CHAPTER-VI
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 reaction. Evans,[199] Polanyi and Eyring[200] 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 irrversibly to give the products.

Thus according to Pelzer,[201] Eyring[202] and coworkers, 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 transition state and 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 energy barrier.

On this basis, Evans[199] and Polanyi and Eyring[200] indeoendently deduced the rate expression for a bimolecular reaction.

$$A + B \rightleftharpoons X \longrightarrow \text{Products}$$
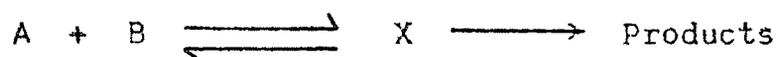
The specific rate kr is given by

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

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

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

Hence the equation (1) reduces to

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

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

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

or

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

Where $\Delta S^{\neq}$ and $\Delta H^{\neq}$ are the entropy and enthalpy changes involved in the formation of the activated complex. Thus a plot of $\ln \frac{kr}{kT/h}$ versus $\frac{1}{T}$ enables one to calculate $\Delta S^{\neq}$ and $\Delta H^{\neq}$.

Equations (4) and (5) show that if entropy change $\triangle S^{\neq}$ is positive then the reaction will be normal or fast from the point of view of simple collision theory, but when $\triangle S^{\neq}$ is negative then the reaction will be very slow.

Frost[203] and Pearson, discussing the significance of entropy of actication point out that the entropy of activation of a bimolecular reaction is related to the frequency factory A by the equation

$$A = \frac{kT}{h} \cdot e^{\triangle S^{\neq}/R} \qquad \ldots(6)$$

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

$$\triangle S^{\neq} = -10 \, Z_A \, Z_B \, (E.U.) \qquad \ldots(7)$$

Where $\triangle S^{\neq}$ 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 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[204,205] ions.

For reactions in solution, the nature of the solvent also plays and important role which has been very well discussed by Amis.[206]

From the point of view of solvent effects, the reaction may be classified into the five following 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 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[207] derived an expression :

$$\ln k_o^S = \ln k_o = \frac{Z_A Z_B e^2}{kT r_x D} \qquad \ldots (8)$$

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, r_x is the radius of the activated complex and k_o is the specific rate in the solvent of infinite dilution. A somewhat different expression has been obtained by Laidler[208] and Eyring on the

basis of a different model for an activated complex. The expression is :

$$\ln k_o = \ln k_c + \frac{e^2}{2kT} \left(\frac{1}{D} - 1 \right) \left[\frac{Z_A^2}{r_A} + \frac{Z_A^2}{r_B} - \frac{(Z_A + Z_B)^2}{r_x} \right] \qquad \ldots (9)$$

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 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 Laidler[208] and Eyring, a deviation from linearity of $\ln k_o^S$ versus $\frac{1}{D}$ in low dielectric sonstant regions in many cases is due to the preferential adsorption of water on the ions.

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

$$\ln k_o^S = \ln ko + \frac{e^2}{2kT} \left(\frac{1}{D} - 1 \right) \left[\frac{Z_A^2}{r_A} - \frac{Z_A^2}{r_X} \right] \qquad \ldots (10)$$

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

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

which will be always positive because r_x 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 the medium.

Unfortunately, in the present stud/, the effect of dielectric constant could not be investigated due to the reactivity of the solvents, methanol, ethanol, formamide, dimethyl-formamide acetone with $S_2O_8^{2-}$ ion.

Another prominent effect of reactions in solution is the influence of ionic strength. Bronsted,[209] Bierrum[210] and Christiansen[211] have applied the Debye-Huckel theory to the influence of neutral salt effect on the velocity of the reactions in solutions. In the first case, the activaties 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 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 Bronstead, Bjerrum is

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

where μ and β are the Debye-Huckel constants.

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

$$\ln\ k = \ln\ ko + 2\ Z_A\ Z_B\ \mu\ \sqrt{\mu}$$

During the 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.[212]

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 redix reactions in general.

For the oxidation reduction reactions, a number of mechanisms have been proposed . The simple process according to Haber[213] and Weiss is the stepwise transfer of an electron from the 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 assumed the rate determining process as,

$$Ag^+ + S_2O_8^{2-} \longrightarrow Ag^{2+} + 2SO_4^{2-}$$
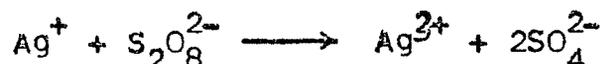
while investigating the oxidation of ammonia, ammonium ion, chromium ion and vanadyl ion in which Ag^{3+} was considered the oxidation species.

On the other hand, Srivastava[135] and Ghosh proposed that the rate determining steps involve the formation of Ag^{2+} and SO_4 according to the following relation.

$$Ag^+ + S_2O_8^{2-} \longrightarrow Ag^{2+} + SO_4^{2-} + \overset{\cdot}{SO_4}$$
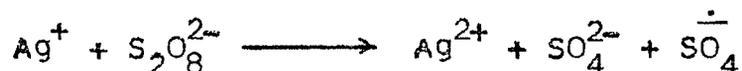
The above reaction mechanism has also been suggested by Bacon,[214] Grime and Munro and by Bawn[17] and Margerison.

On the other hand, Gupta[50] and Ghosh on considerations of entropy of activation proposed that the mechanism involves first, equilibrium between $S_2O_8^{2-}$ and SO_4 ion which is followed by a termolecular rate determining step as follows :

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

$$2\overset{\cdot}{SO_4} + Ag^+ \longrightarrow 2SO_4^{2-} + Ag^{3+} \quad \text{(Slow)}$$
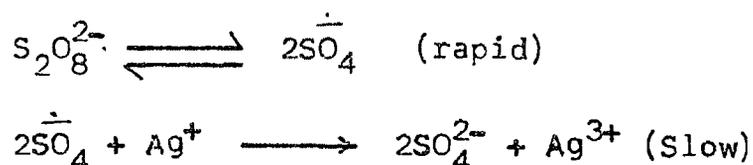
The above mechanism no doubt accounts for the negative value of the entropy of activation observed (of the order of -20 e.u. or more) in Ag^+ catalysed redox reactions of $S_2O_8^{2-}$ ion but the following serious objections have been raised against the mechanism.

(1) The tracer exchange studies (that no exchange of S^{35} between $\bar{SO_4}$ and $S_2O_8^{2-}$ has been observed)[215,216] rule out the possibility of the rapid equilibrium of $S_2O_8^{2-}$ with $\bar{SO_4}$.

(2) It involves a termolecular 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.

Beckier[52] and Kijowski proposed and alternative initial step to explain the catalytic effect of Ag^+ ions which has been later on supported by Chaltykyan[217] and Beileryan.

The various steps proposed may be represented as follows :

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

followed by either

$$Ag\bar{S_2O_8} \longrightarrow Ag^{3+} + 2SO_4^{2-} \quad \ldots(Fast)$$

or

$$Ag\bar{S_2O_8} \longrightarrow Ag^{2+} + SO_4^{2-} + \bar{SO_4} \quad \ldots(Fast)$$

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 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 $S_2O_8^{2-}$ 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 $S_2O_8^{2-}$ 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 :

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

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

Amide	a	b
Pyruvamide	2.525	5.624
Crotonamide	2.575	5.413

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

$$k = a - b \log [Amide]_o$$

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

Amide	a	b
Pyruvamide	0.002381	0.02856
Crotonamide	0.002173	0.02717

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

$$k = a + b [Ag^+]$$

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

Amides	a	b
Pyruvamide	0.125	1.433
Crotonamide	0.123	1.000

(4) The energy of activation, frequency factor and all other energy parameters are recorded in Table - 1.

Table 1 : Arrhenius Parameters

Amides	Temp. 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 $mole^{-1}$
Pyruvamide	1.955	12.353	2.315	22.060	- 32.784	13.155
Crotonamide	1.953	12.572	2.632	21.861	- 32.50	11.721

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 freedon in the formation of the activated complex and, therefore, it is a 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 substantrate which must be naturally a complex molecule.

(5) In all the two 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 two reactions.

$$K^+ > Na^+ > Li^+ > Mg^{++} > Zn^{++}$$
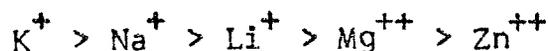
(7) Allyl acetate inhibits the rate of reaction. This may be due to the capture of sulphate radical ions by allyl acetate. The practical evidence for SO_4 has been observed in polymerisation and E.S.R. studies in peroxvdisulphate oxidation reactions.

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

(9) The final oxidation products were formaldehyde and ammonia. In case of pyruvamide, the ammonia was not detected because the solution was prepared in acetic acid. The test for acetaldehyde was carried out according to Feigl as mentioned previously.

Reaction 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 reactions of $S_2O_8^{2-}$ the rate expressions may be explained in

terms of different free radicals. The mechanism upto the formation of formaldehyde which is the major part of the reaction is given below. This mechanism was suggested by Maheshwari[173] and coworkers. The same mechanism can be applied for the oxidation of crotonamide.

$$Ag^+ + S_2O_8^{2-} \xrightarrow{k_1} Ag^{2+} + SO_4^{2-} + \dot{SO_4^-}$$

$$\dot{SO_4^-} + H_2O \longrightarrow HSO_4 + \dot{OH}$$

$$CH_3 \cdot CO \cdot CONH_2 + H_2O \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} CH_3 \cdot CO \cdot COOH + NH_3$$

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

$$CH_3 \cdot CO \cdot COOH + Ag^{2+} \xrightarrow{k_4} CH_3 \cdot CO \cdot CO\dot{O} + H^+ + Ag^+$$

$$CH_3 \cdot CO \cdot CO\dot{O} + S_2O_8^{2-} \xrightarrow{k_5} CH_3\dot{CO} + CO_2 + \dot{SO_4^-} + SO_4^{2-}$$

$$CH_3 \cdot \dot{CO} + Ag^{2+} + H_2O \xrightarrow{k_6} CH_3 \cdot COOH + Ag^+ + H^+$$

$$CH_3COOH + Ag^{2+} \xrightarrow{k_7} CH_3CO\dot{O} + Ag^+ + H^+$$

$$CH_3CO\dot{O} + S_2O_8^{-2} \xrightarrow{k_8} \dot{CH_3} + CO_2 + \dot{SO_4^-} + SO_4^{2-}$$

$$\dot{CH_3} + Ag^{2+} + H_2O \xrightarrow{k_9} CH_3OH + Ag^+ + H^+$$

$$CH_3OH + \dot{OH} \xrightarrow{k_{10}} \dot{CH_2OH} + H_2O$$

$$\dot{CH_2OH} + S_2O_8^{-2} \xrightarrow{k_{11}} HCHO + HSO_4^- + \dot{SO_4^-}$$

$$\dot{CH_2OH} + \dot{SO_4^-} \xrightarrow{k_{12}} HCHO + HSO_4^-$$
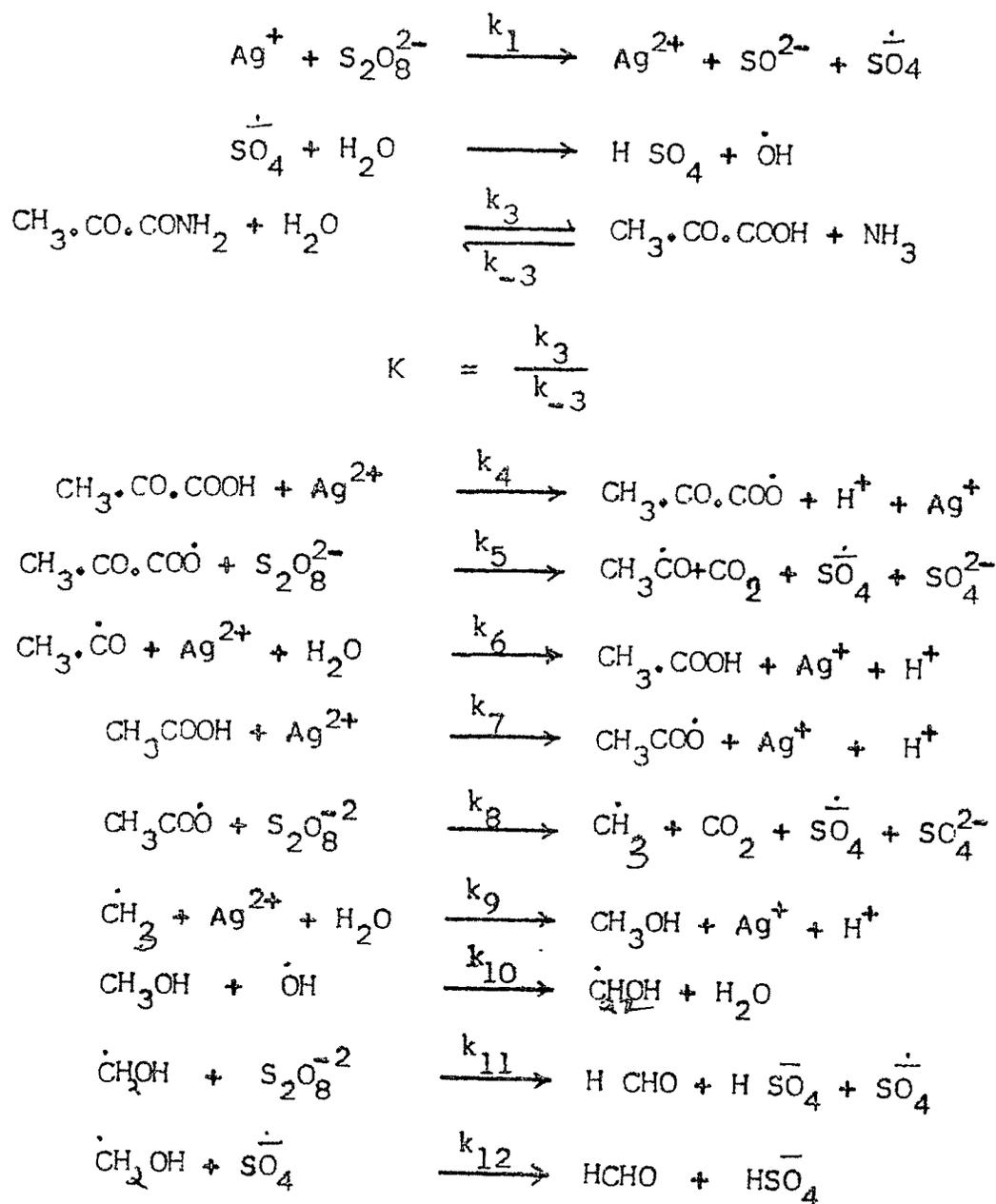
Applying steady state treatment to different radicals and assuming

$$k >> k_1 \text{ and } k_2 \approx k_{12} \text{ and } [Ag^+] \text{ is very small}$$

$$\frac{2k_1 \, k_{12}}{k_2} \, [\, Ag^+] << k_{11} \text{ and may be neglected.}$$

Thus the disappearance is $S_2O_8^{2-}$ is

$$- \frac{d[S_2O_8^{2-}]}{dt} = 3k_1 \, [Ag^+] \, [S_2O_8^{2-}]$$

which is the main feature of the reaction.