

CHAPTER - VIDISCUSSION AND MECHANISM

Chemical kinetics attained a new meaning when Arrhenius¹⁹³ put forth the concept of molecular activation as a pre-requisite to chemical reaction. This concept of molecular activation is now universally accepted and forms the basis of all subsequent theories of chemical reaction. Evans,¹⁹⁴ Polanyi and Eyring¹⁹⁵ and others put forward the absolute reaction rate theory, according to which the activated complex is formed from the reactants by a reversible process, which decompose irreversibly to give the products. Thus according to Eyring,¹⁹⁵ Pelzer,¹⁹⁶ Wynne-Jones,¹⁹⁷ the potential energy of the interacting molecules is considered at the time of collision. There will be a configuration of nuclei of minimum potential energy, related to the activation energy, through which the system would be expected to pass in going from reactants to the products. This region of space is called the transition state. A system in the transition state is called an activated complex.

The rate of reaction is given by the rate of passage through which the transition state or passage over the potential energy barrier.

On this basis, Evans¹⁹⁴ and Polanyi and Eyring^{195,198} independently deduced the rate expression for a bimolecular

reaction.



The specific rate is given by

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

where Q^* and Q_A, Q_B are the partition functions of the reactants A and B and the activated complex. k is the Boltzmann constant. E_0 is the energy of activation referred to zero point energy. Since the equilibrium constant K^\ddagger for the formation of activated complex is given by

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

Hence, the equation (1) reduces to

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

Equation (3) can also be expressed involving the entropy of activation and enthalpy changes.

$$k_r = \frac{kT}{h} \cdot e^{\Delta S^\ddagger/R} \cdot e^{-\Delta H^\ddagger/RT} \quad \dots(4)$$

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

where ΔS^\ddagger and ΔH^\ddagger are the entropy and enthalpy changes involved in the formation of the activated complex respectively.

Thus a plot of $\log \left[\frac{k_r}{kT/h} \right]$ versus $\frac{1}{T} \times 10^3$ enables one to calculate ΔS^\ddagger and ΔH^\ddagger .

Equations (4) and (5) show that, if entropy change ΔS^\ddagger is positive the reaction will be normal or fast from the stand point of simple Collision theory. If ΔS^\ddagger is negative then the reaction will be slow.

Forst¹⁹⁹ and Pearson discussing the significance of the entropy of activation of a bimolecular reaction is related to the frequency factor, A by the relation -

$$A = \frac{kT}{h} \cdot e^{\Delta S^\ddagger/R} \quad \dots(6)$$

and if the radius of the activated complex in the transition state is taken to $2 A^0$ in water then it can be shown that

$$\Delta S^\ddagger \cong - 10Z_A Z_B \text{ e.u.} \quad \dots(7)$$

where ΔS^\ddagger is the entropy change in the formation of activated complex. Z_A, Z_B are the electrostatic contribution of the reacting species A and B respectively. It may be noted that in ionic reactions, electrostatic contribution is the major factor to determine the entropy changes. The equation (7) has been used to predict the nature of the reacting ions in the rate determining step. However, this is in poor accordance with kinetic data of highly charged^{200,201} ions.

For reactions in solution, the nature of the solvent also plays an important role, which has also been very well discussed by Amis.²⁰²

From the point of view of solvent effect, the reaction may be classified into the following categories :

- (1) Ion - Ion reactions
- (2) Ion - Dipolar molecule
- (3) Dipolar molecule - Dipolar molecule reactions
- (4) Electron exchange reactions
- (5) Charge transfer reactions

In the present study the nature of the reaction leading to the formation of activated complex may be either of the first two types, hence only these two effects are discussed here.

From the solvent effect on ion-ion reaction correlating the specific rate k_r with the dielectric constant of the medium D , Scatchard²⁰³ derived the expression :

$$\ln k_0^S = \log k_0 - \frac{Z_A Z_B e^2}{kT r^\ddagger D} \quad \dots(8)$$

where k_0^S is the specific rate in the solvent of dielectric constant D , between two ions of valency Z_A and Z_B ; r^\ddagger is the radius of the activated complex and k_0 is the specific rate in a solvent of infinite dilution. A somewhat different

expression has been obtained by Laidler²⁰⁴ and Eyring on the basis of a different model for the activated complex. The expression is :

$$\ln k_o^S = \ln k_o + \frac{e^2}{2kT} \left(\frac{1}{D} - 1 \right) \left[\frac{z_A^2}{r_A} + \frac{z_B^2}{r_B} - \frac{(z_A + z_B)^2}{r^\ddagger} \right] \dots (9)$$

Equations (8) and (9) enable us to gain information about the nature of the reacting ions from the plot of $\ln k_o^S$ versus $\frac{1}{D}$. The slope of the line will be positive when both the ions A and B are of opposite sign and negative when they are of the same Sign.

In case of ion-dipolar molecule reactions, the charge on dipolar molecule is zero, as such $z_B = 0$ and equation (9) reduces to

$$\ln k_o^S = \ln k_o + \frac{e^2}{2kT} \left(\frac{1}{D} - 1 \right) \left[\frac{z_A^2}{r_A} - \frac{z_B^2}{r^\ddagger} \right] \dots (10)$$

and the plot of $\ln k_o^S$ versus $\frac{1}{D}$ gives a straight line with the slope

$$\frac{e^2 z_A^2}{2kT} \left(\frac{1}{r_A} - \frac{1}{r^\ddagger} \right)$$

which will always be positive, because r^\ddagger is greater than r_A . As such, the rate of the reaction between an ion and dipolar molecule should decrease with increase of dielectric constant of the medium.

Unfortunately in the present study, the effect of dielectric constant could not be investigated due to the reactivity of the solvents such as methanol, ethanol, acetone with $S_2O_8^{2-}$.

Another prominent effect for the reactions in solution is the influence of ionic strength. Bronsted,³³ Bjerrum²⁰⁵ and Christiansen²⁰⁶ have applied the Debye Huckel theory to the influence of neutral salts on the velocity of the reactions in solution. These effects are of two kinds. In the first case, the activities of the reactants, whether ions or polar molecule may be altered by the added electrolytes. This is the primary salt effect. In the second case, the effective concentration of a reactant or a catalytic ion coming from the weak electrolyte may be decreased due to the increase in the ionisation of the electrolyte because of the added salt. This is the secondary salt effect. Primary salt effect can be subdivided into the following two heads :

- (1) Primary exponential salt effect
- (2) Primary linear salt effect

For the former in dilute solutions, the equation of Bronsted, Bjerrum is

$$\ln k = \ln k_0 + \frac{2Z_A Z_B \alpha \sqrt{\mu}}{1 + \beta a_1 \sqrt{\mu}} \quad \dots(11)$$

where α and β are Debye-Huckel constants.

For very dilute solutions where μ is small, the above equation reduces to

$$\ln k \approx \ln k_0 + 2Z_A Z_B \alpha \sqrt{\mu}$$

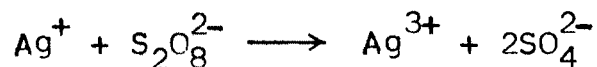
During the last decade, a large number of kinetic studies in solution have been interpreted on the basis of reaction schemes involving atoms, free radicals or radical ions. In many cases, their bond strengths and thermodynamic properties have been experimentally verified as reviewed by Uri.²⁰⁷

Since the present work is concerned with redox reactions involving $S_2O_8^{2-}$, it is necessary to state the present views on the mechanism of redox reactions in general.

For the oxidation reduction reactions a number of mechanisms have been proposed. The simple process according to Haber²⁰⁸ and Weiss is the stepwise transfer of an electron from reductant to oxidant.

Many of the kinetic results on the redox reactions have required the postulation of unstable valency state. Thus the Ag^+ catalysed reactions of $S_2O_8^{2-}$ always involve an electron transfer in each step of oxidation.

Yost⁴⁵ assumed the rate determining process as,



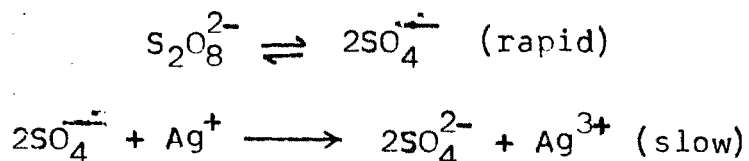
while investigating the oxidation of ammonia, ammonium ion, chromium ion in which Ag^{3+} was considered the oxidising species.

On the other hand Srivastava¹²³ and Ghosh suggested that the rate determining steps involve the formation of Ag^{2+} and $\text{SO}_4^{\cdot-}$ according to the following relation



The above mechanism was also suggested by Bacon, Grime²⁰⁹ and Munro and Bawn and Margerison.¹⁵

On the other hand, Gupta⁴⁹ and Ghosh on considerations of entropy of activation, proposed that the mechanism involves first, equilibrium between $\text{S}_2\text{O}_8^{2-}$ and $\text{SO}_4^{\cdot-}$ ion which is followed by a termolar rate determining step as follows:



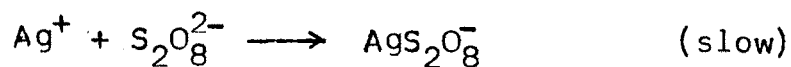
The above mechanism accounts for the negative value of the entropy of activation observed (of the order of - 20 e.u.

or more) in Ag^+ catalysed redox reactions of $\text{S}_2\text{O}_8^{2-}$ ion but the following objections have been raised against the mechanism.

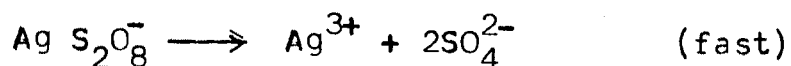
- 1) It involves a termolecular step in the rate determining stage which does not seem to be possible.
- 2) The general opinion now is that much significance cannot be given to the entropy of activation values in order to elucidate the nature of the reacting ions.

Beckier⁵¹ and Kijowski proposed an alternative initial step to explain the catalytic effect of Ag^+ ions which has been supported by Chalatykyan²¹⁰ and Beilerian.

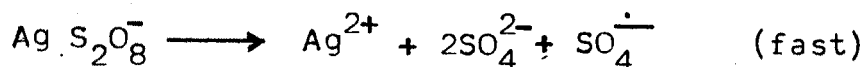
The various steps proposed and are represented as follows :



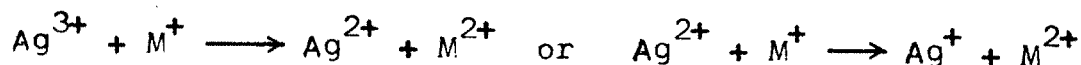
followed by either



or



and the rapid oxidising steps.



The above mechanism avoids the postulation of a termolecular step, but 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 the intermediate AgS_2O_8^- seems rather equally possible, but the opinion is in favour of the former.

Here we summarise the results obtained in this study and we point out the similarities or dissimilarities with the results obtained by the other workers.

(1) The reaction is first order with respect to $\text{S}_2\text{O}_8^{2-}$ ion. Increase in concentration of $\text{S}_2\text{O}_8^{2-}$ at constant ionic strength and at constant K^+ ion concentration brings about a decrease in the specific rate in all the cases. The following relationship can be generalised as :

$$k = a - b \log [\text{S}_2\text{O}_8^{2-}]_0$$

where the values of a and b are given in the following table:

Amide	Cinnamide	Capramide
a	2.717	2.53
b	8.650	14.07

(2) These reactions are zero order with respect to organic substrate. Increase in concentration of the substrate the reaction rate remains constant.

$$k = a - b \log [\text{Amide}]$$

where the values of a and b are given in the following table :

Amide	Cinnamide	Capramide
a	0.001367	0.001721
b	0.01025	0.01032

(3) The specific rate increases linearly with Ag^+ concentration in all the two cases. The relationship followed as

$$k = a + b [\text{Ag}^+]$$

where the values of a and b are given in the following table :

Amide	Cinnamide	Capramide
a	0.53×10^{-3}	0.4×10^{-3}
b	0.365	0.586

(4) All the Arrhenius parameters are given in the following table (Table 1).

TABLE - 1
Arrhenius Parameters

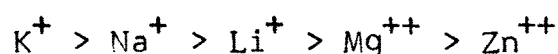
Name of Amide	Temp. Coefficient	E K.Cals. mole ⁻¹	Frequency Factor liter mole ⁻¹ sec ⁻¹ [Ax10 ⁻⁴]	ΔG^\ddagger K.Cals. mole ⁻¹	ΔS^\ddagger e.u.	ΔH^\ddagger K.Cals. mole ⁻¹ (graphically)
Cinnamide	1.933	12.420	1.285	22.235	-33.632	11.503
Capramide	1.986	12.769	3.864	22.008	-31.452	11.440

Thus the two reactions are characterised by a large negative entropy of activation. This suggests that there is a decrease in the degree of freedom in the formation of the activated complex and, therefore, it is a rigid one as is also observed from the low value of frequency factor.

A large negative value of entropy of activation and a low value of frequency factor suggests that the formation of the activated complex in these reactions should involve the redistribution of energy along various degree of freedom in the reacting substrate which must be naturally a complex molecule.

(5) The salt effect is negative in both the cases and of primary exponential type suggesting that the rate determining process in all the two cases is between two oppositely charged ions.

(6) The specific ionic effect of different Cations follow a similar order in all the reactions.



(7) Allyl acetate inhibits the rate of reaction. This may be due to the trapping of sulphate radical ions by allyl acetate, pointing to existence of a radical mechanism.

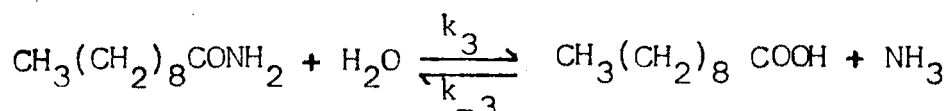
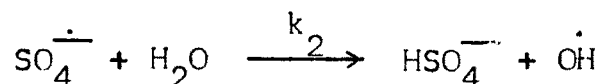
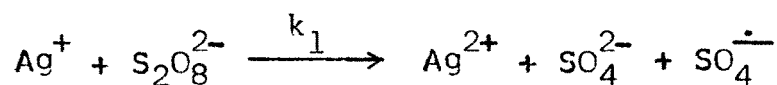
(8) The mole ratio in both the cases is ; One mole of $S_2O_8^{2-}$: One mole of amide.

(9) In the two cases the final oxidation products were acetaldehyde and ammonia. The ammonia could not be detected as the solutions of the two substrates were prepared in acetic acid medium. The test for acetaldehyde was carried out according to Feigl as mentioned previously.

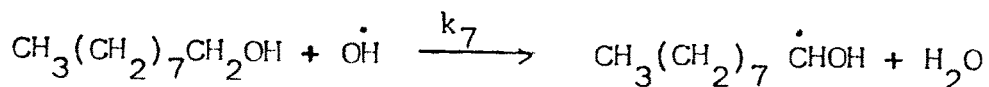
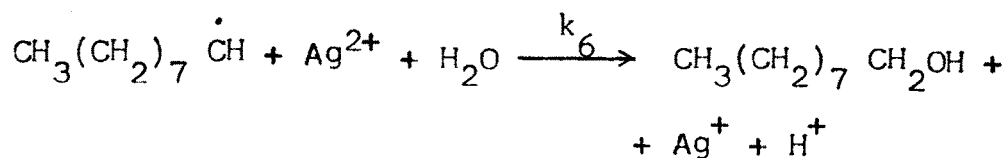
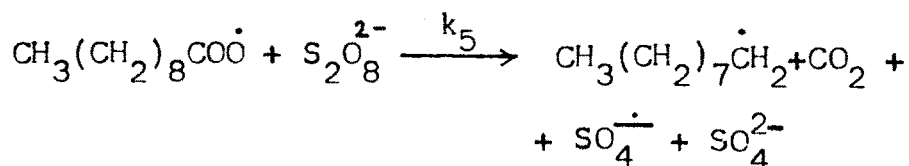
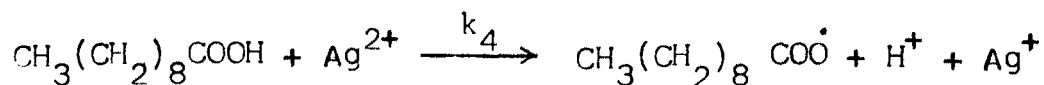
MECHANISM :

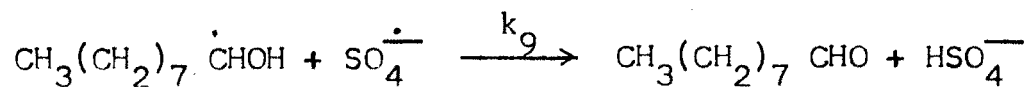
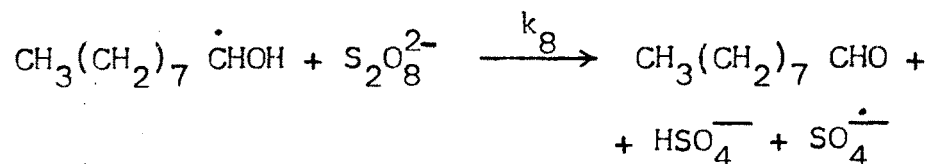
Regarding the nature of the silver species, the recent evidence in literature point out to the fact that in aqueous acid solutions, the existence of Ag(II) is more likely than the higher State of Silver Species.

On the basis of above kinetic results and taking into consideration the previous data available on the redox reaction of $S_2O_8^{2-}$ the rate expressions may be explained in terms of different free radicals. The mechanism upto the formation of acetaldehyde which is the major part of the reaction is given below. This mechanism was suggested by Maheshwari¹⁶¹ and coworkers. The same mechanism can be applied for the oxidation of cinnamide



$$K = \frac{k_3}{k_{-3}}$$





Applying steady state treatment to different radicals and assuming

$k \gg k_1$ and $k_2 \approx k_9$ and $[\text{Ag}^+]$ is very small,

$\frac{2k_1 k_9}{k_2} [\text{Ag}^+] \ll k_8$ and may be neglected.

Thus the rate of disappearance of $[\text{S}_2\text{O}_8^{2-}]$ is

$$-\frac{d[\text{S}_2\text{O}_8^{2-}]}{dt} = 3k_1 [\text{Ag}^+] [\text{S}_2\text{O}_8^{2-}] \text{ which is the main feature}$$

of the reaction.