in velocity that are very often brought about by a rise in temperature.

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 large applications in biochemistry to understand the nature of life.

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

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

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

is 2.01 volts (Latimer).[5] The oxidation by peroxydisulphate ion has been largely used for kinetic study of the various class of compounds, and with this oxidant it is always 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 categorised as follows :

(1) Self decomposition of peroxydisulphate ion

(2) Reactions with inorganic reductants

(3) Polymerisation reactions

(4) Reactions with organic substrates

Since the mechanism of oxidation of peroxydisulphate ion is closely connected with the hydrolytic decomposition (oxidation of water) or peroxydisulphate ion a brief review of the work done to investigate the mechanism of this decomposition is necessary. It may be mentioned here 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 study on the self decomposition of peroxydisulphate ion was made by Elbs[9] and Schonherr and by Caro,[10] follwed by the kinetic studies of Levi[11] and Migliarini, Green[12] and Masson and of Kalian[13] and Olbrich. The results of these kinetic studies may be summarised as follows :

(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

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

(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 substrates, i.e. alcohols was made by Bartlett[14] and Cotman, who found that this decomposition process is greatly enhanced by the presence of organic substrates and suggested that the primary process is the decomposition of $S_2O_8^{2-}$ into two SO_4^- radical ions.

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

Rius[15] and Zuleta studied the decomposition of ammonium persulphate, while Kolthoff[16] and Miller in their study on 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 uncatalysed 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.

$$S_2O_8^{2-} \longrightarrow 2S\dot{O}_4^-$$

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

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

(b) An acid catalysed reaction in which there is unsymmetrical rupture of the O – O hand of the $H\ S_2O_8^-$ ion, yielding sulphate radical and $H\ SO_4^-$, i.e.

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

$$H\ S_2O_8^- \longrightarrow S\dot{O}_4 + HSO_4^-$$

$$S\dot{O}_4 \longrightarrow S\dot{O}_3 + \frac{1}{2}\ O_2$$

$$S\dot{O}_3 + H_2O \longrightarrow H_2\ SO_4$$

While in strongly acidic medium, the SO_4 radical hydrolyses to form Caro's acid according to the following reaction :

$$S\dot{O}_4 + H_2O \longrightarrow H_2SO_5$$

Many[17-20] workers 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 reactions 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 :

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

Where as Yost[21] and Coworkers 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 O_2 formed, concluded that $\overset{\cdot -}{SO}_4$ 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 peroxydisulphate ion has been studied. Uncatalysed oxidation of iodide ion has been studied and work upto 1954 has been reviewed by Morgan[23] and Meeratoja.[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 Brönsted[35] 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 the cation that on the ionic strength.[36-41]

Uncatalysed oxidation of Fe^{2+} ion by $S_2O_8^{2-}$ ion was studied by Kolthoff[42] and coworkers, and was found to obey second order kinetics.

Gupta[43, 44] and Srivastava 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[45] and Nadbalkova 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. Thus Yost[46,47] and coworkers studied the silver catalysed oxidation of chromic salt and came to the following conclusions :

(1) These reactions are first order in $S_2O_8^{2-}$ 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 a negative salt effect.

The above observations were explained by Yost[46,47] and coworkers by postulating the formation of tervalent silver ion as a primary step in all the silver catalysed oxidations.

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

This reaction was taken as the rate determining step which was follwed by the rapid oxidation of the reducing substrate 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[48-50] does not fall in line with the view of Higginson[51] and Marshall according to whom, one electron transfer is more likely in reactions involving ions of transition metals.

Beckier[52] and Kijowski found the Ag^{+} catalysed oxidation of Mn^{2+} by $S_2O_8^{2-}$ to be first order with respect to the catalyst as well as with respect to peroxydisulphate.

King[53,54] studied the Ag^{+} catalysed oxidation of ammonia and ammonium ion and found that the reactions obey first order kinetics but the oxidation of ammonium ion was slightly autocatalytic.

Srivastava[55] 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.

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

Mushran and coworkers[56-58] studied the uncatalysed as well as Ag^+ catalysed oxidation of Thalium (I), Tellurium (IV) and Selenium (IV) by peroxydisulphate ion and found that the reaction to be the first order in peroxydisulphate and Ag^+ and zero order with substrates.

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. Eager[59] and Winkler studies the kinetics of oxidation of mercaptans by peroxydisulphate in acetic acid. The rate was found to be first order in 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 ally acetate by Bartlett[60] and Nozaki initiated by peroxydisulphate showed that the decomposition of peroxydisulphate is a first order reaction. +Evans[61] 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[62] and Rodriguez studied the peroxydisulphate initiated polymerisation of acrylamide using dilatometric technique and found that the reaction follows the expression :

$$[M_1] = k_{1.25} [K_2S_2O_8]^{0.5} [M_1]^{1.25}$$

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 Ag^+ catalysed oxidation of iso-nicotinic, nicotinic hydrazides by peroxydisulphate were studied by Hogale[63] 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[64] and coworkers. Picolinic acid hydrazide undergoes oxidation 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 second step of the reaction.

A kinetic study of the reaction between aromatic amines and peroxydisulphate ion in aqueous base, called Boyland[65-68] - sims oxidation was made by Behrman.[69] The reaction was found to be first order in neutral amine and initially first order in $S_2O_8^{2-}$ ion. Orthoaminoaryl sulphate, ammonia, and humic acid were the products of the oxidation reaction. Behrman proposed a mechanism involving a nucleophillic displacement by the amine nitrogen on the peroxide oxygen to yield the corresponding arylhydroxylamine-O-sulphate. The effect of substituents on this reaction was recently investigated by Venkatsubramanian[70] and Sabesan who found that the reaction is accelerated by electron releasing substituents and retarded by electron withdrawing substituents pointing to an electrophillic attack of $S_2O_8^{2-}$ ion. Srivastava[71-73] studied the oxidation of aromatic amides by peroxydisulphate in acetic acid medium and found that the reaction is of second order - First order with respect to each reactant. Babu[74] J. Shreekanta 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. Chaltykyan[75] and Beilerian studied the kinetic of oxidation of aliphatic amines in aqueous medium. They observed that $(CH_3)_2NH$, $(CHH_5)_2NH$, $C_2H_5NH_2$ follow the second order kinetics, while the amides $(CH_3)_3N$, $(C_2H_5)_3N$ gave fractional orders.

The kinetics of oxidation of some ortho substituted N - N Dimethyl anilines by peroxydisulphate was studied by

Srunivasan[76] and coworkers in 50 % (v/v) aqueous ethanol containing phosphate buffur. They have observed that the reaction was second order overall and first order in each reactant. They have further shown that the rate was not influenced by the present of free radical inhibitor, allyl acetate.

Oxidations of thyamines and uracil with sodium peroxydisulphate was studied by Itahara[77] and coworkers. They have shown that the oxidation of thiamines with $Na_2S_2O_3$ in hydrochloric acid gave S-chloro, 6-hydroxy, 5,6-di-hydrothiamines which were converted to 6-alkoxy, 5-chloro, 5,6-dihydro thiamines. The reactions of uracils also gave similar products together with S-chloro uracils.

The kinetics of oxidation of pyrogallol red by peroxydisulphate, both uncatalysed as well as Ag^+ catalysed was studied by Sevillano[78] and coworkers. The reaction was studied in the presence of 1,10-Phenanthroline (Phen) as an activator. Rate equations for these reactions were derived from the minetic dependences on H^+ and reagent concentrations. The rate constants and the order of reaction were also calculated. A kinetic model was also proposed.

Kinetics of reaction between peroxydisulphate and iodide ions in aqueous medium was studied by Lai[79] 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^{o}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 discussed.

Kinetics of the oxidation of ethylenediamine tetraceto cobaltate (II) complexes by peroxydisulphate ion, induced by irradiation with visible light of aqueous solutions containing tris (2'-2'-bipyridine) rethenium(II) ion was studied by Nishida[80] Suzuko and coworkers. They have shown that the oxidation of ethylenediamine tetraceto cobaltate (II) $[Co(Edta)^{2-}]$ by $S_2O_8^{2-}$ was greatly accelerated by irradiation with visible light of aqueous solutions containing tris (2,2'-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 (2,2'-bipyridine) ruthenium ion was studied by Nishida[81] SuZuKo and Kimura Masura. They studied the reaction is $HCO_2^{-} + S_2O_8^{2-} \longrightarrow H^{+} + CO_2 + 2SO_4^{2-}$ constituting a chain reaction initiated by the reaction between $S_2O_8^{2-}$ and $[Ru(bpy)_3]^{2}$. A reaction mechanism was also presented.

The kinetics of oxidation of aldehydes and katones, both uncatalysed as well as Ag^+ catalysed by peroxydisulphate was studied by Khulbe[82,83] and Srivastava. The Subraman[84] and Santapa 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 have 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[85] and coworkers. They have shown that the reaction was found to be first order in $S_2O_8^{2-}$ and zero order in benzaldehyde.

The kinetics of reaction between ammonium and potassium peroxydisulphate with formaldehyde in aqueous medium was studied by Nikolaev[86] and Kochetkova. They have shown that the reaction was second order w.r.t. persulphate and zero order w.r.t. 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 25°C was studied by Okoh[87] Joseph and Krishnamurthy. They have shown that the reaction was first order in both Ag(I) and $S_2O_8^{2-}$ and zero order in porphyrin.

Bacon[88] and coworkers studied the Ag^+ catalysed oxidation of primary and secondary amines as well as α-amino acids by peroxydisulphate. Srivastava[89,90] and Chandra studied the oxidation of glycine and alanine 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[91] and coworkers. They have shown that the reaction is first order w.r.t. $S_2O_8^{2-}$ and Ag(I), and Zero order w.r.t. amino acid. The rate law is explained by assuming Ag^{2+}, SO_4 and amino acid radicals as intermediates. When Cu^{2+} was added to the system under similar conditions the rates of these reactions were shown to be higher. Silver (I) and Copper (II) catalysed oxidation glycine by peroxydisulphate in aqueous medium was studied by Reddy[92] and coworkers. 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. Oxidation study of glutamic acid was made by Srivastava[93] 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[94,95] and Santappa and others[96-99] studied the Ag^+ catalysed oxidation of methanol and ethanol by $S_2O_8^{2-}$ ion and found the order as $\frac{3}{2}$ and $\frac{1}{2}$ respectively. Bisht[100] and Srivastava studied the Ag^+ catalysed oxidation of alcohols. They have observed that the reaction was first order w.r.t. $S_2O_8^{2-}$ and zero order w.r.t. 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[101] and Srivastava studied the Ag^+ catalysed oxidation of n-propanol and found that the rate constant increases with an increase in alcohol concentration. Srivastava[102] and Gupta studied the oxidation of alicyclic alcohols by peroxydisulphate in the presence of Ag(I) as a catalyst. They have shown that the reaction was first order w.r.t. $S_2O_8^{2-}$ and Ag^+ and zero order in alcohol. A free radical mechanism was suggested. Kinetics of oxidation of both aliphatic[103-105] and aromatic alcohols have also been reported by many workers.[106,107]

Edward[108] and coworkers following the kinetics of methanol, ethanol, spectrophotometrically reported 3/2 order in S_2O_8 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[109-111] and Menghani. They have shown that the reaction was first order in $S_2O_8^{2-}$ and zero order in reductant. Bakore[111] and Menghani postulated hivalent Silver ion (Ag^{2+}) formed by the interaction of $S_2O_8^{2-}$ and Ag^+ playing an important role in the oxidation of pinacol. Khan[112] and Srivastava, studied the Ag(I) catalysed oxidation of 1, 3-diol, propane 1,2-diol by $S_2O_8^{2-}$ ion.

They have shown that the reaction was first order in $S_2O_8^{2-}$ and zero order in reductant. Mishra[113] and Ghosh in the silver catalysed oxidation of glycerol found that the order of the reaction w.r.t. glycerol was slightly negative (-0.06 for glycerol concentration from 0.8 to 0.1 M) but the order tends to approach zero when the temperature increases.

Silver (I) catalysed oxidation of 1-3 propanediol by peroxydisulphate was studied by Srivastava[114] and coworkers. (re-investigation). A mechanism different from that reported by Bakore[115] and Meghani was proposed on the basis of the oxidation products.

Ag^+ catalysed oxidation of benzyl alcohol by peroxydisulphate was studied by Srivastava[116] and coworkers. They found that the order w.r.t. $S_2O_8^{2-}$ and Ag^+ was one and order w.r.t. benzyl alcohol was zero.

Silver (I) catalysed oxidation of isoamyl alcohol by peroxydisulphate was studied by Singh[117] and coworkers. They found that the order w.r.t. $S_2O_8^{2-}$, was first one and the reaction was zero order w.r.t. 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[118] and coworkers. They have proposed a free radical mechanism for this reaction.

Ag (I) catalysed oxidation of tert-alcohol by peroxydisulphate was studied by Singh.[119] He suggested that the reaction was first order in $S_2O_8^{2-}$ and Ag^+ and zero order in alcohol.

Kinetic study on the oxidation of hexane-1,6-diol by peroxydisulphate (in presence of Ag^+ as a catalyst) was studied by Srivastava[120] 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[121,122] 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[123] and Walker and Bacon[124] and Munro.

The oxidation of phenols by peroxydisulphate ion in alkaline medium has been studied by many workers[125-129] and has been reviewed by Sethna.[130]

Oxidation of phenols by $S_2O_8^{2-}$ ion in aqueous ethanol, tert-butanol, acetonitrile and acetone was studied by

Panigrahi[131] and coworkers. They found that the reaction was first order in $S_2O_8^{2-}$ and reductant and the order w.r.t. 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 mucic and benzilic acid by $S_2O_8^{2-}$ ion in presence of Ag(I) as a catalyst was studied by Gupta[132] and Saksena. They have studied the reaction in dioxane conductivity water 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.[133] 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.

Uncatalysed oxidation of some organic acids, such as acrylic, cinnamic was studied by Khan[134] and coworkers. They found that the reaction was first order in $S_2O_8^{2-}$ and zero order in organic substrates. A radical mechanism was proposed for this reaction.

Srivastava[135] and Ghosh studied the uncatalysed oxidation of formic acid and formate ion. They found that the reaction was first order in $S_2O_8^{2-}$ and zero order in substrates, while Kappana[136] reported the oxidation of formate ion by peroxydisulphate to be a second order reaction. Gupta[137] and Nigam after studying the Ag^+ catalysed reaction supported the view point of Srivastava[135] and Ghosh that the reaction is first order in formate ion. Chaltykyan[138] and coworkers 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 the variation of order with temperature. The reaction is second order upto 30°C while at 40-45°C the order decreases.

Mishra[139] and Ghosh studied the Ag(I) catalysed oxidation of lactic acid. They have reported a first order behaviour w.r.t. to $S_2O_8^{2-}$ and a slight retarding effect due to H^+ ions, while the rate was found to increase linearly when the concentration of Ag(I) was increased. Bakore[140,141] 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[142] and Sabesan reported a strong dependence of first order rate constant on lactic acid concentration, a result which was quite different to that of Mishra[139] and Ghosh and Bakore[140,141] and Joshi.

Copper (II) catalysed oxidation of lactic acid by peroxydisulphate was also studied by Agrawal[143] and coworkers. A reaction mechanism involving reactions of copperlactate complexes was suggested.

Hambir[144] Singh and coworkers studied the Ag(I) catalysed oxidation of di-atrolactic acid by peroxydisulphate. They found that the reaction was first order in S_2O^{2-} and Ag(I) and zero order w.r.t. di-atrolactic acid. A free radical mechanism was suggested.

The oxidation of malic acid was studied by Kumar[145] and saxena. They found 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.

The oxidation of tartaric acid was studied by Saxena[146] and Singhal. They have reported a dependence of order on temperature and its variation with time.

Srivastava[147] and Vasudeva have reported a first order behaviour independent of temperature for the uncatalysed oxidation of citric acid. Mhalal[48] and Iyer studied the Ag^+ catalysed oxidation of citric acid and found that the reaction is first order w.r.t. peroxydisulphate and zero order with citric acid.

Anderson[149] and Kochi studied the decarboxylation of acids in presence of Ag(I) by $S_2O_8^{2-}$ ion in aqueous medium. The rate of decarboxylation was found to be first 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 dicarboxylic acids both catalysed as well as uncatalysed oxidation of oxalic[150-153] acid and oxalate[154,155] ion, was studied by a number of workers. There is no general agreement about the exact mechanism of this reaction. According to Allen,[151] the Cu^{2+} catalysed reaction is first order in catalyst and zero order in substrate as well as in peroxydisulphate. Srivastava[152] and Bhakuni reported first order w.r.t. the catalyst and peroxydisulphate Kemp[156] observed that kinetic results were not reproducible where as Srivastava[155] and Ghosh reported that, when proper precautions of the 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 Srivastava[152] and Bhakuni reported the existence of autocatalysis followed by auto-inhibition for both Ag^{+} as well as Cu^{2+} catalysed oxidation of oxalic acid. Allen[151] found that the Cu^{2+} catalysed reaction is first order w.r.t. catalyst and zero order w.r.t. oxalate ion and $S_2O_8^{2-}$ which is contradictory to the results obtained by Srivastava[152] and Bhakuni. Benzvi[157] and Allen reinvestigated this reaction and found it to be of first order in $S_2O_8^{2-}$ and of half order in the catalyst. They further observed that the reaction exhibits an induction period followed by autocatalysis and then inhibition. This inhibition was also confirmed by Saxena and Singhal. Allen[159] 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.

The kinetics of reaction between peroxydisulphate with tartaric acid was studied by Agrawal[160] and coworkers. They have observed that the reaction exhibits a variation in order. The reaction starts as bimolecular and ends as monomolecular. H^+ and O_2 accelerates the reaction which is also dependent on the surface volume ratio of the reaction vessel. The oxidation involves a radical chain mechanism.

Ag(I) catalysed oxidation of dicarboxylic acids by peroxydisulphate was studied by Radhakrishnamurti[161] and coworkers. They have shown that the reaction was first order with respect to peroxydisulphate and Ag^+ and zero order with respect to substrate. A free radical mechanism was suggested.

Ag(I) catalysed oxidation of glyoxal and glyoxalic acid by peroxydisulphate was studied by Singh[162] and coworkers. They found that the reaction was first order in $S_2O_8^{2-}$ and Ag^+ and zero order in substrate. Uncatalysed oxidation of glyoxalic acid was also studied by Vasudeva[163] and coworkers. They have shown that the reaction was first order in $S_2O_8^{2-}$ and zero order in glyoxalic acid. A radical mechanism was suggested.

The kinetics of oxidation of propionic acid in presence of Ag^+ as a catalyst by peroxydisulphate was studied by Malhotra[164] and Saxena. They have shown that the reaction was first order in $S_2O_8^{2-}$ and Ag^+. Complex formation between Ag^+ and propionic acid was indicated.

Vasudeva[165] and coworkers studied the oxidation of glycolic acid by peroxydisulphate. They found that the reaction was first order in $S_2O_8^{2-}$ and zero order in glycolic acid. The final products of oxidation were glyoxalic acid and formaldehyde. A free radical mechanism was suggested by them for this reaction.

Vasudeva[166] 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[167] Singh and coworkers studied the uncatalysed oxidation of p-bromomandelic acid by peroxydisulphate. They found that the reaction was first order in $S_2O_8^{2-}$ ion and zero order in substrate. The final oxidation product was p-Br C_6H_4CHO. A free radical mechanism was suggested.

Agrawal[168] and coworkers studied the Cu(II) catalysed oxidation of malic acid by peroxydisulphate. They found that the reaction who first order in $S_2O_8^{2-}$ and zero order in substrate.

Cu(II) catalysed oxidation of succinic acid by $S_2O_8^{2-}$ was also studied by Agrawal[169] and coworkers. They have shown that the reaction was first order in $S_2O_8^{2-}$ and zero order in $S_2O_8^{2-}$ and zero order in succinic acid and half order in catalyst. A nine step radical chain mechanism involving a Cu(II) - Succinate intermediate was proposed.

Silver (I) and copper (II) catalysed oxidation oxidation of glycolic, malic, tartaric and succinic acids by percxydisulphate was also studied by Agrawal[170] and coworkers. They have shown that, Ag(I) initials 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.

Copper (II) catalysed oxidation of malic acid by Meyerstein.[171] 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[170] for this reaction is unreasonable. because no other decomposition reaction of a Cu(II) complex is known with simultaneous formation of free radicals and it is difficult to state how oxidation of a carboxylate will result in carbon dioxide formation. An alternative mechanism was proposed based on the known properties of copper complexes.

Srivastava[172] and coworkers studied the Ag(I) catalysed oxidation of malonic, succinic, and adipic acids by peroxydisulphate. They found that the reaction was first order in $S_2O_8^{2}$ and in Ag^+ and zero order in substrates. A free radical mechanism was proposed by them for this reaction.

Ag(I) catalysed oxidation of β-Phenyl propionic acid by peroxydisulphate in sulphuric acid medium was studied by Maheshwari[173] and coworkers. They have shown that the reaction was first order in $S_2O_8^{2}$ and Ag^+ and zero order in substrate.

Arumugam[174] and coworkers studied the 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.

Silver catalysed oxidation of some aromatic azo compounds by peroxydisulphate was studied by Murty[175] 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.

Srinivasan[176] and coworkers studied the substituent and steric effects in the oxidation of alkyl aryl sulfides by peroxydisulphate. 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 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[177] and coworkers. They found that the reaction was first order in $S_2O_8^{2-}$ and Ag^+ and fractional order in substrate.

Srivastava[178] and coworkers studied the Ag(I) catalysed oxidation of sulfanilamide by peroxydisulphate. The reaction 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 radical mechanism was suggested for this reaction.

Ag(I) catalysed oxidation of phthalimide by peroxydisulphate was studied by Kadam[179] 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.

Hambir[180] 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[181] 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[182,183] and coworkers. They found that the reaction was first order in $S_2O_8^{2-}$ and Ag^+ and zero order in substrate.

Srivastava[184,185] 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 SO_4^{2-} and Ag^+.

Srivastava, Hambir Singh and Anil Kumar[186] studied the Ag(I) catalysed oxidation of for amide by peroxydisulphate. CO_2 and NH_3 were the final products of oxidation. A free radical mechanism was proposed.

Oxidation study of acetamide by peroxydisulphate was also reported by Vasudeva[187] and coworkers. They have shown that the reaction was first order in $S_2O_8^{2-}$ and zero order in substrate.

A literature survey shows that very little work on the oxidation of amides by peroxydisulphate has been reported by previous[188-190] workers.

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 pyruvamide and crotonamide are presented in different chapters and the reactions mechanism is proposed in the chapter of discussion.