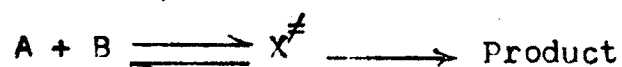


DISCUSSION :

Chemical kinetics attained a new meaning when Arrhenius (202) put forward the concept of molecular activation as a prerequisite to chemical reaction. This concept of activation is now universally accepted and forms a basis of all subsequent theories of chemical reactions. The nature of activated complex, formed as a result of molecular collisions between energised molecules, was considered by Evans and Polanyi (203), Eyring (204). According to Eyring's point of view it is necessary for the reacting atoms or molecules to approach each other to form the activated complex after collision and then pass over an energy barrier to give the products. The molecular species corresponding to the top of such energy barrier are referred to as activated complexes and the rate of the reaction is controlled by the rate by which these complexes travel over the top of the barrier.

As far as oxidation reactions are considered they do not take place in a single step but are complicated due to simultaneous occurrence of a number of steps, some of them are relatively fast or slow. Each step is preferably accompanied by single electron transfer (205). The slowest step is the rate determining step.

According to Evans, Eyring and Polanyi the reaction sequence for a bimolecular reaction is represented as



The expression for the rate constant k_r of reaction, on the basis of absolute reaction rate theory, can be put in the form.

$$k_r = \frac{kT}{h} \cdot \frac{Q^\ddagger}{Q_A \cdot Q_B} \cdot e^{-E_0/RT} \quad \dots (1)$$

where the ' Q ' terms refer to the appropriate partition functions.

k = Boltzmann constant.

E_0 = Energy of activation referred to zero point energy.

Since the equilibrium constant K^* for the formation of the activated complex is given by

$$K^* = \frac{Q^\ddagger}{Q_A \cdot Q_B} \cdot e^{-E_0/RT} \quad \dots (2)$$

Hence equation (1) reduces to

$$k_r = \frac{kT}{h} \cdot K^* \quad \dots (3)$$

$$\text{therefore, } k_r = \frac{kT}{h} \cdot e^{-\Delta G^\ddagger/RT} \quad \dots (4)$$

Where ΔG^\ddagger is the free energy of activation.

But $\Delta G = \Delta H - T\Delta S$. It can be expressed as

$$k_r = \frac{kT}{h} \cdot e^{\Delta S^\ddagger/R} \cdot e^{-\Delta H/RT} \quad \dots (5)$$

$$\ln \left[\frac{k_r}{kT/h} \right] = \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT} \quad \dots (6)$$

where ΔS^\ddagger and ΔH^\ddagger are the entropy and enthalpy changes involved in the formation of the activated complex. Thus, a plot of $\ln \left[\frac{k_r}{kT/h} \right]$ against $\frac{1}{T}$ enables one to calculate ΔS^\ddagger and ΔH^\ddagger .

Since the experimental energy of activation E_{exp} is related to ΔH^\ddagger by the expression.

$$E_{\text{exp}} = \Delta H^\ddagger - P\Delta V^\ddagger + RT \quad (7)$$

Equation (5) for unimolecular reactions or for reactions in solutions, in which ΔV^\ddagger is zero, reduce to

$$k_r = e \cdot \frac{kT}{h} \cdot e^{\Delta S^\ddagger/R} \cdot e^{-E_{\text{exp}}/RT} \quad (8)$$

and in the case of bimolecular reactions

$$k_r = e^2 \cdot \frac{kT}{h} \cdot e^{\Delta S^\ddagger/R} \cdot e^{-E_{\text{exp}}/RT} \quad (9)$$

Thus the equations (8) and (9) (ref. 206) can be used to evaluate the energy of activation for a reaction by the study of effect of temperature on the rate of the reaction.

The prominent effect for reactions in solution is the influence of ionic strength. Bjerrum (207), Bjerrum (208) and Christiansan (209) have applied the Debye Huckel theory to the influence of neutral salts on the rate of reaction in solution.

These effects are of two kinds. In the first case, the activities of the reactants whether ions or polar molecules, may be altered by the added electrolytes. This is the primary salt effect. In the second case, the effect



concentration of a reagent or a catalytic ion coming from a weak electrolytes, may be decreased due to a decrease in the ionisation of the electrolyte because of the added salt. This is the secondary salt effect.

The primary salt effect can be sub-divided into the following two types :

- i) Primary exponential salt effect.
- ii) Primary linear salt effect.

The former for the dilute solutions is given by the Brønsted-Bjerrum equation.

$$\ln k = \ln k_0 + \frac{2Z_A \cdot Z_B \alpha \sqrt{\mu}}{1 + \beta \cdot a_1 \sqrt{\mu}} \quad \dots (10)$$

and for very dilute solution, where μ is small, it reduces to

$$\ln k \approx \ln k_0 + 2Z_A \cdot Z_B \cdot \alpha \sqrt{\mu} \quad \dots (11)$$

Where Z_A and Z_B are the charges of the reacting ions forming the activated complex, μ is the ionic strength of the medium, a , is the mean distance of the closest approach of ions and α and β are the Debye-Huckel constants, while 'k' and 'k₀' are the observed rate constant at ionic strength, and the rate constant at zero ionic strength.

Equation (11) has been verified by many workers in the case of large number of reactions in dilute solutions, and such studies have helped in gaining information regarding the nature of the charge on the reacting ions A and B going to form the activated complex.

According to ~~Bjerrum~~ extended equation a reaction involving ions and dipolar molecules should be independent of the ionic strength of the medium, but this is true only for very dilute solutions. At moderately concentrated solutions the rate will vary with ionic strength. For such reactions between an ion and a dipolar molecules, Amis and Jaffe (210) deduced an equation correlating the rate with the dielectric constant of the medium, which was latter on modified by Amis (211), because of the element of uncertainty about the extrapolation to a reference state of dielectric constant in the Amis - Jaffe approach. Amis, using coulombic considerations, deduced the equation,

$$\ln k_D = \ln k_{\infty} + \frac{Z \cdot \epsilon \cdot \mu_0}{k.T.r^2.D} \quad (12)$$

Where, μ = dipole moment of the dipolar molecule at zero ionic strength.

ϵ = electronic charge.

In case of ion-ion type of reaction, it may be pointed out that in any reaction of this type, instead of equations (10) or (11), the following equation is found to be obeyed by many such reactions.

$$\ln k_r = \ln k_0 + \frac{2 Z_A.Z_B \sqrt{\mu}}{1 + \sqrt{\mu}} + \beta \quad (13)$$

indicating thereby the presence of specific ion effect.

~~Bjerrum~~-Bjerrum theory of salt effect has been criticised by Olson and Simonson (212), according to whom, the effect of addition of salts for reactions between ions of the same

charge sign is caused almost exclusively by the concentration and character of the ions of charge sign opposite to that of the reactants, and that the rate is not dependent upon the ionic strength of the solution. It is true that for reactions between ions, allowance must be made for the role played by the ion pairs, but the role of ion pairs must be accepted as a supplement to, rather than as a replacement of the role of activity coefficient.

The identification of reaction products is another important factor which leads to the elucidation of the reaction mechanism. There may be a number of intermediates which are, extremely reactive and hence short-lived. The existence of these intermediates and free radicals can be demonstrated by addition of radical trap such as allyl acetate (195, 196), allyl alcohol (195, 11, 213), and diphenylpicrylhydrazyl (DPPH) (214) which acts as excellent free radical capture. Recently, it has been reported that the electron paramagnetic resonance (epr) studies directly supply information about the structure (215, 216) of the activated complex. Isotonic method has also offered a very powerful tool for getting information about the mechanism of organic as well as inorganic reactions. The study of the step by step oxidation in the above mentioned ways gives results which can be interpreted mechanistically. The mechanism is nothing but mental model to explain facts obtained by the kinetic studies and in several cases, it predicts very successfully the optimum

conditions for carrying out a chemical reaction.

The present study involves the redox reactions involving $S_2O_8^{2-}$ ion, it is rather necessary to state the present views on mechanism of redox reactions in general.

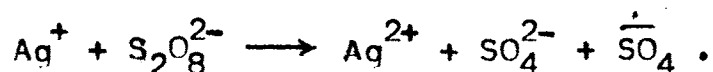
Many times the kinetic results of redox reactions have required the postulation of the existence of species of unstable valency states. Thus, the Ag^+ catalysed reactions of $S_2O_8^{2-}$ (Reviewed in detail in Chapter I) frequently involve an electron transfer in each step of the oxidation as pointed out by Haber and Weiss (217).

Yost (26) assumed that the rate determining process as



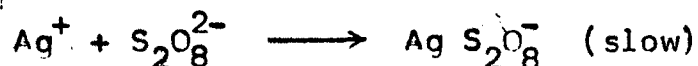
While investigating the oxidation of ammonia, ammonium ion, chromium ion and vanadyl ion in which the Ag^{3+} was considered as the oxidising species.

Srivastava and Ghosh (218) proposed that the rate determining step involves the formation of Ag^{2+} and $\dot{S}O_4$, according to the following relation.

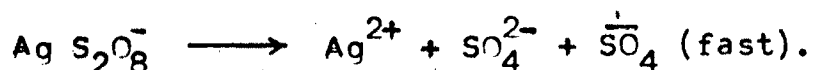
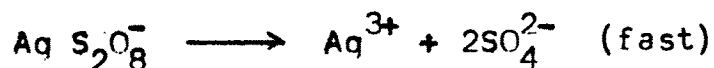


Beckier and Kijowski (219) proposed an alternative initial step to explain the catalyst effect of Ag^+ ions which has been latter supported by Chaltykyan and Beileryan (121).

The various steps may be represented as follows :



followed by either



The above mechanism avoids the postulation of a termolecular step, but it fails to account for the observed negative entropy of activation of large magnitude.

Thus, the formation of bivalent silver ion and a sulphate radical ion, either directly or through the formation of intermediate $\text{Ag S}_2\text{O}_8^-$, seems rather equally possible. However, overwhelming opinion is in favour of the former.

In order to discuss the possible mechanism for the Ag^+ catalysed oxidation of n-caproic and n-heptanoic acid hydrazides by peroxydisulphate ion, it is necessary to summarise the results obtained in the present investigation.

- 1) The oxidation of n-caproic and n-heptanoic acid hydrazides is first order w.r.t. $\text{S}_2\text{O}_8^{2-}$ ion. An increase in $\text{S}_2\text{O}_8^{2-}$ concentration resulted in decrease in specific rate in the oxidation reactions of both the hydrazides studied. The effect is eliminated when these reactions are studied at constant ionic strength and at constant K^+ ion concentration.
- 2) Both these reactions are zero order w.r.t. organic substrate (hydrazide) but the specific rate increases with an increase in the concentration of organic substrate (hydrazide).

The specific rate of the reaction is governed by the following expression

$$k = k_{\max} \times \frac{[\text{Reductant}]_0}{b + [\text{Reductant}]_0}$$

where the values of 'k max' and 'b' are -

Organic substrate (Reductant)	'kmax'	'b'
a) n-Caproic and hydrazide	0.0208	0.007916
b) n-heptanoic acid hydrazide	0.0277	0.009444

3) The specific rate of the reaction is directly proportional to AgNO_3 concentration in both the cases.

4) The various thermodynamic parameters determined are as follows :

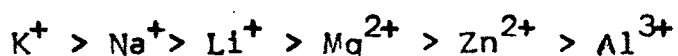
Reaction oxidation	Temp. coefficient	E k cal mole ⁻¹	A x 10 ² Sec ⁻¹	ΔG^\ddagger k cal mole ⁻¹	ΔS^\ddagger (E.u)	ΔH^\ddagger k cal mole ⁻¹ (Graphically)
n-caproic acid hydrazide	1.71	10.52	6.15	20.70	-35.17	9.59
n-heptanoic acid hydrazide	1.56	8.66	3.65	20.80	-43.43	7.69

Both the reactions are characterised by large negative entropy of activation but the free energy of activation as well as enthalpy of activation are of same order of magnitude in each case. The energy of activation for both the reactions is lower than that for the Ag^+ catalysed decomposition of $\text{S}_2\text{O}_8^{2-}$ ion in water (17.9 k cal mole⁻¹).

This suggests that the $S_2O_8^{2-}$ ion should be involved in some subsequent stage either with the organic substrate or with any radical derived there from.

5) The reaction exhibited a negative salt effect and apparently of primary exponential type in the region of low ionic strength. This suggests that the rate determining process is between two oppositely charged ions.

6) The specific inhibitory effect of different cations follows a general order in both reactions, as given below :



7) In an investigation of the effect of hydrogen ion on the rate of reaction it was found that the reaction did not take place in acidic medium indicating that protonated species did not undergo oxidation by $S_2O_8^{2-}$ ion.

8) Allyl acetate exerted appreciable inhibitory effect on the reaction rate.

9) The oxidation products identified in these reactions are as follows :

i) n-caproic acid hydrazide \longrightarrow n-caproic acid.

ii) n-Heptanoic acid hydrazide \longrightarrow n-Heptanoic acid.

In addition to these products, nitrogen is also detected by lime test (201).

10) The values of first order rate constants for both these reactions are given below. (for standard runs)

Hydrazides	Mean $k \times 10^2 \text{ min}^{-1}$
i) n-Caproic acid hydrazide	1.25
ii) n-Heptanoic acid hydrazide	1.54

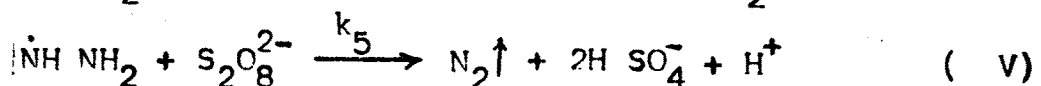
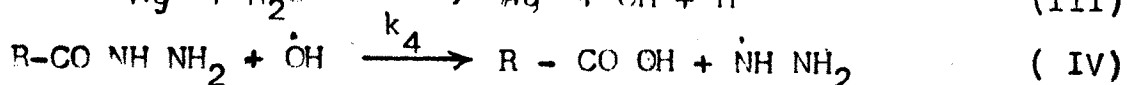
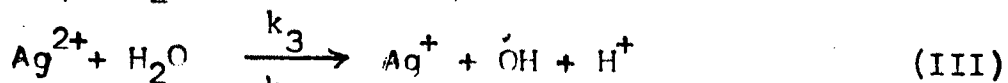
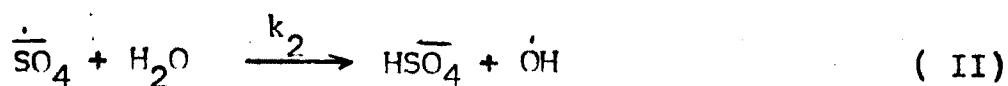
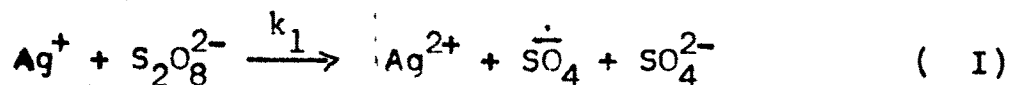
The kinetic data for both hydrazides show that they are reacting almost with the same rate. This observation is in favour of the fact that the order w.r.t. substrate is zero or nearly zero, i.e. substrate is not involved in the rate determining step.

From the results obtained, it is observed that the rate of silver catalysed oxidation of n-heptanoic acid hydrazide is slightly faster than that of n-caproic acid hydrazide. Which may be attributed to addition of one methylene group in the straight chain hydrazide. So increase in the length of hydrazide chain has resulted in increase in rate of oxidation. Similar results have been reported by P. Musala-Reddy (220) in their study of oxidation of aliphatic esters by chromic acid in presence and absence of oxalic acid in acetic acid-water medium, and also by V. Thiagarajan and Co-workers (221) in their study of oxidation of alcohols with bromine i.e. Propane 2-Ol, Butane 2-Ol, Pentane 2-Ol, Pentane 3-Ol, Hexane 2-Ol.

Allyl acetate inhibits the reaction rate because it acts as sulphate radical capture agent leading to subsequent polymerisation by radical anion formed by the catalysed

decomposition of peroxydisulphate. This indicates that the oxidation of hydrazides follows the free radical mechanism. Taking into consideration the close similarity in the kinetic behaviour of n-caproic and n-heptanoic acid hydrazides oxidation it can be suggested that Ag^+ catalysed oxidation of these hydrazides by peroxydisulphate ion follows an identical reaction mechanism. Thus on the basis of kinetic evidences, the following sequence of steps may be proposed for the Ag^+ catalysed oxidation of hydrazides i.e. in general R-CO-NH-NH_2 .

Where $\text{R} = \text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$, for n-Caproic acid hydrazide and $\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$, for n-Heptanoic acid hydrazide.



It is worth while to mention that the first two steps have been proposed earlier by Backier and Kijowski (219), Chaltykyan and Beileryan (121), Bawn and Margerison (15) proposed that the rate determining step involves a one electron release reaction with the formation of Ag^{2+} . It was also proposed by these authors that Ag^{2+} further reacted with water according to step (III). Frank and Krishna Rao (159)

have shown the formation of $\dot{\text{N}}\text{H NH}_2$ radical in the oxidation of hydrazides by other reagents. N_2 was detected as one of the final products in the present study. Hence $\dot{\text{N}}\text{H NH}_2$ may be the intermediate which further reacts with $\text{S}_2\text{O}_8^{2-}$ and gives N_2 .

The rate of disappearance of peroxydisulphate is given as

$$-\frac{d(\text{S}_2\text{O}_8^{2-})}{dt} = k_1(\text{Ag}^+) (\text{S}_2\text{O}_8^{2-}) + k_5 (\dot{\text{N}}\text{H NH}_2)(\text{S}_2\text{O}_8^{2-}) \quad (\text{VI})$$

Applying steady state treatment to the intermediates Ag^{2+} , $\dot{\text{S}}\text{O}_4$, $\dot{\text{O}}\text{H}$ and $\dot{\text{N}}\text{H NH}_2$ the following equations are obtained :

$$\begin{aligned} \frac{d(\dot{\text{S}}\text{O}_4)}{dt} &= k_1(\text{Ag}^+) (\text{S}_2\text{O}_8^{2-}) - k_2(\dot{\text{S}}\text{O}_4) = 0 \\ k_1(\text{Ag}^+) (\text{S}_2\text{O}_8^{2-}) &= k_2(\dot{\text{S}}\text{O}_4) \end{aligned} \quad (1)$$

$$\begin{aligned} -\frac{d(\text{Ag}^{2+})}{dt} &= k_1(\text{Ag}^+) (\text{S}_2\text{O}_8^{2-}) - k_3(\text{Ag}^{2+}) = 0 \\ k_1(\text{Ag}^+) (\text{S}_2\text{O}_8^{2-}) &= k_3(\text{Ag}^{2+}) \end{aligned} \quad (2)$$

from (1) and (2)

$$k_2(\dot{\text{S}}\text{O}_4) = k_3(\text{Ag}^{2+}) \quad (3)$$

$$-\frac{d(\dot{\text{O}}\text{H})}{dt} = k_2(\dot{\text{S}}\text{O}_4) + k_3(\text{Ag}^{2+}) - k_4(\dot{\text{O}}\text{H})(\text{R CO NH NH}_2) = 0$$

$$k_2(\dot{\text{S}}\text{O}_4) + k_3(\text{Ag}^{2+}) = k_4(\dot{\text{O}}\text{H})(\text{R CO NH NH}_2) \quad (4)$$

from (3) and (4)

$$2k_3(\text{Ag}^{2+}) = k_4(\dot{\text{O}}\text{H})(\text{R CO NH NH}_2) \quad (5)$$

From (2) and (5)

$$2k_1(\text{Ag}^+) (\text{S}_2\text{O}_8^{2-}) = k_4(\dot{\text{O}}\text{H})(\text{R CO NH NH}_2) \quad (6)$$

$$\frac{d(\text{NH NH}_2)}{dt} = k_4(\dot{\text{O}}\text{H})(\text{R CO NH NH}_2) - k_5(\dot{\text{N}}\text{H NH}_2)(\text{S}_2\text{O}_8^{2-}) = 0$$

$$k_4(\dot{\text{O}}\text{H})(\text{R CO NH NH}_2) = k_5(\dot{\text{N}}\text{H NH}_2)(\text{S}_2\text{O}_8^{2-}) \quad (7)$$

From (6) and (7)

$$2k_1(\text{Ag}^+) (\text{S}_2\text{O}_8^{2-}) = k_5(\dot{\text{N}}\text{H NH}_2) (\text{S}_2\text{O}_8^{2-}) \quad (8)$$

On substituting equation (8) in (VI) we get

$$= \frac{d(\text{S}_2\text{O}_8^{2-})}{dt} = k_1(\text{Ag}^+) (\text{S}_2\text{O}_8^{2-}) + 2k_1(\text{Ag}^+) (\text{S}_2\text{O}_8^{2-}) \quad (9)$$

$$= 3k_1(\text{Ag}^+) (\text{S}_2\text{O}_8^{2-}) \quad (10)$$

Therefore, the rate of disappearance of peroxydisulphate is given by

$$- \frac{d(\text{S}_2\text{O}_8^{2-})}{dt} = 3k_1(\text{Ag}^+) (\text{S}_2\text{O}_8^{2-}) \quad (11)$$

The above rate expression (11) satisfactorily accounts for the main general kinetic features of the oxidation of hydrazides, viz. the first order w.r.t. $S_2O_8^{2-}$ and Ag^+ catalyst each and zero order w.r.t. substrate. It also accounts for the negative salt effect observed and further suggests that the rate of oxidation of hydrazides should be of the same order of magnitude which has been experimentally observed. It is also noted that the equation (11) fails to explain the facts that the velocity constant is dependent on initial concentration of hydrazides because of the complexity of the system. The existence of radical mechanism has been proved experimentally by investigating the effect of allyl acetate on the specific rate of oxidation. The specific rate of the reaction is inhibited by allyl acetate and thereby confirming radical mechanism.

Thus in conclusion on the basis of the kinetic results presented in this dissertation, it can be stated that the silver catalysed oxidation of hydrazides by $S_2O_8^{2-}$ ion follows the mechanism as proposed previously on page 86.