

# I

## CHAPTER - I

### I N T R O D U C T I O N

Kinetics is a part of the science of motion. In Physics the science of motion is termed dynamics and is subdivided into kinematics, which treats of the motion of bodies, and kinetics, which deals with the effect of forces on motion. In chemistry, no such distinction is made. Kinetics deals with the rate of chemical reaction, with all factors which influence the rate of reaction, and with the explanation of the rate in terms of the reaction mechanism. Chemical kinetics might very well be called chemical dynamics.

Chemical kinetics with its dynamic view point may be contrasted with thermodynamics with its static view point. Thermodynamics is interested only in the initial and final states of a system; the mechanism whereby the system is converted from one state to another and the time required are of no importance. Time is not one of the thermodynamic variables. The most important subject in thermodynamics is the state of equilibrium, and, consequently, thermodynamics is the more powerful tool for investigating the conditions at equilibrium. Kinetics is concerned fundamentally with the details of the progress whereby a system gets from one state to another and with the time required for transition. Equilibrium can also be treated in principle on the basis of kinetics

as that situation in which the rates of the forward and reverse reactions are equal. The converse is not true; a reaction rate cannot be understood on the basis of thermodynamics alone. Therefore, chemical kinetics may be considered a more fundamental science than thermodynamics. Unfortunately, the complexities are such that the theory of chemical kinetics is difficult to apply with accuracy. As a result, we find that thermodynamics will tell with precision the extent of reaction, but only kinetics will tell the rate of the reaction.

Thus, in every branch of chemistry the study of kinetics is very 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 the 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.

The first accurate kinetic study of a chemical reaction was carried out in 1850 by Wilhelmy<sup>1</sup> who measured the rate of conversion of an acidic solution of sucrose into glucose and fructose. The 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 the solution.

In 1862, Berthelot<sup>2</sup> and St. Gilles made a careful study of the equilibrium between acetic acid, ethanol, ethyl acetate and water.

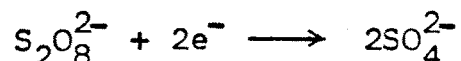


They were able to show that in this reversible reaction the rate of the forward reaction was proportional to the concentration of ethanol multiplied by the concentration of acetic acid.

In the year of 1865 to 1867 Harcourt and Esson<sup>3</sup> published the results of their investigations on the reaction between potassium permanganate and oxalic acid. Very detail experimental studies of the rate of this reaction and of its variation with the concentrations of the reacting substances were carried out by Harcourt and the results were analysed mathematically by Esson in the manner in which this is still frequently done today. Expressions for the amount of reaction as a function of time were worked out for a "first order" reaction, in which the rate is proportional to the concentration of only one reacting

substance, and for a "Second order" reaction, in which the rate is proportional to the product of two concentrations. The theory of successive first order reactions, in which the product of one reaction undergoes a second reaction, was also developed.

In oxidation reactions, the common oxidising agents used are nitric acid, chlorine, bromine, ceric sulphate, potassium iodate, potassium permanganate and potassium dichromate. These oxidising agents are strong and the oxidation is rather fast. The use of potassium peroxydisulphate is comparatively recent. It is a mild oxidising agent, although the standard redox potential of the system,



is 2.01 Volts (Latimer<sup>4</sup>). The oxidation by peroxydisulphate ion, generally takes place slowly.<sup>5</sup> 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 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) The self decomposition of peroxydisulphate ion

- 2) Reactions with inorganic reactants
- 3) Polymerisation reactions
- 4) Reactions with organic substrates.

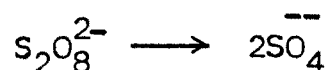
Since the mechanism of oxidation by peroxydisulphate ion is closely related with the hydrolytic decomposition (oxidation of water) of peroxydisulphate ion, a brief review of the work done to investigate the mechanism of this decomposition is necessary. It may be mentioned that the work on the kinetic studies involving peroxydisulphate ion upto 1961 has been reviewed by D.A. House<sup>6</sup> and Wilmarth<sup>7</sup> and Haim.

The first study on the self decomposition of peroxydisulphate ion was made by Elbs<sup>8</sup> and Coworkers and by Caro.<sup>9</sup> Similarly the further study was made by Green<sup>10</sup> and Masson and by Kailan and Olbrich.<sup>11</sup> The results of their study are summarised as follows :

- (1) Decomposition of potassium and 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 permonosulphuric acid is formed while in aqueous solution acid sulphate is formed with the evolution of oxygen.

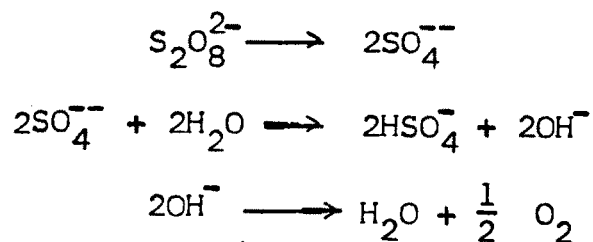
- (4) The specific rate is a function of peroxydisulphate concentration which was explained as due to the specific inhibitory effect of  $K^+$  ions.

The kinetics of decomposition of peroxydisulphate ion in presence of organic substrates, i.e. alcohols was made by Bartlett<sup>12</sup> 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  $SO_4^{\cdot-}$  radical ions.

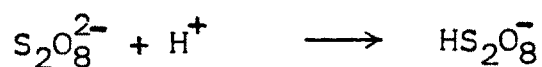


Rius and Zulueta<sup>13</sup> studied the decomposition of  $(NH_4)_2S_2O_8$  while Kolthoff<sup>14</sup> and Miller in their study of the thermal decomposition of aqueous peroxydisulphate solution concluded that the decomposition occurs by means of two reactions, both of which occur simultaneously and are independent.

- (a) An 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.



- (b) An acid catalysed reaction in which there is unsymmetrical rupture of the O - O bond of the  $\text{HS}_2\text{O}_8^-$  ion, yielding sulphate radical and  $\text{HSO}_4^-$ , i.e.



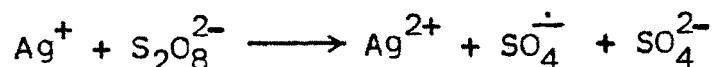
while in strongly acidic medium, the  $\text{SO}_4^\cdot$  radical hydrolyses to form caro's acid according to the following reaction :



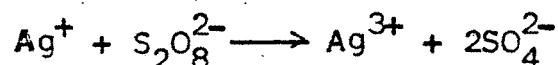
Several workers<sup>15-18</sup> studied the kinetics of decomposition of peroxydisulphate ion from different point of view and from all these studies it can be concluded that the primary process involved in the uncatalysed decomposition of peroxydisulphate ion is the breaking of  $\text{S}_2\text{O}_8^{2-}$  into two sulphate radical ions.

Silver ions ( $\text{Ag}^+$ ) has been found to be 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 :



where as, Yost and Coworkers<sup>19</sup> were of the view that the primary step is the formation of  $Ag^{3+}$  ion.



Recently, Franchuk,<sup>20</sup> on the basis of his study of the determination of isotopic composition of  $O_2$  formed, concluded that  $SO_4^{\cdot-}$  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<sup>21</sup> and Meeratoja.<sup>22</sup> This reaction has been generally found to be bimolecular in nature.<sup>23-26</sup> Since this reaction is between ions of like charges, so it has been investigated by many workers<sup>27-32</sup> to test the predictions of Bronsted<sup>33</sup> 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 than on the ionic strength.<sup>34-39</sup>

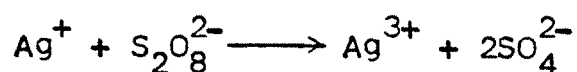


Uncatalysed oxidation of  $\text{Fe}^{2+}$  ion by  $\text{S}_2\text{O}_8^{2-}$  ion was studied by Kolthoff and coworkers<sup>40</sup> and was found to obey second order kinetics.

Gupta and Srivastava<sup>41,42</sup> studied the uncatalysed oxidation of mercurous nitrate and stannous ion by  $\text{S}_2\text{O}_8^{2-}$  ion in aqueous medium and found the order of the reaction to be one and two respectively. Stehlik<sup>43</sup> and Nedbalkova studied the kinetics of oxidation of Silver(I) with  $\text{S}_2\text{O}_8^{2-}$  forming Silver(III) oxide and suggested the first step to be the oxidation of  $\text{Ag}^+$  to  $\text{Ag}^{2+}$  ion. Thus Yost<sup>44-46</sup> and coworkers studied the silver catalysed oxidation of chromic salt, ammonia, vanadyl ion and manganous ion by  $\text{S}_2\text{O}_8^{2-}$  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 characterised by a negative salt effect.

The above observations were explained by Yost<sup>44-46</sup> and coworkers by postulating the formation of trivalent silver ion as a primary step in all the silver catalysed oxidations.

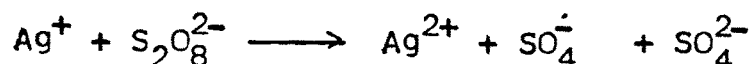


This reaction was taken as the rate determining step which was followed by the rapid oxidation of the reducing substrate by the tervalent silver ion formed in the first process with the reproduction of silver ion ( $\text{Ag}^+$ ). The formation of  $\text{Ag}^{3+}$  ion although supported by many other workers<sup>47-49</sup> does not fall in line with the view of Higginson<sup>50</sup> and Marshall according to whom, one electron transfer is more likely in reactions involving ions of transition metals.

Beckier<sup>51</sup> and Kijowski found the  $\text{Ag}^+$  catalysed oxidation of  $\text{Mn}^{2+}$  by  $\text{S}_2\text{O}_8^{2-}$  to be first order with respect to the catalyst as well as with respect to peroxydisulphate.

King,<sup>52,53</sup> studied  $\text{Ag}^+$  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<sup>54</sup> and Ghosh in their study of  $\text{Ag}^+$  catalysed decomposition of  $\text{H}_2\text{O}_2$  by  $\text{S}_2\text{O}_8^{2-}$  proposed the formation of  $\text{Ag}^{2+}$  in the rate determining step.



Mushran<sup>55-57</sup> and coworkers studied the uncatalysed as well as  $\text{Ag}^+$  catalysed oxidation of Thallium(I), Tellurium(IV) and Selenium(IV) by peroxydisulphate ion and found that the

reaction to be of the first order in peroxydisulphate and  $\text{Ag}^+$  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. Eager<sup>58</sup> and Winkler studied the kinetics of oxidation of mercaptans by peroxydisulphate in concentrated acetic acid. Like most of the reactions of peroxydisulphate, 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 allyl acetate by Nozaki<sup>59</sup> and Bartlett initiated by peroxydisulphate showed that the decomposition of peroxydisulphate is a first order reaction. In the earlier studies, Evans<sup>60</sup> 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  $\text{S}_2\text{O}_8^{2-}$  into two sulphate radical ions.

Recently Riggs<sup>61</sup> and Rodriguez studied the peroxydisulphate initiated polymerisation of acrylamide using dilatometric technique and found that the reaction follows the expression :

$$\frac{d}{dt} [ M_1 ] = K_{1.25} [ \text{K}_2\text{S}_2\text{O}_8 ]^{0.5} [ M_1 ]^{1.25}$$

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 oxidation of aldehydes and ketones by peroxydisulphate, both uncatalysed as well as  $Ag^+$  catalysed was studied by many workers.<sup>62-64</sup> Thus Subraman<sup>62</sup> and Santappa studied 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.

$Ag^+$  catalysed oxidation of benzaldehyde by peroxydisulphate in sulphuric acid medium was studied of Srivastava<sup>65</sup> and coworkers. The reaction was found to be first order in  $S_2O_8^{2-}$  and zero order in benzaldehyde.

Bacon<sup>66</sup> and coworkers studied the  $Ag^+$  catalysed oxidation of primary and secondary amines  $\alpha$  - amino acids by peroxydisulphate. Srivastava and Chandra studied the oxidation of glycine<sup>67</sup> and alanine<sup>68</sup> 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 peroxydisulphate ion was studied by Reddy<sup>69</sup> and coworkers. They have shown that the reaction is first order with respect to peroxydisulphate and ( $\text{Ag}^+$ ) and zero order with respect to amino acid. The rate law is explained by assuming  $\text{Ag}^{2+}$ ,  $\text{SO}_4^{\cdot-}$  and amino acid radicals as intermediates. The rates of these reactions were shown to be higher when  $\text{Cu}^{2+}$  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<sup>70</sup> and coworkers. The oxidation was first order in  $\text{S}_2\text{O}_8^{2-}$  and 1/2 order in  $\text{Ag}^+$  in the presence of  $\text{Ag}^{2+}$ ,  $\text{Cu}^{2+}$  mixtures. Oxidation study of glutamic acid was made by Srivastava<sup>71</sup> and Mathur. They have shown that the reaction is first order in  $\text{S}_2\text{O}_8^{2-}$  and  $\text{Ag}^{2+}$  and zero order in glutamic acid. A free radical mechanism was proposed.

A kinetic study of the reaction between aromatic amines and peroxydisulphate ion in aqueous base, Called Royland<sup>72-75</sup> sims oxidation was made by Behrman.<sup>76</sup> 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<sup>77</sup> 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<sup>78-80</sup> and coworkers 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<sup>81</sup> 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<sup>82</sup> 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.

Subraman<sup>83,84</sup> and Santappa and others<sup>85-88</sup> 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<sup>89</sup> and Srivastava studied the  $Ag^+$  catalysed oxidation of alcohols. They have shown that the reaction follows first order behaviour with respect to  $S_2O_8^{2-}$  and zero order with respect to alcohol. They also suggested that, the fractional order reported by earlier workers is due to the variation in ionic strength and faulty kinetic experimentation. Khulbe<sup>90</sup> and Srivastava

studied  $\text{Ag}^+$  catalysed oxidation of n-propanol and found that the rate constant increases with an increase in alcohol concentration. Srivastava<sup>91</sup> and Gupta studied the oxidation of alicyclic alcohols by peroxydisulphate in presence of  $\text{Ag(I)}$  as a catalyst. They have shown that the reaction was first order  $\text{S}_2\text{O}_8^{2-}$  and  $\text{Ag}^+$  and zero order in alcohol. They have proposed a free radical mechanism. Kinetics of oxidation of both aliphatic<sup>92-94</sup> and aromatic<sup>95,96</sup> alcohols have also been reported by many coworkers.

Edward<sup>97</sup> and coworkers following the kinetics of methanol and ethanol spectrophotometrically reported 3/2 order in  $\text{S}_2\text{O}_8^{2-}$  and zero order in alcohol. Thus the results are contradictory regarding the order of the reaction.

Kinetic study on the oxidation of butane 1,3-diol, propane 1,2-diol and pinacol by peroxydisulphate ion have been recently carried out by Bakore<sup>98-100</sup> and Menghani, Khan<sup>101</sup> and Srivastava, in their  $\text{Ag}^+$  catalysed oxidation of ethylene glycol and Bakore and Menghani,<sup>100</sup> in the oxidation of pinacol observed a first order behaviour in  $\text{S}_2\text{O}_8^{2-}$  and zero order in reductant. Bakore and Menghani<sup>100</sup> postulated bivalent silver ion ( $\text{Ag}^{2+}$ ) formed by the interaction of  $\text{S}_2\text{O}_8^{2-}$  and  $\text{Ag}^+$  playing an important role in the oxidation of pinacol. Mishra<sup>102</sup> 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.

$\text{Ag}^+$  catalysed oxidation of benzyl alcohol by peroxydisulphate was studied by Srivastava<sup>103</sup> and coworkers. They have shown that the order with respect to peroxydisulphate and  $\text{Ag}^+$  was one and order with respect to benzyl alcohol was zero. Kinetics of silver catalysed oxidation of isoamyl alcohol by peroxydisulphate was carried out by Singh<sup>104</sup> and coworkers. They have shown that the order with respect to  $\text{S}_2\text{O}_8^{2-}$  was first one and the reaction was zero order with respect to iso-amyl alcohol. A free radical mechanism involving  $\text{Ag}^{2+}$  was suggested.

Silver(I) catalysed oxidation of 1-3 propanediol by peroxydisulphate was studied by Srivastava<sup>105</sup> and coworkers (re-investigation). A mechanism different from that reported by Bakore<sup>106</sup> 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.<sup>107</sup> He suggested that the reaction was first order in  $\text{S}_2\text{O}_8^{2-}$  and  $\text{Ag}^+$  while the reaction was zero order in alcohol.



$\text{Ag}^+(\text{I})$  catalysed oxidation of iso-amyl alcohol, crotyl alcohol by peroxydisulphate was studied by Gupta<sup>108</sup> and coworkers. They have proposed a free radical mechanism for this reaction.

Silver(I) catalysed oxidation of hexane-1,6 diol by peroxydisulphate ion was studied by Srivastava<sup>109</sup> 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 product of oxidation was 6 - hydroxyhexanol. A free radical mechanism was discussed.

Srivastava<sup>110,111</sup> and Dutta carried out the kinetic study of  $\text{Ag}^+$  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<sup>112</sup> and Walker and Bacon<sup>113</sup> and Munro.

The oxidation of phenols by peroxydisulphate ion in alkaline medium has been studied previously by a number of workers<sup>114-118</sup> and has been reviewed by Sethna.<sup>119</sup>

Oxidation of phenols by peroxydisulphate ion in aqueous ethanol, tert-butanol, acetonitrile and acetone was studied by

Panagrahi<sup>120</sup> and coworkers. The reaction was first order in both oxidant and substrates. 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.

$Ag^+$  catalysed oxidation of acrylic acid by peroxydisulphate ion was studied by Agrawal.<sup>121</sup> He found that the reaction was first order in  $S_2O_8^{2-}$  and zero order in substrate. He proposed a radical chain mechanism for this reaction. Uncatalysed oxidation study of some organic acids (acrylic, cinnamic) was studied by Khan<sup>122</sup> and coworkers. They have shown that the reaction was first order in  $S_2O_8^{2-}$  and zero order in the substrate. A radical mechanism was proposed.

Uncatalysed oxidation of formic acid and formate ion was studied by Srivastava<sup>123</sup> and Ghosh. They found that the reaction was first order in peroxydisulphate and zero order in organic substrates, while Kappana<sup>124</sup> reported the oxidation of formate ion by peroxydisulphate to be a second order reaction. Gupta<sup>125</sup> 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. Chaltykyan<sup>126</sup> and coworkers while studying

the  $\text{Cu}^{2+}$  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  $30^{\circ}\text{C}$  while at  $40-45^{\circ}\text{C}$  the order decreases.

Silver catalysed oxidation of lactic acid was investigated by Mishra<sup>127</sup> and Ghosh. They have reported a first order behaviour with respect to peroxydisulphate and a slight retarding effect due to  $\text{H}^{+}$  ions, while the rate was found to increase linearly when the concentration of  $\text{Ag}^{+}$  was increased. Bakore<sup>128,129</sup> 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<sup>130</sup> and Sabesan reported a strong dependence of first order rate constant on lactic acid concentration, a result quite different to that of Mishra and Ghosh and Bakore and Joshi.

Oxidation of lactic acid catalysed by copper(II) by peroxydisulphate was also studied by Agrawal<sup>131</sup> and Coworkers. A reaction mechanism involving reactions of copper-lactate complexes was proposed.

Silver catalysed oxidation of di-atrolactic acid by peroxydisulphate was studied by Hambir<sup>132</sup> Singh and coworkers.

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.

Oxidation of malic acid was studied by Kumar<sup>133</sup> 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 beginning and unimolecularity to completion. In oxidation of tartaric acid, Saxena<sup>134</sup> and Singhal has reported a dependence of order on temperature and its variation with time. Srivastava<sup>135</sup> and Vasudeva have reported a first order behaviour independent of temperature for the uncatalysed oxidation of citric acid.

Mhala<sup>136</sup> 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<sup>137</sup> 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<sup>138-141</sup> and uncatalysed<sup>142-143</sup> 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<sup>139</sup> the  $\text{Cu}^{2+}$  catalysed reaction is first order in catalyst and zero order with substrate as well as in peroxydisulphate. Bhakuni<sup>140</sup> and Srivastava reported first order with respect to the catalyst and peroxydisulphate. Kemp<sup>144</sup> observed that the kinetic results were not reproducible where as Srivastava<sup>143</sup> 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  $\text{Cu}^{2+}$  has a great catalytic activity for oxalate oxidation while Bhakuni<sup>140</sup> and Srivastava reported the existence of autocatalysis followed by auto-inhibition for both  $\text{Ag}^+$  as well as  $\text{Cu}^{2+}$  catalysed oxidation of oxalic acid. Allen<sup>139</sup> found that  $\text{Cu}^{2+}$  catalysed reaction is first order with respect to the catalyst and zero order with respect to oxalate ion and  $\text{S}_2\text{O}_8^{2-}$  which is contradictory to the results obtained by Bhakuni<sup>140</sup> and Srivastava. Allen<sup>145</sup> and Benzvi reinvestigated this reaction and found it to be of first order in  $\text{S}_2\text{O}_8^{2-}$  and of half order in catalyst. Allen<sup>145</sup> 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<sup>146</sup> and Singhal.

Recently, Allen<sup>147</sup> and Kalb studied the  $\text{Ag}^+$  catalysed oxidation of oxalate by  $\text{S}_2\text{O}_8^{2-}$  ion in air free solution and found that the rate law varies with concentration of  $\text{S}_2\text{O}_8^{2-}$  ion.

Oxidation reaction between peroxydisulphate and tartaric acid was studied by Agrawal<sup>148</sup> and coworkers. The reaction exhibits a variation in order. The reaction starts as bimolecular and ends as monomolecular.  $\text{H}^+$  and  $\text{O}_2$  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<sup>149</sup> and coworkers. They have shown that the reaction was first order with respect to the oxidant and  $\text{Ag}^+$  but shows zero order dependence on the substrate. A free radical mechanism was proposed.

Singh<sup>150</sup> and coworkers studied the silver catalysed oxidation of glyoxal and glyoxalic acid by peroxydisulphate. They have shown that the reaction was first order in  $\text{S}_2\text{O}_8^{2-}$  and  $\text{Ag}^+$  and zero order in substrate.

Silver(I) catalysed oxidation of propionic acid by peroxydisulphate ion was investigated by Malhotra<sup>151</sup> 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<sup>152</sup> 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<sup>153</sup> and coworkers. 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<sup>154</sup> and coworkers. They have shown that the reaction was first order in peroxydisulphate and zero order in fumaric acid. A radical mechanism was proposed.

Hambir<sup>155</sup> 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<sup>156</sup> 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<sup>157</sup> 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 involving 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<sup>158</sup> and coworkers. 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.

Kinetics and mechanism of copper(II) catalysed oxidation of malic acid by peroxydisulphate ion was reinvestigated by Meyerstein.<sup>159</sup> He suggested that the mechanism proposed by Agrawal<sup>156</sup> 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 a 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<sup>160</sup> 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  $\beta$ -Phenyl propionic acid by peroxydisulphate in sulphuric acid medium was studied by Maheshwari<sup>161</sup> and coworkers. They have shown that the reaction was first order with respect to  $S_2O_8^{2-}$  and  $Ag^+$  and zero order with respect to substrate.

Arumugam<sup>162</sup> 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 proposed.

Silver catalysed oxidation of some aromatic azo compounds by peroxydisulphate was studied by Murty<sup>163</sup> and coworkers. 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 mechanism was suggested for this reaction.

Substituent and Steric effects in the oxidation of alkyl aryl sulfides by peroxydisulphate was studied by Srinivasan<sup>164</sup> and coworkers. 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 sulphur atom.

Silver catalysed oxidation of methyl, ethyl and n-propyl acetates by peroxydisulphate in aqueous medium was studied by Reddy<sup>165</sup> and coworkers. The reaction was shown to be first order in the catalyst  $Ag^+$  and oxidant  $S_2O_8^{2-}$  and fractional order in substrate. A reaction scheme is presented in which  $Ag(I)$ -ACOR (R=Me, Et, Pr.) adduct reacts with  $S_2O_8^{2-}$  in the rate determining step to yield  $Ag(II)$ -ACOR adduct.

Silver(I) catalysed oxidation of sulfanilamide by peroxydisulphate was studied by Srivastava<sup>166</sup> and coworkers. 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 possible radical mechanism is suggested and the rate law is derived therefrom.

Silver(I) catalysed oxidation of phthalimide by peroxydisulphate was studied by Kadam<sup>167</sup> and coworkers. 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 suggested.

Silver catalysed oxidation of N-methylacetamide by peroxydisulphate was studied by Hambir<sup>168</sup> Singh and coworkers. The reaction was first order in  $S_2O_8^{2-}$  and in  $Ag^+$  and zero order with respect to substrate. A radical mechanism was suggested.

Silver catalysed oxidation of Thiourea by peroxydisulphate was studied by Anees<sup>169</sup> Quaiser and Nand. The oxidation showed first order kinetics with respect to  $S_2O_8^{2-}$  and  $Ag^+$ . The rate was independent of the thiourea concentration. A mechanism involving free radicals was proposed.

Mushran and Agrawal studied the  $Ag^+$  catalysed oxidation of Urea<sup>170</sup> and acetamide<sup>171</sup> by peroxydisulphate. They have shown that the reaction was first order in  $Ag^+$  and  $S_2O_8^{2-}$  and zero order in substrate. The mode of attack of oxidation species was not considered. Srivastava and Singh<sup>172-73</sup> studied the oxidation of amides by peroxydisulphate in presence of silver catalyst. They have shown that the amides undergo hydrolytic decomposition and the hydrolytic products were

further oxidised by  $\text{SO}_4^{2-}$  and  $\text{Ag}^+$ . Srivastava<sup>174</sup> and coworkers further studied the oxidation of formamide by peroxydisulphate. It was shown that the  $\text{Ag}^+$  catalysed oxidation of formamide gave  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{NH}_3$  as the oxidation products. They have proposed a free radical mechanism. Oxidation study of acetamide was also reported by Vasudeva<sup>175</sup> and coworkers. It was shown that the reaction was first order in  $\text{S}_2\text{O}_8^{2-}$  and zero order in substrate.

A literature survey reveals that very little work (on the oxidation of amides) has been reported by previous workers.<sup>176-184.</sup>

The kinetic results of oxidation study (Oxidation of Cinnamide and capramide in acetic acid medium) are presented in different chapters and the probable mechanism is suggested in the chapter of discussion.