

CHAPTER - VI

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DISCUSSION AND MECHANISM :

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The concept of molecular activation is universally accepted and forms the basis of all the theories of chemical reactions. Polanyi¹⁹⁴⁶, Evans and Eyring¹⁹³⁷ put forward the absolute reaction rate theory. According to this theory, the rate of the reaction is given by the rate at which the activated complex is formed from the reactants by the reversible process, which decompose irreversibly to give the products. Thus according to Felzer¹⁹³⁸, Eyring¹⁹³⁹ and Wynne - Jones, 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 the reactants to products. This region of configuration space is called the transitional state. The 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 barrier.

On this basis, Evans and Polanyi¹⁹³⁶ and Eyring¹⁹³⁷ independently deduced the rate expression for a bimolecular reaction.



The specific rate k_r is given by the expression :

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

Where Q^* , Q_A and 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 the zero point energy. The equilibrium constant K for the formation of activated complex is given by :

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

Hence the equation (1) reduces to

$$k_r = (kT/h) \times K^\ddagger \quad \dots (3)$$

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

$$\text{OR } k_r = (kT/h) \times e^{\Delta S^\ddagger/R} \times e^{\Delta H^\ddagger/RT} \quad \dots (4)$$

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

Where ΔS^\ddagger and ΔH^\ddagger are the entropy and enthalpy changes involved in the formation of an activated complex. Thus a plot of $\log [k_r / (kT/h)]$ versus $1/T \times 10^3$ enables one to calculate ΔS^\ddagger and ΔH^\ddagger

Equations (4) and (5) also indicates that, when the entropy change ΔS^\ddagger is positive then the reaction will be normal or fast from the point of view of collision

theory, but when ΔS^\ddagger is negative then the reaction will be very slow.

Frost²⁰⁰ and Pearson, while discussing the significance of entropy of activation, point out that, the entropy of activation of a bimolecular reaction is related to the frequency factor A by the equation :

$$A = \frac{KT}{h} \times (\Delta S)^\ddagger/R \quad \dots (6)$$

and when the radius of the activated complex in the transition state is considered to be $2A^\circ$ in water, then it can be shown that,

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

Where S^\ddagger is the entropy change in the formation of an activated complex. Z_A , Z_B are the electrostatic contribution of the reacting species A and B respectively. It must be remembered that, in ionic reactions, electrostatic contribution is the major factor to determine the entropy changes. The equation (7) can be employed to predict the nature of the reacting ions in the rate determining step. However, this is in poor accordance with the kinetic data of highly.^{201,202} charged ions. For reactions in solution, the nature of the solvent also plays an important role which has been discussed in detail by Amis²⁰³.

From the point of view of solvent effects, the reaction may be classified into the five major categories :

- 1) Ion - Ion reactions.
- 2) Ion - Dipolar molecule reactions
- 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 an activated complex may be either of the first two types and hence only these two effects will be discussed here.

For the solvent effect on ion-ion reaction correlating the specific rate k_r with dielectric constant, D of the medium. Scatchard derived the following expression :

$$\ln k_r^s = \ln k_o - \frac{Z_A Z_B e^2}{kT\gamma^{\ddagger}D} \quad \dots (8)$$

Where k_o^s is the specific rate in the solvent of the dielectric constant D between two ions of valency Z_A and Z_B . γ^{\ddagger} is the radius of the activated constant. k_o is the specific rate in the solvent of infinite dilution. Laidler²⁰⁴ and Eyring, on the basis of a different model for an activated complex obtained a different expression :

$$\ln k_o = \ln k_o + \frac{e^2}{2kT} \left[\frac{1}{D} - 1 \right] \left[\frac{Z_A}{\gamma_A} + \frac{Z_B}{\gamma_B} - \frac{(Z_A + Z_B)^2}{\gamma^{\ddagger}} \right] \quad \dots (9)$$

Equations (8) and (9) enable us to gain information about the nature of the reacting ions, from the plot of $\ln k_o$ versus $1/D$. The slope of this plot will be positive when

both the ions A and B are of opposite sign and negative when they are of the same sign.

According to Laidler²⁰⁴ and Eyring a deviation from linearity of $\ln K_o$ versus $1/D$ in low dielectric constant regions in many cases is due to the adsorption of water on the ions.

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

$$\ln K_o^S = \ln K_o + \frac{e^2}{2KT} \left[\frac{1}{D} - 1 \right] \left[\frac{Z_A^2}{r_A} - \frac{Z_A^2}{r^{\mu}} \right] \dots (10)$$

and a plot of $\ln K_o$ versus $1/D$ gives a straight line with a slope

$$\frac{e^2 Z_A}{2 KT} \left[\frac{1}{r_A} - \frac{1}{r^{\mu}} \right]$$

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

Another prominent effect of reactions in solution is the influence of ionic strength. Bronsted²⁰⁵, Bjerrum²⁰⁶ and Christiansen²⁰⁷ have applied the Debye - Huckel theory to the influence of neutral salt effect on the velocity of the reactions in solution. 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 effective concentration of the reactant or a catalytic ion coming from a weak electrolyte may be decreased due to a decrease in the ionisation of the electrolyte because of the added salt. This is the secondary salt effect.

Primary salt effect may be subdivided into the following heads :

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

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

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

Where α and β are the Debye - Huckel constants.

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

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

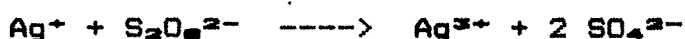
During the last twenty years, a larger number of kinetic studies in solution have been interpreted on the basis of reaction schemes involving atoms free radicals or radical ions. In many cases, their bond strengths and thermodynamic properties have been further reviewed by Uri²⁰⁸.

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

For the oxidation - reduction reactions, many different mechanisms have been suggested. According to Haber²⁰⁹ and Weiss, the simple process is the stepwise transfer of an electron from the reductant to the oxidant. Redox reactions may take place via simple electron transfer or through an agency of the atom or ion transfer.

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.

Yost¹⁸ assumed the rate determining process as,



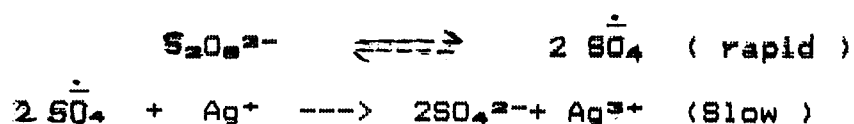
While investigating the oxidation of ammonia, ammonium ion, chromium ion and vanadyl ion in which Ag^{3+} was considered the oxidation species.

On the other hand, Srivastava¹³³ and Ghosh suggested that the rate determining steps involve the formation of Ag^{2+} and $\overset{\ominus}{SO}_4$ according to the following relation



The above mechanism was also suggested by Bacon²¹⁰, Grime and Munro and by Bawn¹⁴ and Margerison. On the other hand, Gupta and Ghosh on considerations of entropy of

activation, proposed that the mechanism involves equilibrium between $S_2O_8^{2-}$ and $SO_4^{\cdot-}$ radical ion which is followed by a termolecular rate determining step as follows :



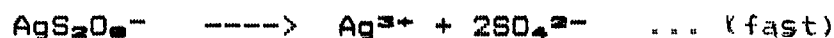
The above mechanism accounts for the negative value of the entropy of activation observed (of the order of -20 e.u. or more) in Ag^+ catalysed redox reactions of $S_2O_8^{2-}$ ion but the following serious objections have been raised against the mechanism

- 1) The tracer exchange studies (that no exchange of S^{35} between $SO_4^{\cdot-}$ and $S_2O_8^{2-}$ has been observed^{211,212}) rule out the possibility of the rapid equilibrium of $S_2O_8^{2-}$ with $SO_4^{\cdot-}$
- 2) It involves a termolar step in the rate determining stage which does not seem to be possible.
- 3) 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.

Beckier⁴⁹ and Kijowski proposed an alternative initial step to explain the catalytic effect of Ag^+ ions which has been later on supported by Chaltykyan²¹³ and Beileryan. The various steps suggested may be represented as follows



followed by either



and the rapid oxidising steps,



The above mechanism avoids the postulation of a termolar 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. However, overwhelming opinion is in favour of the former.

Thus in order to discuss the reaction mechanism for silver catalysed oxidation of amides by $\text{S}_2\text{O}_8^{2-}$ ion, it is necessary to summarise the results obtained in this study. These results are summarised as follows:-

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

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

where the values of a and b are recorded in the

following table

Amide	a	b
Fumaramide	2.443	5.90
Azelaic - amide	2.480	6.5

2> These reactions are zero order with respect to organic substrate. Increase in the concentration of the substrate does not affect on the specific rate. The specific rate remains practically constant indicating the zero order behaviour of the reaction. The following relationship has been followed :-

$$k = a - b \text{ Log } [\text{amide}]_0$$

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

Amide	a	b
Fumaramide	0.00272	0.02675
Azelaic - amide	0.0030	0.03105

3> The specific rate increases linearly with Ag^+ concentration in all the two cases. The following relationship is followed :-

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

Where the values of a and b are recorded in the following table :-

Amide	a	b
Fumaramide	1.56×10^{-3}	0.9375
Azelaic - amide	2.1×10^{-3}	0.4861

4> The energy of activation, frequency factor along with the all energy parameters are recorded in the following table.

TABLE - 1

Arrhenius Parameters

Amide	Temp. Coeff.	E Kcals mole ⁻¹	Frequency Factor A x 10 ⁴ litre.mole ⁻¹ .sec ⁻¹	ΔG^\ddagger K.cals mole ⁻¹	ΔS^\ddagger e.u.	ΔH^\ddagger K.cals. mole ⁻¹
Fumaramide	1.901	12.116	8.544	22.19	-34.72	11.722
Azelaic- amide	1.968	12.743	1.789	22.236	-32.78	11.842

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

An abnormally large negative value of entropy of activation and rather 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 reacting

substrate which must be naturally a complex molecule.

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

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



7) Allyl acetate inhibits the rate of reaction.

This may be due to the capture of sulphate radical ions by allyl acetate. The practical evidence for $\dot{S}O_4$ has been observed in Polymerisation^{214,215} and E.S.R.²¹⁶ studies in peroxydisulphate oxidation reactions.

8) The mole ratio in both the cases is one mole of $S_2O_8^{2-}$: one mole of the substrate.

9) In the two cases the final oxidation products are their parent acids and nitrogen. These final products were detected according to Feigl¹⁹² as mentioned previously.

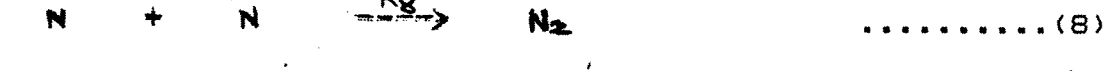
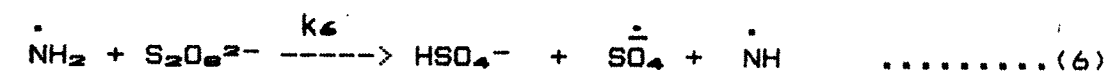
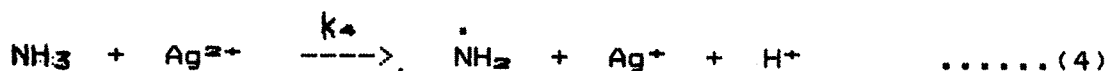
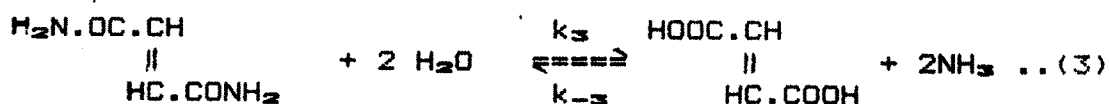
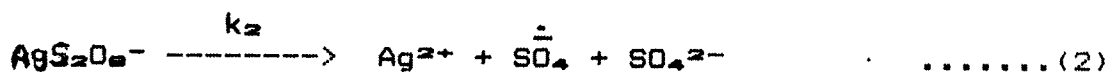
From the kinetic results summarised above for the oxidation of amides, it can be concluded that the kinetic behaviour in the two cases is nearly the same. Further the large negative value of entropy of activation in the two cases suggests the formation of the complex between Ag^+ and $S_2O_8^{2-}$, also proposed by Beckier⁴⁹ and Kijowski and later on supported by Chaltrykian²¹³ and Beilerian.

We discuss the mechanism for the oxidation of fumaramide. The same mechanism can be operative for the oxidation of azelaic-amide. This mechanism was suggested by Srivastava^{1,2} and Hambir Singh for the oxidation of amides by peroxydisulphate.

The steps involved in the proposed mechanism are presented in the following scheme :



$$K = \frac{k_1}{k_{-1}}$$



Applying the steady state treatment to the radicals Ag^{2+} , $\overset{\cdot}{\text{SO}}_4$, $\overset{\cdot}{\text{NH}}_2$ and $\overset{\cdot}{\text{NH}}$ the following equations are obtained

$$d/dt [\overset{\cdot}{\text{SO}}_4] = k_2 [\text{AgS}_2\text{O}_8^-] - k_5 [\text{NH}_3] [\overset{\cdot}{\text{SO}}_4]$$



$$+ K_6 [\text{NH}_2] [\text{S}_2\text{O}_8^{2-}] - K_7 [\text{NH}] [\text{SO}_4] = 0 \dots (I)$$

$$d/dt [\text{Ag}^{2+}] = K_2 [\text{AgS}_2\text{O}_8^-] - K_4 [\text{NH}_3] [\text{Ag}^{2+}] = 0 \dots (II)$$

$$d/dt [\text{NH}_2] = K_4 [\text{NH}_3] [\text{Ag}^{2+}] + K_5 [\text{NH}_3] [\text{SO}_4] - K_6 [\text{NH}_2] [\text{S}_2\text{O}_8^{2-}] = 0 \dots (III)$$

$$d/dt [\text{NH}] = K_6 [\text{NH}_2] [\text{S}_2\text{O}_8^{2-}] - K_7 [\text{NH}] [\text{SO}_4] = 0 \dots (IV)$$

$$d/dt [\text{S}_2\text{O}_8^{2-}] = K_1 [\text{Ag}^+] [\text{S}_2\text{O}_8^{2-}] - K_2 [\text{AgS}_2\text{O}_8^-] + K_4 [\text{NH}_2] [\text{S}_2\text{O}_8^{2-}] = 0 \dots (V)$$

$$K = \frac{[\text{AgS}_2\text{O}_8^-]}{[\text{Ag}^+] [\text{S}_2\text{O}_8^{2-}]} \dots (VI)$$

$$d/dt [\text{S}_2\text{O}_8^{2-}] = K_2 K [\text{Ag}^+] [\text{S}_2\text{O}_8^{2-}] + K_4 [\text{NH}_2] [\text{S}_2\text{O}_8^{2-}] \dots (VII)$$

From equation (II) we have

$$K_2 [\text{AgS}_2\text{O}_8^-] = K_4 [\text{NH}_3] [\text{Ag}^{2+}] \dots (VIII)$$

and from equation (IV) we get

$$K_6 [\text{NH}_2] [\text{S}_2\text{O}_8^{2-}] = K_7 [\text{NH}] [\text{SO}_4] \dots (IX)$$

subtracting equation (IV) from equation (I) we get

$$K_2 [\text{AgS}_2\text{O}_8^-] = K_5 [\text{NH}_3] [\text{SO}_4] = 0$$

$$\text{OR } [\text{SO}_4] = \frac{K_2 [\text{AgS}_2\text{O}_8^-]}{K_5 [\text{NH}_3]} \dots (X)$$

Adding equation (I) and (III), we get

$$K_2 [\text{AgS}_2\text{O}_8^-] + K_4 [\text{NH}_3] [\text{Ag}^{2+}] - K_7 [\text{NH}] [\text{SO}_4] = 0$$

$$\text{OR } 2K_2 [\text{AgS}_2\text{O}_8^-] = K_7 [\text{NH}] [\text{SO}_4] \dots (XI)$$

substituting value of SO_4 from equation (X)

$$2 K_2 [\text{AgS}_2\text{O}_8^-] = \frac{K_7 [\text{NH}] K_2 [\text{AgS}_2\text{O}_8^-]}{K_5 [\text{NH}_3]}$$

$$\text{OR } \frac{2 k_5}{k_7} \times [\text{NH}_3] = [\dot{\text{N}}\text{H}] \quad \dots\dots\dots(\text{XII})$$

substituting the value of $k_7 [\dot{\text{N}}\text{H}] [\text{SO}_4^{\cdot-}]$ in equation (IX) we get

$$k_6 [\dot{\text{N}}\text{H}_2] [\text{S}_2\text{O}_8^{2-}] = 2 k_2 [\text{AgS}_2\text{O}_8^-]$$

OR

$$\begin{aligned} [\dot{\text{N}}\text{H}_2] &= \frac{2 k_2 [\text{AgS}_2\text{O}_8^-]}{k_6 [\text{S}_2\text{O}_8^{2-}]} \\ &= \frac{2 k_2}{k_6} \times \frac{[\text{Ag}^+] [\text{S}_2\text{O}_8^{2-}]}{[\text{S}_2\text{O}_8^{2-}]} \\ &= \frac{2 k_2 k}{k_6} [\text{Ag}^+] \quad \dots\dots\dots(\text{XIII}) \end{aligned}$$

$$d/dt [\text{S}_2\text{O}_8^{2-}] = k_2 \cdot k [\text{Ag}^+] [\text{S}_2\text{O}_8^{2-}]$$

$$\pm 2k_6 + \frac{k_2 \cdot k}{k_6} \times [\text{Ag}^+] [\text{S}_2\text{O}_8^{2-}] \quad \dots(\text{XIV})$$

$$d/dt [\text{S}_2\text{O}_8^{2-}] = 3k_2 k [\text{Ag}^+] [\text{S}_2\text{O}_8^{2-}] \quad \dots(\text{XV})$$

The above rate expression (XV) accounts the salient kinetic features of the silver catalysed oxidation of fumaramide by peroxydisulphate ion, namely, first order in $\text{S}_2\text{O}_8^{2-}$ and first order in Ag^+ . The zero order behaviour in amide is also accounted for. However, the above rate expression does not account for the dependence of first order rate constant on the concentration of $\text{S}_2\text{O}_8^{2-}$ ion and that of amide taken. As explained earlier, this seems to be a trace impurity effect and naturally cannot be incorporated in the rate expression. The existence of radical mechanism has been proved, experimentally by investigating the effect of allyl

acetate and this supports the postulation of trace impurity effect, suggested by Srivastava²⁴ and Coworkers.

The first two steps have been proposed earlier by Beckier⁴⁹ and Kijowski and Chaltykyan²¹³ and Beilerian. Step (3) is an equilibrium process gives a small concentration of ammonia which actually undergoes oxidation in subsequent steps.