CHAPTER - VI

DISCUSSION AND MECHANISM

The concept of molecular activation is now universally accepted and forms the basis of all subsequent theories of chemical reaction. Evans[190], Polanyi and Eyring[191] put forward the absolute reaction rate theory according to which the rate of the reaction is given by the rate at which the activated complex is formed from the reactants by a reversible process, which decompose irreversibly to give the products. Thus according to Eyring[191] Pelser[192], Wynne[193] 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 reactants to products. This region of configuration 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, Evans[190], Polanyi and Eyring[191] independently deduced the rate expression for a bi-molecular reaction.

$$A + B \rightleftharpoons X \longrightarrow \text{Products}$$

The specific rate kr is given by

$$kr = \frac{kT}{h} \cdot \frac{Q^*}{Q_A Q_B} \cdot e^{-Eo/RT} \quad \ldots \quad (1)$$

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 and Eo is the energy of activation referred to the zero point energy. Since the equilibrium constant $K^{\neq}$ for the formation of the activated complex is given by :

$$K^{\neq} = \frac{Q^*}{Q_A\ Q_B} \cdot e^{-Eo/RT} \quad \ldots \quad (2)$$

Hence the equation (1) reduces to

$$kr = \frac{kT}{h} K^{\neq} \quad \ldots \quad (3)$$

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

$$kr = \frac{kT}{h} . e^{\Delta S^{\neq}/R} . e^{-\Delta H^{\neq}/RT} \quad \ldots \quad (4)$$

or

$$\ln. \frac{kr}{kT/h} = \frac{\Delta S^{\neq}}{R} - \frac{\Delta H^{\neq}}{RT} \quad \ldots \quad (5)$$

where $\Delta S^{\neq}$ and $\Delta H^{\neq}$ are the entropy and enthalpy changes involved in the formation of the activated complex respectively.

Thus a plot of $\log\left[\frac{kr}{kT/h}\right]$ versus $\frac{1}{T}$ enables one to calculate $\Delta S^{\neq}$ and $\Delta H^{\neq}$.

Equation (4) and (5) also show that if entropy change $\Delta S^{\neq}$ is positive the reaction will be normal or fast from the stand point of simple collison theory, but if $\Delta S^{\neq}$ is negative then the reaction will be slow one.

Frost and Pearson[195] discussing the significance of the entropy of activation of a bimolecular reaction is related to the frequency factor, A by the equation

$$A = \frac{kT}{h} e^{\Delta S^{\neq}/R} \quad \ldots\ldots \quad (6)$$

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

$$\Delta S^{\neq} \overset{\frown}{=} - 10 Z_A \, Z_B \text{ e.u.} \quad \ldots \quad (7)$$

where $\Delta S^{\neq}$ 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[196,197] ions.

For reactions in solution, the nature of the solvent also plays an important role, which has also been very well discussed by Amis.[198]

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

1. Ion-Ion reactions.
2. Ion-Dipolar molecule reactions.
3. Dipolar molecule-Dipolar molecule reaction.
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 will be discussed here.

For the solvent effect on ion-ion reaction correlating the specific rate kr with the dielectric constant, D , of the medium Scatchard[199] derived an expression :

$$\ln k_o^s = \ln k_o - \frac{Z_A Z_B e^2}{kT\, rx\, D} \qquad \ldots\ldots \quad (8)$$

where k_o^s is the specific rate in the solvent of dielectric constant D, between two ions of valency Z_A and Z_B; rx is the radius of the activated complex and k_o is the specific rate in a solvent of infinite dilution. Somewhat different expression has been obtained by Laidler[200] and Eyring on the basis of a different model for the activated complex. The expression is :

$$\ln k_o^s = \ln k_o + \frac{e^2}{2kT} \left(\frac{1}{D} - 1 \right) \left[\frac{Z_A^2}{r_A} + \frac{Z_B^2}{r_B} - \frac{(Z_A + Z_B)^2}{rx} \right] . \quad (9)$$

Equation (8) and (9) enable us to gain information about the nature of the reacting ions, from the plot of $\ln k_o^s$ versus 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.

According to Laidler[200] and Eyring[200], a deviation from linearity of $\ln k_o^s$ versus $\frac{1}{D}$ in low dielectric constant regions in many cases is due to peeferential adsorption of water on the ions.

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

$$\ln k_o^s = \ln k_o + \frac{e^2}{2kT}\left(\frac{1}{D} - 1\right)\left[\frac{Z_A^2}{r_A} - \frac{Z_A^2}{rx}\right] \quad \ldots \quad (10)$$

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

$$\frac{e^2 Z_A^2}{2kT}\left(\frac{1}{r_A} - \frac{1}{rx}\right)$$

which will always be positive, since rx is greater than r_A. As such the rate of 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, methanol, ethanol, dioxane, formamide, dimethyl-formamide, acetone with $S_2O_8^{2-}$ ion and the failure of the analytical method employed in presence of acetic acid.

Another prominent effect of reactions in solution is the influence of ionic strength. Bronsted[201], Bjerrum[202] and Christeanean[203] have applied the Debye-Huckel theory to the influence of neutral salt 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 a 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 can be subdivided into the following heads.

A) Primary exponential salt effect.

B) Primary linear salt effect.

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

$$\ln k = \ln k_o + \frac{2Z_A\, Z_B\, \alpha \sqrt{\mu}}{1 + \beta a_1 \sqrt{\mu}} \qquad \ldots\ldots \quad (11\ )$$

where α and β are Debye-Huckel constants.

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

$$\ln k \ \overset{\Omega}{\equiv}\ \ln k_o + 2Z_A Z_B\, \alpha \sqrt{\mu}$$

During the last decade, 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 experimentally verified as reviewed by Uri.[204]

Since 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, a number of mechanism have been proposed. The simple process according to Haber[205] and Weiss is the stepwise transfer of an electron from reductant to oxidant. Redox reactions may take place via simple electron transfer or through the 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.

Yost[48] assumed the rate determining process as,

$$Ag^+ + S_2O_8^{2-} \longrightarrow Ag^{3+} + 2SO_4^{2-}$$

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

On the other hand, Srivastava[123] and Ghosh proposed that the rate determining steps involve the formation of Ag^{2+} and $SO_4^{\dot{-}}$ according to the following relation

$$Ag^+ + S_2O_8^{2-} \longrightarrow Ag^{2+} + SO_4^{2-} + SO_4^{\dot{-}}$$

The above reaction mechanism has also been suggested by Bacon,[206] Grime and Munro and Bawn[17] and Margerison.

On the other hand, Gupta[52] and Ghosh on considerations of entropy of activation, proposed that the mechanism involves first, equilibrium between $S_2O_8^{2-}$ and $SO_4^{\dot{-}}$ ion which is followed by a termolecular rate determining step as follows :

$$S_2O_8^{2-} \rightleftharpoons 2\ SO_4^- \quad (\text{ rapid })$$

$$2\ SO_4^- + Ag^+ \longrightarrow 2\ SO_4^{2-} + Ag^{3+} \quad (\text{ slow })$$

The above mechanism no doubt 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 above mechanism.

1. The tracer exchange studies (that no exchange of S^{35} between SO_4^- and $S_2O_8^{2-}$ has been observed)[207,208] rule out the possibility of the rapid equilibrium of $S_2O_8^{2-}$ with SO_4^-.
2. It involves a termolecular step in the rate determining stage which does not seem 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.

Beckier[54] and Kijowski proposed an alternative initial step to explain the catalytic effect of Ag^+ ions which has been later on supported by Chaltykyan[209] and Beileryan.

The various steps proposed may be represented as follows :

$$Ag^+ + S_2O_8^{2-} \longrightarrow AgS_2O_8^- \quad \ldots \quad \text{(Slow)}$$

followed by either

$$AgS_2O_8^- \longrightarrow Ag^{3+} + 2SO_4^{2-} \ldots \quad \text{(fast)}$$

or

$$AgS_2O_8^- \longrightarrow Ag^{2+} + SO_4^{2-} + SO_4^{\dot{-}} \, .. \quad \text{(fast)}$$

and the rapid oxidising steps,

$$Ag^{3+} + M^+ \longrightarrow Ag^{2+} + M^{2+}$$

or

$$Ag^{2+} + M^+ \longrightarrow Ag^+ + M^{2+}$$

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. However, overwhelming opinion is in favour of the former.

In order to discuss the probable mechanism for the Ag^+ catalysed oxidation of amides by peroxydisulphate ion, it would be necessary to summarise the results obtained in this study and to point out the similarities or dissimilarities with the kinetic results of other workers. These results are a summarised as follows :

1. The reaction is first order with respect to $S_2O_8^{2-}$ ion. Increase in concentration of $S_2O_8^{2-}$ at constant ionic strength and at constant K^+ ion concentration brings about a decrease in the specific rate in all the cases. The relationship followed can be generalised as :

$$k = a - b \log \left[S_2O_8^{2-}\right]_o$$

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

Amide	Amino-acetamide	Acetylaminoacetamide
a	2.83	1.85
b	1.80	1.55

2. These reactions are zero order with respect to the organic substrate. Increase in concentration of the reductants , decreases the specific rate. The relationship followed as :

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

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

Amide	Amino-acetamide	Acetylaminoacetamide
a	0.00833	0.009817
b	0.04375	0.01090

TABLE - 1

Arrhenius Parameters

Name of the amide	Temperature Coefficient	E K.Cals. mole^{-1}	Frequency Factor'A' litre mole^{-1} sec^{-1}	$\Delta G^{\neq}$ K.Cals. mole^{-1}	$\Delta S^{\neq}$ e.u.	$\Delta H^{\neq}$ K.Cals. mole^{-1}
Amino-acetamide	1.969	12.613	7.956×10^{4}	21.27	-29.77	12.170
Acetylamino-acetamide	2.068	13.690	3.6904×10^{5}	21.11	-26.21	11.745

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

$$k = a + b \left[Ag^+\right]$$

where a and b for the two amides are

Amides	Amino-acetamide	Acetylaminoacetamide
a	2.0×10^{-3}	3.9×10^{-3}
b	3.9	3.3

4. The temperature coefficient, energy of activation and other thermodynamic parameters are given in Table- 1.

Thus all 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 rigid one as is also 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 the reacting substrate which must be naturally a complex molecule.

5. In all the cases, the salt effect is negative and of 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 reactions.

$$K^+ > Na^+ > Li^+ > Zn^{++} > Mg^{++}$$

7. Allyl alcohol and allyl acetate inhibits the rate of reaction. This may be due to the capture of sulphate radical ions by allyl alcohol and allyl acetate.

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 formaldehyde and ammonia. These final products were detected according to Feigl as mentioned previously.

From the kinetic results summarised above for the oxidation of amides, it can be concluded that the kinetic behaviour is nearly the same in the two cases studied above. In all the cases the reaction is inhibited by allyl acetate pointing to the existence of a radical mechanism.

Taking into account all the above considerations, the following mechanism seems to be reasonable :

REACTION MECHANISM

The first order with respect to $S_2O_8^{2-}$ and Ag^+, zero order with respect to aminoacetamide and acetylaminoacetamide, inhibitory action of metal ions and allyl acetate together with the fact that the mole ratio is one, lead that the following mechanism may be operative.

We discuss here the mechanism for the oxidation of aminoacetamide. The same mechanism can be operative for acetylaminoacetamide. The steps involved in the proposed mechanism are presented in the scheme :

$$Ag^+ + S_2O_8^{2-} \underset{k-1}{\overset{k_1}{\rightleftharpoons}} Ag\,S_2O_8^-$$

$$K = \frac{k_1}{k-1} \qquad \ldots\ldots \quad (1)$$

$$AgS_2O_8^- \xrightarrow{k_2} Ag^{2+} + SO_4^{\cdot-} + SO_4^{2-} \qquad \ldots\ldots \quad (2)$$

$$\underset{\text{Amide}}{H_2N.CH_2.CONH_2} + H_2O \underset{k-3}{\overset{k_3}{\rightleftharpoons}} \underset{\text{Amino-acetic acid}}{H_2N.CH_2COOH} + NH_3 \quad \ldots \quad (3)$$

$$H_2N.CH_2COOH + Ag^{2+} \xrightarrow{k_4} H_2N\dot{C}H_2 + CO_2 + Ag^+ + H^+ \quad (4)$$

$$H_2N\dot{C}H_2 + S_2O_8^{2-} \xrightarrow[H_2O]{k_5} HCHO + NH_3 + HSO_4^- + SO_4^{\cdot-} \quad (5)$$

$$SO_4^{\cdot-} + H_2O \xrightarrow{k_6} HSO_4^- + \dot{O}H \qquad \ldots\ldots \quad (6)$$

$$H_2NCH_2COOH + \dot{O}H \xrightarrow{k_7} H_2N\dot{C}H_2 + CO_2 + H_2O \qquad \ldots\ldots \quad (7)$$

$$Ag^+ + SO_4^{\cdot-} \xrightarrow{k_8} Ag^{2+} + SO_4^{2-} \qquad \ldots\ldots \quad (8)$$

$$H_2N\dot{C}H_2 + SO_4^{\cdot-} \xrightarrow[H_2O]{k_9} HCHO + NH_3 + HSO_4^- \quad \ldots\ldots \quad (9)$$

It may be pointed out that the first two steps have also been proposed by Bawn[17] and Margerison and other steps were suggested by Ram[85] Reddy and their Co-workers, in the Ag^+ catalysed reactions by $S_2O_8^{2-}$ ion.

Applying steady state treatments to the intermediates namely, Ag^{2+}, $SO_4^{\dot{-}}$, $\dot{O}H$ and amino acid radical , The following differential equations set up :

$$\frac{d}{dt}[\dot{S}\bar{O}_4] = k_2[AgS_2O_8^-] - k_6[SO_4^{\dot{-}}] - k_8[Ag^+][\dot{S}\bar{O}_4] - k_9[H_2N\dot{C}H_2][\dot{S}\bar{O}_4] + k_5[H_2N\dot{C}H_2][S_2O_8^{2-}] = 0 \quad \ldots\ldots (1)$$

$$\frac{d}{dt}[Ag^{2+}] = k_2[AgS_2O_8^-] - k_4[Ag^{2+}][H_2NCH_2COOH] + k_8[Ag^+][SO_4^{\dot{-}}] = 0 \quad \ldots\ldots (2)$$

$$\frac{d}{dt}[H_2N\dot{C}H_2] = k_4[H_2NCH_2COOH][Ag^{2+}] - k_5[H_2N\dot{C}H_2][S_2O_8^{2-}] + k_9[SO_4^{\dot{-}}][H_2N\dot{C}H_2] + k_7[H_2NCH_2COOH][\dot{O}H^-] = 0 \quad (3)$$

$$\frac{d}{dt}[\dot{O}H] = k_6[SO_4^{\dot{-}}] - k_7[H_2NCH_2COOH][\dot{O}H] = 0 \quad \ldots . (4)$$

Solving all the above differential equations we get,

$$-\frac{d[S_2O_8^{2-}]}{dt} = k'[S_2O_8^{2-}][Ag^+] \quad \ldots . (5)$$

where $k' = \left[\frac{k_2k_4k_8}{k_9}\right]^{\frac{1}{2}}$

Thus the equation (5) shows that the reaction is first order in $S_2O_8^{2-}$ and also in Ag^+ and Zero order in substrate as found experimentally. The above rate expression does not account for the slight dependence of the first order rate constant on the concentration of peroxydisulphate or the organic substrate. Since the reaction involves a free radical mechanism, it is likely that this slight decrease in the rate constant with increase in the concentration of either of the reactants is due to the presence of trace impurity in them.

Thus the mechanism furnishes a sound explanation of the salient kinetic features of the data obtained in the oxidation of all the above reactions studied.

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