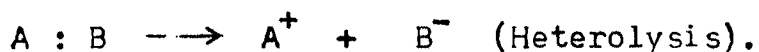


INTRODUCTION :

Chemical kinetics plays an important role in the field of Chemistry, and is concerned with the quantitative study of the rates of chemical reactions and of the factors upon which they depend. The study of kinetics of chemical reaction lies in the fact that its usefulness in furnishing the information, not only about the products formed but also of the reactive intermediates controlling the overall reaction. The mechanism of the reaction is known if the detailed picture of all the individual or other elementary processes involving atoms, molecules, radicals, ions and other reactive species, that take part simultaneously and/or consecutively in the overall reaction process. The mechanism of the reaction gives a detailed picture of the activated complex (1) not only in terms of the constituent molecules but also in terms of geometry. Generally, in most of the reactions, particularly the organic ones, the products obtained are dependent on the course of reaction adopted which is controlled by the reaction rates of several complicating and competing reactions, so, the kinetic study, very often, is capable of predicting favourable conditions necessary for commercial production of a desired product. Although, sometimes, it may not be possible to obtain extensive information about the path traversed by a reaction,

sufficient data can be had to suggest the most likely mechanism of the reaction.

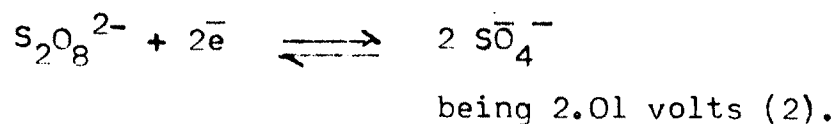
Oxidation reaction occupies an important role in synthetic chemistry. In fact oxidation is de-electronation. The study of the oxidation of organic compounds is an examination of the way by which the electron can be removed from them. The organic compounds involve covalent bonding and are mainly composed of a carbon skeleton, surrounded by skin of hydrogen and consequently, have a few superficial electrons accessible for direct attack by colliding reagents. The covalent bond rupture is an essential feature of organic reactions, which can be effected by two different ways, viz. Homolysis in which electron pair bond is broken symmetrically, so that each fragment acquires complete control over one of the electrons and thus becomes free, uncharged atom or compound radical. Heterolysis in which the electron pair bond is broken unsymmetrically so that the two fragments become oppositely charged ions.



Electron removal by these two ways has clearly distinguishable characteristics. In homolytic oxidations the

electrons are removed singly from substrate molecule by active atoms or by active free radicals. They usually involve the removal, from an organic molecule, of one electron together with a hydrogen nucleus. Heterolytic oxidation involves the attack on substrate of electrophilic reagent which can, by a single process, gain control of a further electron pair. Heterolytic oxidants, therefore, attack the exposed electron pairs of atoms such as oxygen, nitrogen or sulphur, or loosely held π electrons of olefins, rather than the electron pairs of C-H, O-H or N-H bonds. A heterolytic oxidant thus approaches a substrate molecule, toward the region in which its valency electrons are most exposed.

In oxidation reactions, the common oxidising agents used are nitric acid, potassium dichromate, potassium periodate, Potassium permanganate, chlorine, bromine, ceric sulphate, and V^{+5} . 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. On the other hand, peroxydisulphate ion is comparatively milder oxidizing agent, the standard redox potential of the system,



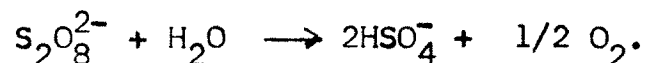
The use of peroxydisulphate as mild oxidant is comparatively recent and has been used in the oxidation of a large number of various classes of compounds, with this oxidant it is very often possible to isolate and identify the intermediate products formed during the course of reaction.

Kinetic study involving peroxydisulphate ion may be categorised as follows :

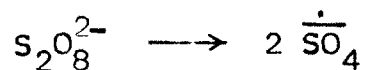
- a) Self-decomposition of $S_2O_8^{2-}$ ion,
- b) reactions with inorganic reductants,
- c) Polymerization reactions,
- d) reactions with organic compounds.

It may be mentioned that the work on the kinetic studies involving peroxydisulphate ion up to 1961 has been reviewed by D.A. House (3) and by Wilmarth and Haim (4). The first studies on the self-decomposition of peroxydisulphate ion were made by Elbs and Schonherr(5) and by Caro (6) followed by the kinetic studies of Levi and Migliorini (7) reported decomposition of $K_2S_2O_8$ and $Na_2S_2O_8$ to be of the first order but not that of $(NH_4)_2S_2O_8$. They also observed the decomposition to be catalysed by H^+ , OH^- , Pt black and Pb etc. Confirming the observations of Levi, Green and Masson (8) suggested

the evolution of O_2 in the following way,



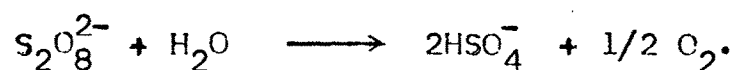
They suggested the ionisation of acid sulphate only into metal ions and HSO_4^- ions to avoid the formation of H^+ and thereby explaining the absence of any auto-catalytic activity. After having studied the decomposition of $K_2S_2O_8$, Kailan and Olbrich (9) observed that the rate constant is a function of its own concentration, which they explained on the assumption of the specific inhibitory effect of K^+ ions. However, they did not agree with Greens and Masson's opinion that H^+ ions are not produced and instead, suggested that the catalytic activity of H^+ ions is counter balanced by the inhibitory effect of SO_4^{2-} ions. The recent observations made by Breuer and Jenkins (10) on the pH dependence of the decomposition of $K_2S_2O_8$ showed that the pH dependence of the reaction was more complicated than was previously thought. Studying the effect of organic substances on the decomposition of $K_2S_2O_8$, Bartlett and Cotman (11) suggested primary process as,



which has been in support of the earlier suggestion of Evans and Baxendale (12). The work of Nozaki and

Bartlett (13), Smith and Campbell (14) and latter on that of Bawn and Margerison (15) also supported this suggestion. The results of these studies may be summerized as under :

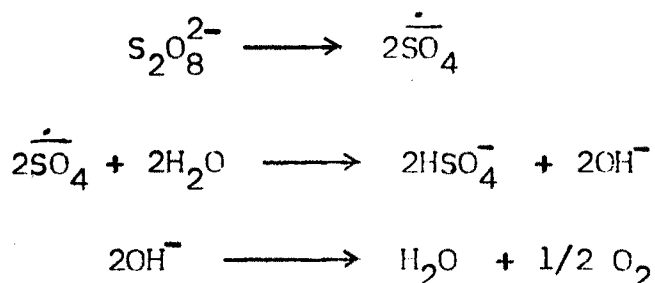
- (a) Decomposition of potassium and sodium peroxydisulphate follows first order kinetics but not that of ammonium salt.
- (b) The reaction is catalysed by H^+ and OH^- , platinum black, lead and by certain other metals.
- (c) In strongly acidic solution, H_2SO_5 is formed, where as in aqueous solution, acid sulphate is formed with evolution of O_2 as follows :



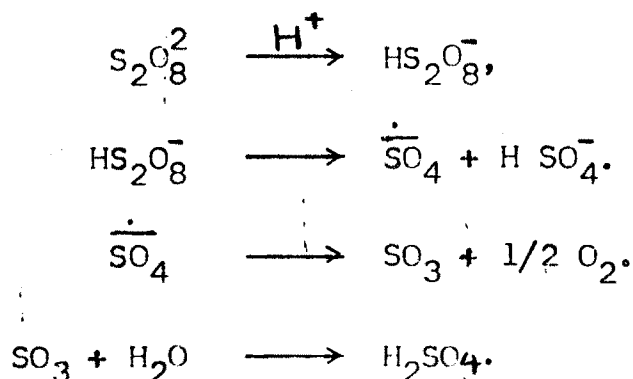
- (d) The specific rate is a function of peroxydisulphate concentration which was explained as due to the specific inhibitory effect of K^+ ions.

The study of Ruis and Zulueta (16), on the decomposition of strongly acidic solution of $(NH_4)_2 S_2O_8$, and that of Kolthoff and Miller (17) on thermal decomposition of $K_2S_2O_8$ concluded that the decomposition occurs through two independent reactions taking place simultaneously.

i) An uncatalysed reaction in which there is a symmetrical rupture of the O-O bond to form two sulphate radical ions ($\dot{\text{S}}\text{O}_4$) which are removed by the reaction with water, liberating O_2 .



ii) An acid catalysed reaction in which there is an unsymmetrical rupture of O-O bond of the HS_2O_8^- ion yielding sulphate radical and HSO_4^- i.e.



Caro's acid is produced in strongly acidic solution.

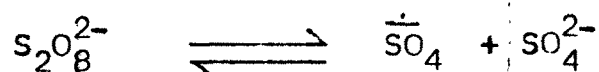


Srivastava and Ghosh (18), on the other hand, suggested the following equilibrium to be the primary step in the

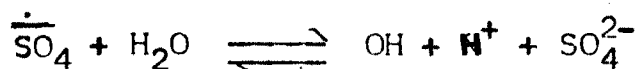
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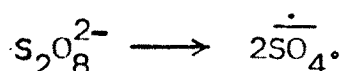
decomposition of $S_2O_8^{2-}$



This suggestion, however, is not acceptable to Eager and McCallum (19). The photolytic decomposition of $S_2O_8^{2-}$ is found to occur through two parallel reactions, as suggested by Tsao and Wilmarth (20), one of the reactions generates SO_4 ion followed by a rapid reversible equilibrium.



While the second reaction initially gives HSO_5 which, however, rapidly destroyed, forming O_2 . All this is in favour of the belief that the primary process is the uncatalysed decomposition of $S_2O_8^{2-}$ in the formation of two $\dot{S}O_4$ radical ions,



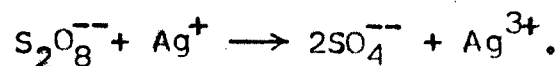
It may be noted that the uncatalysed oxidation of oxalic acid or oxalate ion (18, 21) follows complex kinetics involving radical chain mechanism.

For the catalysed reactions, Ag^+ has been found to be an efficient catalyst during the decomposition of $S_2O_8^{2-}$ while Cu^{2+} is generally less efficient, except in the case of $S_2O_8^{2-} - S_2O_3^{2-}$ (22) and in few other cases. The Ag^+

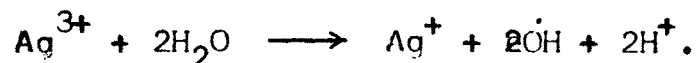
catalysis of Peroxydisulphate ion oxidation was first observed by Marshall (23). Various kinetic investigations (24-33) show that for the majority of the reducing agents studied, the rate law is given by equation -

$$-\frac{d(S_2O_8^{2-})}{dt} = K (S_2O_8^{2-}) (Ag^+).$$

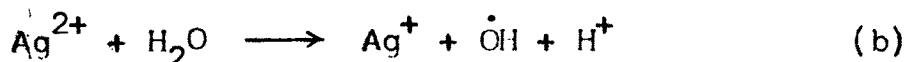
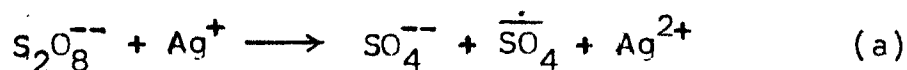
Most of the work done on the kinetics of Ag^+ catalysed oxidation by $S_2O_8^{2-}$ has been with the aim of deciding the catalytic role of Ag^+ . Yost (24) proposed that, the catalytic effect of Ag^+ ion was due to the formation of Ag^{3+} followed by a rapid reaction between Ag^{3+} and the reducing agent.



Morgan (34) suggested that Ag^{3+} formed in the rate determining step reacts rapidly with water to form hydroxyl radicals.

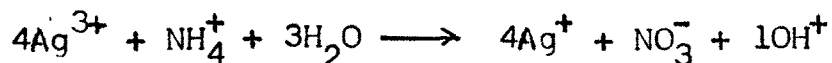


and that the hydroxyl radicals were responsible for the oxidation of reducing reagents, where as Bawn and Margerison (15) proposed that the rate determining step involves a one electron release reaction with the formation of Ag^{2+} followed by reaction of Ag^{2+} with water.

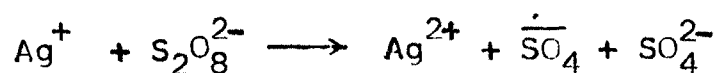


Equation (a) has been proposed by Fronaeus and Ostman (32). Recently, Frankchuk (35) on the basis of his study of the determination of isotopic composition of O_2 formed, concluded that $\overset{\cdot}{\text{SO}}_4$ ion is formed in the decomposition of $\text{S}_2\text{O}_8^{2-}$ ion and that its formation is especially catalysed by Ag^+ ion.

The formation of Ag^{3+} ion, eventhough supported by many other workers (33,36,37), is not in agreement with the view of Higginson and Marshall (38), suggesting the transfer of one electron more likely, with which a number of other workers (15, 18, 32, 39, 40) agree. One more objection raised against the mechanism proposed by Yost was that it failed to explain the auto-catalytic behaviour of many reactions involving $\text{S}_2\text{O}_8^{2-}$ ion. King, in his study of Ag^+ catalysed oxidation of ammonia (28) and ammonium ion (29), found that although the reactions obey first order kinetics, but the oxidation of ammonium ion was found to be slightly auto-catalysed for which, he suggested the following fast reaction accounting for the auto-catalytic nature of the reaction.



Srivastava and Ghosh (18), in their study of Ag^+ catalysed decomposition of H_2O_2 by $\text{S}_2\text{O}_8^{2-}$ proposed the formation of Ag^{2+} in the rate determining step



Kinetic studies involving peroxydisulphate ion have lately been of great interest for the chemist because of the fact that the peroxydisulphate ion acts as a catalyst in the polymerisation processes. The use of this ion as an indicator of polymerisation has been recently recognised. Eager and Winkler (41) studied the kinetics of oxidation of mercaptans by $\text{K}_2\text{S}_2\text{O}_8$ in concentrated acetic acid and found the reaction to be first order in $\text{S}_2\text{O}_8^{2-}$ and zero order in mercaptan. They proposed that the rate determining process is the dissociation of peroxydisulphate ion into two sulphate radical ions ($\overset{\cdot}{\text{S}}\text{O}_4$) with an activation energy of the order of 26.0 K Cal mole⁻¹. The reaction was reinvestigated by Kolthoff and Miller (42), from emulsion polymerisation point of view and quite similar results have been reported in the peroxydisulphate oxidation of organic sulphides and sulphoxides (43), Levitt (44) proposed the heterocyclic dissociation of $\text{S}_2\text{O}_8^{2-}$ into one

sulphate radical ($\dot{\text{S}}\text{O}_4$) and one sulphate ion (SO_4^{2-}) to be the first step of the reaction followed by the reaction of $\dot{\text{S}}\text{O}_4$ with the organic substrate. Emulsion polymerisation studies of allyl acetate by Nozaki and Bartlett (13) initiated by $\text{K}_2\text{S}_2\text{O}_8$ also showed that the decomposition of $\text{K}_2\text{S}_2\text{O}_8$ is a first order reaction.

In the earlier studies Evans (12) and others had suggested that in the polymerisation processes in aqueous medium and in 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. Thus, Smith and Campbell (14) using $\text{K}_2\text{S}_2\text{O}_8$ containing radio active S^{35} established the presence of fragments of the peroxydisulphate on the polymer chain of emulsion polymerised styrene. Nozaki and Bartlett (13) showed the presence of terminal sulphate groups on 75 % of the molecules formed in the emulsion polymerised polyallyl acetate.

Riggs and Rodriguez (45) 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 it is evident that they favour a cage effect thereby rather than a complex formation theory to explain the order with respect to monomer.

An important class of reactions involving peroxydisulphate ion as an oxidant is the "oxidation of organic compounds". Kinetic studies of various organic compounds by peroxydisulphate ion were reviewed recently by House (3) and Wilmarth and Haim (4).

The kinetics of oxidation of alcohols by $S_2O_8^{2-}$ has been widely studied. Bartlett and Cotman (11) found a $3/2$ order for the uncatalysed oxidation of methanol by $S_2O_8^{2-}$. On the other hand, Levitt and Malinowski (46), in the uncatalysed oxidation of 2-Propanol by $S_2O_8^{2-}$ showed that at higher concentration of alcohol, the order w.r.t. alcohol is zero while at low concentration it is unity. Recently many other workers (47-51) also studied the oxidation of alcohols, thus Subbaraman and Santappa (47) studying the Ag^+ catalysed oxidation of alcohols by $S_2O_8^{2-}$, in deaerated buffered and unbuffered solutions reported $3/2$ order in $S_2O_8^{2-}$ and $1/2$ order in methanol and

ethanol, while the order w.r.t. Ag^+ was 1/2, They further observed an inhibition period in the presence of O_2 in all cases. Mishra and Ghosh (52) studied the uncatalysed as well as Ag^+ catalysed oxidation of ethanol and dioxan by $\text{S}_2\text{O}_8^{2-}$ and reported first order in $\text{S}_2\text{O}_8^{2-}$ and zero order in organic substrates. Stehlik and Fiala (53) found that the Ag^+ catalysed oxidation of CH_3OH and $\text{C}_2\text{H}_5\text{OH}$ by $\text{S}_2\text{O}_8^{2-}$ can be represented by following equations

$$-\frac{d(\text{S}_2\text{O}_8^{2-})}{dt} = (2.9 \pm 0.1) \cdot (\text{S}_2\text{O}_8^{2-}) \left[\frac{(\text{Ag}^+)}{(\text{CH}_3\text{OH})} \right]$$

and

$$-\frac{d(\text{S}_2\text{O}_8^{2-})}{dt} = (7.8 \pm 0.1) (\text{S}_2\text{O}_8^{2-}) (\text{Ag}^+)$$

Spectrophotometric studies of Edward et. al. (54), for uncatalysed oxidation of CH_3OH and $\text{C}_2\text{H}_5\text{OH}$ by $\text{S}_2\text{O}_8^{2-}$ showed a 3/2 order in $\text{S}_2\text{O}_8^{2-}$ and zero order in alcohols in the absence of O_2 . Subbaraman and Santappa (47) studied the uncatalysed and Ag^+ catalysed oxidation of 2-butanol, cyclohexanol and 3-butanol by $\text{S}_2\text{O}_8^{2-}$ in the absence of O_2 , and found the reaction first order in $\text{S}_2\text{O}_8^{2-}$, 1/2 order in 2-butanol, zero order in other alcohols and 1/2 order in Ag^+ . So these results are rather contradictory regarding the order of the reaction. Kinetic studies on the oxidation of methanol (51) butane - 1,3 diol (55), Propane, 1,2-diol(56),

ethylene glycol (57), Pinacol (58), glycerol (59), diphenyl carbinol (60), methyl mandelate (61), 1,4-butane diol and 1,5 pentane diol (62) benzyl alcohol (63), iso amyl alcohol (64) and 2-phenyl ethanol (65) have been carried out recently. The kinetics of Ag^+ catalysed oxidation of aromatic alcohols (66) and aliphatic alcohols (67) by peroxydisulphate ion in aqueous medium is first order in $\text{K}_2\text{S}_2\text{O}_8$ and Ag^+ zero order w.r.t. aromatic as well as aliphatic alcohols but kinetics of Cu^{2+} catalysed oxidation of Polyalcohols like sorbitol, erythritol and glycerol (68) by $\text{S}_2\text{O}_8^{2-}$ ion follows the following rate law.

$$-\frac{d(\text{S}_2\text{O}_8^{2-})}{dt} = k (\text{S}_2\text{O}_8^{2-}) (\text{Cu}^{2+})^{1/2}$$

Recently, oxidation of unsaturated aliphatic and arylalkyl alcohols by peroxydisulphate is studied (69). Kinetics of oxidation of the aldehydes and ketones was carried out by Subbaraman and Santappa (70), Srivastava and Khulbe (71), and by Srivastava and Maheshwari (72), and they reported that these reactions follow similar mechanism to that of alcohol oxidation.

Some important kinetic studies of the organic acids include the Ag^+ - catalysed oxidation of lactic acid (73-77), Citric acid (78-79), malic acid (80), phthalic acid (81),

ascorbic acid (82), phenyl acetic acid (83) and mandelic acid, malic acid (84) by $S_2O_8^{2-}$ ion while those of uncatalysed oxidations include O-phenoxy benzoic acid(85), tartaric acid (86), glycolic acid (87) phenyl acetic acid(88). Generally all of them are reported to be first order in $S_2O_8^{2-}$ and zero order in organic substrate. However, Kumar and Saxena (80) in the case of malic acid, reported variation of order with increase in temperature, the reaction being bimolecular second order in the beginning and unimolecular first order at completion. Reduction of ascorbic acid ^{reported} by Mushran and Mehrotra (82), was found to be strongly affected by allyl acetate, suggesting the formation of $\overset{\cdot}{S}O_4$ ion and thereby to a chain mechanism involving hydroxyl radical and ascorbate free radical. Formation of Ag^{2+} was generally suggested in the rate determining step in all these reactions. Very recently, Cu^{2+} catalysed oxidation of glycolic acid by peroxydisulphate ion has been reported by Agarwal and Saxena (89) and they found that first order peroxydisulphate decomposition is disturbed initially for a period of 60-75 min. and thereafter fair constancy is obtained. They attributed it to a considerable pH drop. Interesting study has been carried out by Ram Reddy and Sethuram (90) involving the effect of Cu^{2+} on the Ag^+ catalysed oxidation of some amino acids by peroxydisulphate ion in aqueous medium. Ag^+ ion catalysed oxidation of some amino acids were studied and specific rates of these

reactions were compared with those of $\text{Ag}^+ - \text{Cu}^{2+}$ catalysed reactions. The rate of these reactions were found to be significantly higher, when Cu^{2+} was added to system under similar conditions. However, then Cu^{2+} alone was added instead of Ag^+ , no reaction was observed. Kinetics of silver catalysed oxidation of α -hydroxy monocarboxylic acid (91), succinic acid (92) and Cu(II) catalysed oxidation of lactic acid (93) had been studied. In the former case the reaction shows first order dependence on $\text{S}_2\text{O}_8^{2-}$ and zero order in acid while in latter case the reaction obeys rate law.

$$-\frac{d(\text{S}_2\text{O}_8^{2-})}{dt} = k [\text{S}_2\text{O}_8^{2-}] [\text{lactic acid}]^{1,2} [(\text{Cu III})]^{0.3}$$

The mechanism involves oxidation of Cu(II) acetate complex by $\overset{\cdot}{\text{S}}\text{O}_4$.

The study of oxidation of aromatic compounds like phenols, aromatic amines by $\text{S}_2\text{O}_8^{2-}$ has attracted considerably during the recent years, firstly because of the formation of polymeric products, and secondly due to the inherent complications involved. The oxidation of phenols by $\text{S}_2\text{O}_8^{2-}$ ion in alkaline medium was first of all reported by Elbs (94). Since then this reaction has been the subject to study of different groups of workers (95-97) and the work upto 1950 has been reviewed by Sethana (98).

The phenol oxidation from the view point of the kinetics was first studied by Behrman and Walker (96) taking 2-hydroxypyridine and O-nitrophenol as typical phenols. They reported that the reaction was first order both in peroxydisulphate ion and phenolate ion and suggested that the rate determining step in the Elbs peroxydisulphate oxidation is an electrophilic attack by $S_2O_8^{2-}$ on the phenolate ion. Behrman (97) later on, studied the effect of various substituents on the rate of this reaction and considered a rate of limiting attack at oxygen or at carbon and confirmed Hammett's Correlation. The mechanism of the Elbs peroxydisulphate oxidation, in which the rate limiting attack by $S_2O_8^{2-}$ on the phenoxide occurs at the 'O' atom. The rate constant for p-chloro, p-bromo, p-iodo phenols were determined by Srinivasan and Rajagopal (99) and found that the rate constants were either equal to or lower than for *ph*-OH, since the halo-d-orbital resonance reduces the electron density at oxygen. The higher rate constant of P-F C_6H_4OH is due to the +M effect of fluorine. Bacon and Co-workers (39; 100) after a comprehensive study, found that the resinous polyphenols constitute the entire oxidation products of phenol and cresols except p-cresol.

Recently, following the preliminary work of Khulbe and Srivastava (101) on the colour changes during the oxidation of different phenols by $S_2O_8^{2-}$ in aqueous medium, Datt and Srivastava in their laboratory carried out kinetic studies of the Ag^+ catalysed oxidation of phenol (102), O-Cresol (103) and quinol (104) in acetone medium and found that the reaction is first order and reached the conclusion that the mechanism of Ag^+ catalysed oxidation of phenols by $S_2O_8^{2-}$ in acid or neutral medium is different from that of Elbs peroxydisulphate reaction. Srivastava and Dua (105), reported that the silver catalysed oxidation of nitrophenol by $S_2O_8^{2-}$ ion gave nitro P-benzoquinone. Kinetic study of Ag^+ catalysed oxidation of o-Chlorophenol by peroxydisulphate has been carried out by Srivastava and Shukla (106). The role of the substituent on the rate of oxidation of some phenols has been reported by Sharma and Srivastava (107), and they investigated that the reaction was accelerated by electron releasing groups and retarded by electron withdrawing groups.

Ag^+ ion catalysed oxidation of glycine, α -alanine and α -valine has been carried out by Chandra and Srivastava (108) and rates of these oxidation reactions are

in the order glycine > α -valine > α -alanine. It has been shown that the increase in alkyl chain retards the reaction rate considerably and, therefore, the reaction rate of alanine oxidation is much slower than the glycine oxidation. However, the slightly higher values obtained with the valine oxidation than those of alanine are due to the presence of a branched chain which makes the molecule more reactive.

Ag^+ ion catalysed oxidation of aliphatic amines by $\text{S}_2\text{O}_8^{2-}$ has been recently carried out by Bacon et. al (109-114) and co-workers (115-122). According to Bacon et.al. (113-114), Ag^+ catalysed oxidation of primary aliphatic amine $\text{R-CH}_2\text{-NH}_2$ in alkaline medium gave aldimine $\text{R-CH=N-CH}_2\text{R}$, which subsequently hydrolysed to the aldehyde, R-CHO and the original amine or was hydrogenated to the corresponding secondary amine of the type $\text{R}'\text{, R}''\text{CH NH}_2$ which was converted into ketone $\text{R}'\text{ CO R}''$ without separation of the ketimine. On the other hand secondary amines of the type $(\text{R CH}_2)_2\text{NH}$ and $(\text{R}'\text{ R}''\text{-CH}_2)_2\text{-NH}$ gave proper yield of the aldehydes and ketones under similar conditions while a kinetic study of Chaltykyan and co-workers showed that the reaction is second order, being first order w.r.t. each of the two reactants. The rate

constant was found to be proportional to the first power of catalyst concentration.

Oxidation of some aliphatic amines and amino alcohols have been carried out (123) by $S_2O_8^{2-}$ in presence of Ag^+ as catalyst at $20^\circ C$. The mono amino aquo complex of catalyst ions kinetically active. The catalytical activity of Ag^+ increased with decreasing basicity of amines. The rate of oxidation of amines in the presence of Ag^+ ion is the linear function of basicity of amines. The rate of oxidation of piperidine was higher than was expected according to the observed regular increase. Probably this can be attributed to the formation of the intermediate active complex, peroxydisulphate aquoamine Ag . It was concluded that an increase of electron density by the 'N' of amines inhibits the formation of kinetically active mono-amino aquocomplex of Ag^+ , decreasing its catalytic activity.

Bhattacharya and Joshi (124) reported uncatalysed oxidation of n-butylamine at $45^\circ C$ by $S_2O_8^{2-}$ ion and they found that the reaction is first order in n-butylamine and first order in peroxydisulphate. Similar observations have been reported in the oxidation of di-iso-propylamine and bis (2-hydroxypropylamine) (125). It is also reported

that added acid retards the rate of the reaction. Kinetics of oxidation of glycine (126) in presence of $\text{Ag}^+ - \text{Cu}^{2+}$ catalyst by $\text{S}_2\text{O}_8^{2-}$ ion indicates that the rate constant in presence of mixed catalyst is far higher than sum of rate constants in presence of Ag^+ or Cu^{2+} . The reaction between aromatic amines and peroxydisulphate in aqueous base to form *o*-amino-aryl sulphate was first reported in 1953 (127). The preparative aspects of this reaction were explored in a series of further papers, which established the scope of the reaction (128-130). The reaction might appropriately be named the Boyland-Sims oxidation. The primary, secondary and tertiary amines are all successfully converted to the *O*-sulphate esters although the yields of the isolated materials are frequently poor. If both the ortho positions are blocked, para substitution takes place, otherwise, ortho position is exclusive except for the peroxydisulphate oxidation of anthranilic acid (131) in which a small portion of the para isomer was detected. The reaction of aromatic amines and $\text{S}_2\text{O}_8^{2-}$ leads to the formation of coloured products (128-132) and a number of products in addition to the sulphate esters have been reported. Azo and Azoxy compounds have been found as a product of the oxidation of 2-naphthyl amine (129). In such oxidation reactions (127, 130, 131)

a brown amorphous material, frequently in substantial amount has been detected. The scope of the reaction was extended to include indoles and amino-pyridines. The results of a preliminary mechanistic study of this reaction (133) suggested that it proceeds via nucleophilic displacement on the peroxide oxygen (134) rather than by a radical mechanism and therefore, closely allied to the Elbs - peroxydisulphate oxidation of phenols (96) with notable exception of the orientation of the sulphate group.

A kinetic study of reactions was made by Behrman (135), who reported a first order dependence on amine concentration and initially first order in $S_2O_8^{2-}$ ion concentration. Furthermore, he suggested a nucleophilic displacement by the amine nitrogen on peroxide oxygen to give the corresponding arylhydroxylamine-O-sulphonate. This postulated intermediate was then supposed to rearrange to the O-amino arylsulphate or to get oxidised to humic acid and ammonia.

Following Behrman's work, Venkatasubramanian and Sabesan (136) in a recent kinetic study of the effect of substituents on the rate of the reaction, between aromatic amines and peroxydisulphate ion in alkaline medium have also reported that the reaction is accelerated by the electron

releasing substituents and is retarded by electron withdrawing substituents pointing to an electrophilic attack by the $S_2O_8^{2-}$ ion on the nitrogen of the amine. It is hoped that the reaction proceeds through the different paths in different media (acidic/alkaline etc.) as was reported in the electrolytic oxidation of aromatic amines using different electrolytes (137). The contradictory results, to that of Venkatsubramanian and Sabesan's (136) study, have been reported by Srivastava and Gupta (138). They have studied the reaction between different mono and disubstituted anilines and $K_2S_2O_8$ in acetic acid medium and found that the reaction is accelerated by electron withdrawing substituents and retarded by mono and dimethyl substituents i.e. by electron donating substituents. These observations (136-138) clearly exhibit that the effect of Substituents, on the rate of the reaction between aromatic amines and peroxydisulphate ion in alkaline medium, is different from that of acidic medium. Substituent effect on the oxidation of N, N-dimethylaniline (139) by peroxydisulphate was studied. The reaction rate is accelerated by electron releasing and retarded by electron withdrawing substituents.

Ag^+ ion catalysed oxidation of amides by peroxydisulphate has been studied (139-140) and it was observed that in the case of acetamide (139), the reaction was first order in peroxydisulphate ion and zero order in substrate. However, Remy et. al. (140) found that in the case of other amides viz. $\text{CH}_3\text{CO NH CH}_3$, $\text{CH}_3\text{CO N}(\text{CH}_3)_2$, $\text{CH}_3\text{CO NH C}_2\text{H}_5$ etc. the order is $3/2$. Mushran and Agarwal (141) also studied the Ag^+ catalysed oxidation of urea and found a similar order as in the case of acetamide. As a result of a systematic kinetic study of the Ag^+ catalysed oxidation of amides in their laboratory Singh and Srivastava (142, 143) have concluded that the reaction involves the oxidation of the hydrolytic products of amides. Srivastava et. al. (144) studied the oxidation of formamide and showed that Ag^+ catalysed oxidation gives CO_2 , NH_4^+ as products, and on this basis, they suggested a general mechanism. Oxidation of acetamide and formamide by $\text{S}_2\text{O}_8^{2-}$ was carried out by Wasif, Saad et. al. (145) and they have also shown that the reaction was first order in $\text{S}_2\text{O}_8^{2-}$ and zero order in amide. Ag^+ - catalysed oxidation of malonamide and nicotinamide (146), N-ethyl acetamide (147), iso-nicotinamide (148), n-caproamide (149), iso-caproamide (150), Picolinamide (151), n-valeramide (152), phthalimide (153) by $\text{S}_2\text{O}_8^{2-}$ has been studied. Similarly Sankpal and Jagdale (154) studied the Ag^+ catalysed oxidation of n-butyramide, iso-butyramide

and found that the reaction was first order in $S_2O_8^{2-}$ and zero order in amide. Patil and Sankpal (155) studied Ag^+ catalysed oxidation of glutaramide and adipamide and found that the reaction was first order in $S_2O_8^{2-}$ and zero order in amide. Hambir Singh, Chauhan and Rathi (156) studied silver catalysed oxidation of n-methyl acetamide and shown that the reaction was first order in $S_2O_8^{2-}$ and zero order w.r.t. substrate. The oxidation of thioacetamide by $S_2O_8^{2-}$ catalysed by Ag^+ shows independence of reaction on thioacetamide concentration. Recently Kinetic study of peroxydisulphate oxidation of sulfanamide (157) follows the second order kinetics, first order in each of the reactants.

The kinetics of oxidation of hydrazides has been studied recently and it has been shown that di-imides or free radicals have been formed as intermediates. The oxidation of hydrazides (158) by lead tetraacetate leads to the formation of corresponding acids and nitrogen through the formation of aroyl-dimides, where aroyl radical is formed at room temperature.

The kinetics of oxidation of nicotinoyl and iso-nicotinoyl hydrazides by iron (III) (159) in the presence of 1,10-phenanthroline has been investigated. The oxidation reaction involves the formation of 1:1 complex

with substrate. The retardation of the rate by the presence of H^+ ions was observed and formation of di-imide radical intermediate has been proposed.

The oxidation of phenyl hydrazides (160) by MnO_2 is though a preliminary oxidation of the hydrazide to azo compounds which is solvolysed to acid. The kinetics of oxidation of hydrazides by iodine in aqueous hydrochloric acid has been studied by Krishna Rao and Frank (161) and found that at high concentration of iodine, reaction was first order w.r.t. both oxidant and substrate.

The kinetics of the oxidation of phenyl acetyl hydrazide (162) by Vanadium (V) in aqueous perchloric acid has been studied. The reaction was found to be first order in [oxidant] and in [substrate]. When [substrate] \gg [vanadium(V)] the pseudo first order rate constant decreases with an increase in substrate concentration and the order with respect to H^+ is found to be unity.

The oxidation of salicylic acid hydrazide (163) and substituted salicylic acid hydrazide by active MnO_2 was studied by Haskar and confirmed that acid and nitrogen were the major products.

Hogale and Jagdale investigated the kinetics of Ag^+ catalysed oxidation of Picolinic, nicotinic and isonicotinic acid hydrazides (164) and also studied oxidation of phenylacetic acid hydrazide (165), Benzhydrazide (166), and found that the reaction was first order in $\text{S}_2\text{O}_8^{2-}$ and zero order in hydrazides.

The chemistry of hydrazide is very important and interesting branch of organic chemistry due to physiological activity of hydrazides. In particular various modified aromatic carboxylic acid hydrazides have been tested for the physiological effects. The high activity of certain derivatives is assumed to be due to the diacylhydrazine group as the biologically active centre(167). Carboxylic acid 1, 2 diarylhydrazides have been reported to possess anti-inflammatory properties (168) and diuretic action has been ascribed to benzoic acid hydrazide derivatives (169). iso-Nicotinic acid hydrazide has a strong antituberculous action (170) and hence many derivatives of this compound have been synthesised and tested for antibacterial properties (170-172). Isoxazole carboxylic acid hydrazides (173) are active against leprosy and an anticonvulsive action has been reported for phenothiazine carboxylic acid hydrazide (174) Dihydrazides have been introduced as anthelmintics (175).

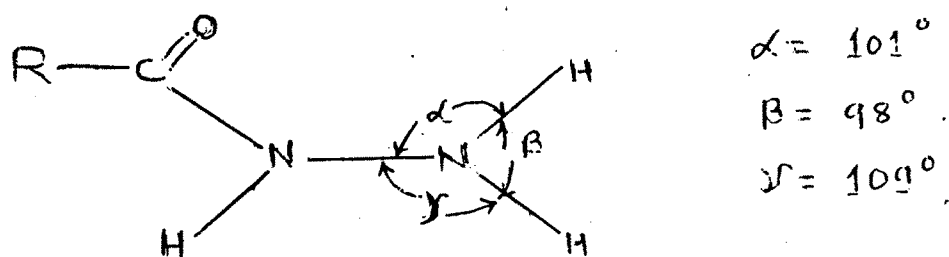
Due to their high reactivity, hydrazides are important starting materials and intermediates in the synthesis of certain amines, aldehydes and heterocyclic compounds. Hydrazides are used for heat and corrosion stabilization of cellulose and cellulose derivatives (176) and as antioxidants for polyolefins and polyurethanes, which are otherwise oxidised in presence of copper. Dihydrazides can be used in cigarette filters for the selective removal of aldehydes from tobacco smoke.

The hydrazides are derivatives of carboxylic acids and hydrazine. The preferred nomenclature is to describe any hydrazide as carboxylic acid hydrazide. The nomenclature is also used in chemical abstract.

The properties of hydrazides are important in their relevance to the chemistry of proteins, substances that are fundamental to all lives, their characteristic properties being primarily due to polyamide structure. Hence, the structure of hydrazides is determined carefully using modern techniques of structure determination.

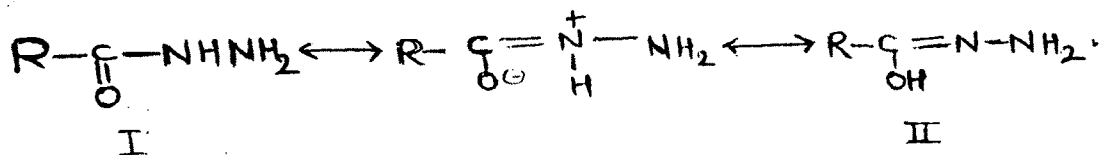
The nitrogen atoms of hydrazide are designated as 1 and 2 or α and β or N and N' the first number of each pair denoting the nitrogen where the acyl group is inserted.

The structure of isonicotinic acid hydrazide has been determined by x-ray crystallography (177).



The N-N bond length is always between 1.39 and 1.42 A° which is shorter than that in hydrazine which is always between 1.46 and 1.47 A° . This is due to formal charge effect and to the fact that the electron attracting acyl group reduces the repulsion between the lone pair of electrons on nitrogen atoms. The C - N bond length is 1.33 A° , which is same as in the pyridine ring. This bond has, therefore, roughly a 50 % double bond character. The two hydrogen atoms point in the direction almost exactly in the same plane.

The hydrazide group can change from its resonance stabilised amide form (I) to the tautomeric enol form (II) by the shift of a hydrogen from nitrogen to oxygen.



Due to resonance stabilization of hydrazide group, its basicity is decreased. In addition to this, the electron attracting phenyl group, so much lowers the basicity of hydrazides that the compounds assume an acidic character.

In the NMR spectra of hydrazides, the chemical shift of the protons of similar hydrazides are similar to those of protons with a comparable chemical environment in other compounds such as amides. The I.R. spectra of crystalline hydrazides show an amide (N-N disuccinimide) band at 1625-1670 cm^{-1} , due to the carbonyl group whose double bond character is reduced by the mesomeric effect of the amide system. A weak band at 1610-1620 cm^{-1} is attributed to NH_2 deformation (182-183). The spectra recorded for hydrazides in solution are different as regards the position and the number of absorption bands, u.v. absorption spectra of hydrazides have not been investigated extensively but they are expected to resemble those of amides.

PRESENT STUDY AND ITS OBJECTS :

Although the kinetics of oxidation of hydrazides by variety of oxidants have been studied, but that of aliphatic acid hydrazides seems to have received much little attention. From the above discussion and previous survey it is clear that very little information regarding mechanism of oxidation of hydrazides by peroxydisulphate ion is available. Hence the study of the kinetics of Ag^+ catalysed oxidation of aliphatic acid hydrazides by $\text{K}_2\text{S}_2\text{O}_8$ has been undertaken. The hydrazides chosen being to a homologous series, so that the effect of chain length on reaction rate and on the mechanism of the reaction can be established.

The two aliphatic acid hydrazides selected for kinetic study are :

- (1) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CONH}\text{NH}_2$ -n-Caproic acid hydrazide.
(n-Cap.A.H.β)
- (2) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CONH}\text{NH}_2$ -n-Heptanoic acid hydrazide.
(n-Hep.A.H.)