CHAPTER V : DISCUSSION

Chemical kinetics attained a new meaning when Arrhenius[1] put forth the concept of molecular activation as a prerequisite to chemical reaction. This concept of activation forms the basis of all subsequent theories of chemical reactions. It was established by Evans, Polanyi[2] and Eyring[3] that the activated complex forms as a result of molecular collisions between energised molecules. Each and every chemical reaction involves first formation of the activated complex in a reversible process, which then leads to give products of the reaction. Thus, it is necessary, according to Eyring, for occurance of any chemical reaction that the reacting atoms or molecules should approach each other and then pass over a free energy barrier. The molecular species corresponding to the top of such a free energy barrier are referred to as activated complexes and the rate of the reaction is controlled by the rate at which these complexes travel over the barrier.

Most oxidation reactions are complicated by the simultaneous occurrence of the number of steps, some of which are fast and some are slow. Each step is preferably accompanied by a single electron transfer.[4] The kinetic study is simple, if there is only one rate determining step.

Kinetic study involves the following determinations, for to elucidate the reaction mechanism of a chemical reaction.

1) Order with respect to each of the reactants.
2) Effect of electrolyte (Ionic strength).

3) Entropy of activation.
4) Effect of solvent.
5) Stoichiometry of the reaction.

In addition to above mentioned determinations, the determinations of chemical stoichiometry and the detection of intermediates helps to establish reaction mechanism.

1) Order of reaction :

The order of the reaction with respect to the different reactants indicate whether the rate determining step involves one reactant or more. If the rate of the reaction depends on the concentration of just one reactant, the rate determining step involves only that reactant.

In permanganate oxidations of amides, it has been observed that the order of reaction with respect to $KMnO_4$ is zero, amide is one and alkali is one. The overall order of reaction is two. Hence the rate of disappearance of permanganate is proportional to the first power of concentration of amide and the first power of concentration of alkali, i.e.

$$- \frac{d}{dt} \left[MnO_4^- \right] \propto \left[Amide \right] \left[OH^- \right] \qquad (1)$$

2) Effect of electrolyte :

For a bimolecular reaction, the relationship between the rate constant and the ionic strength is given by

$$\log k = \log k_o + 2\, z_A . z_B . \alpha \sqrt{\mu} \qquad (2)$$

where z_A and z_B are the charges of the reacting ions A and B.

μ = ionic strength,

α = constant,

k_o = the velocity constant at zero ionic strength

Equation (1) is only an approximation of an expression of Bronsted[5] and is valid only for dilute solutions, where ionic strength is small. The above equation predicts a relationship of log k when plotted against square root of the ionic strength, with a slope proportional to the product z_A and z_B, which may either be negative or positive, depending on the nature of the ionic charges. Hence if z_A and z_B are of the same charges, an increase in the rate of the reaction; an increase in ionic strength decreases the rate of reaction, in case of oppositely charged ion. If one of the reactants is neutral so that z_B is zero, equation (2) predicts no effect of ionic strength on the rate of reaction.

The results of oxidation of nicotinamide and isonicotinamide show that the rate of the oxidation reaction, increases as the ionic strength (salt concentration) increases. Hence it means that z_A, z_B must be positive or the reactants A and B must carry either the positive charges or negative charges, because the product of charges should result in positive value.

3) <u>Entropy changes</u> :

For a unimolecular reaction thermodynamic treatment gives

$$k_r = \frac{kT}{h} \; e^{\Delta S/R} \; e^{-Ea/RT} \quad \text{------------} (3)$$

where k_r = velocity constant,

k = Boltzmann constant,

h = Plank's constant,

Ea = Energy of activation,

ΔS = Change in entropy.

Also,

$$k_r = A \cdot e^{-Ea/RT} \quad \text{------------} (4)$$

where A = Frequency factor.

Hence, $$A = \frac{kT}{h} \cdot e^{\Delta S/R} \quad \text{------------} (5)$$

Now $$\frac{kT}{h} = 10^{13} \quad \text{------------} (6)$$

Hence $$A = 10^{13} \cdot e^{\Delta S/R} \quad \text{------------} (7)$$

It is evident that ΔS is positive if A is greater than 10^{13}. The frequency factor, A, can be calculated from equation (5) by determination of energy of activation, and E_a from well known Arrhenius equation. If ΔS is positive, it corresponds to less rigid probable complex and the reaction is faster. If ΔS is negative, the formation of activated complex is more rigid and the rate is slower. For reactions between ions of unlike charges there is generally an entropy increase going from reactants to activated complex. For ions of like charges, there is an entropy decrease as in the present work of oxidation of nicotinamide and iso-nicotinamide.

In terms of frequency factor, A, it is found that for reactions between ions of unlike charge, frequency factor is greater than 10^{13}, for ions of like charges the frequency factor is much less than 10^{13}. The reactions which have much larger or much smaller frequency factor values than 10^{13} can be described as "Abnormal" reactions, for which an explaination must be sought in terms of the complex mechanism. In most cases where an ion and a neutral molecules are involved frequency factor has been found to be of the order of 10^{11}. The utility of calculations for the increase or decrease of entropy has been well established by Moelwyn-Hughes[6] and Frost and Pearson.[7]

The decomposition of ring compound should be accompanied by an increase in entropy and a high frequency factor.[8]

(a) The negative values of entropy of activation of oxidation of amides suggest that the rate of disappearance of amide is slow.

(b) In case of oxidations of amide by permanganate the frequency factor is much smaller than 10^{13} and hence these oxidations can be described as "Abnormal reactions" for which an explaination must be sought in terms of the complex mechanism.

4) <u>Effect of Solvent</u> :

For reactions in solution, the nature of the solvent plays an important role, which has been discussed in detail by Amis.[9] It is observed that in the present study, the effect of dielectric constant could not be investigated due to the reactivity of the solvent such as alcohols, dioxane, acetone etc. with potassium permanganate.

Related work of Kennth B.Wiberg on the Kinetics of Permanganate Oxidation of Acetone

The kinetics of the permanganate oxidation of acetone was examined by Wiberg.[10] During the oxidation enolate ion is an intermediate, and it is oxidised by permanganate ion via an electron transfer rather than addition to the double bond.

The two possible schemes are suggested by Wiberg for the oxidation of acetone.

Scheme-I :

The enolate ion is formed on equilibrium state and is oxidised by permanganate in the rate determining step. The steps are as follows :

$$\text{Acetone} + \text{OH}^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{enolate} + \text{H}_2\text{O}$$

$$\text{enolate} + \text{Mn}^{\text{VII}} \xrightarrow{k_3} \text{Product} + \text{Mn}^{\text{V}}$$

$$\text{Mn}^{\text{V}} + \text{Mn}^{\text{VII}} \xrightarrow{k_4} 2\ \text{Mn}^{\text{VI}}$$

The last step is assumed to be faster than the others. Assuming a steady state concentration for the enolate, the rate law becomes

$$-\frac{d}{dt}\left[Mn^{VII}\right] = \frac{2\ k_1\ k_3\ \left[Mn^{VII}\right]\left[Acetone\right]\left[OH^-\right]}{k_3\ \left[H_2O\right]\ +\ k_3\ \left[Mn^{VII}\right]}$$

It is observed that as the concentration of permanganate increases, $k_3 \left[Mn^{VII}\right] \gg k_2 \left[H_2O\right]$ and this will qualitatively account for the decrease in observed rate constant with increasing permanganate oxidation.

<u>Scheme-II</u> :

In first scheme, it was assumed that enolate ion reacted with permanganate. Another possibility is that it reacts with enol which is in equilibrium with the enolate ion. The steps would be then

$$\text{Acetone} + OH^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{enolate} + H_2O$$

$$\text{enolate} + H_2O \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \text{enol} + OH^-$$

$$\text{enol} + Mn^{VII} \xrightarrow{k_5} \text{Product} + Mn^{V}$$

$$Mn^{V} + Mn^{VII} \xrightarrow{k_6} 2\ Mn^{VI}$$

Applying the steady state approximation, the rate law for this sequence of steps becomes

$$-\frac{d}{dt}\left[Mn^{VII}\right] = \frac{2\ k_1\ k_3\ k_5\ \left[Acetone\right]\left[OH^-\right]\left[MnO_4^-\right]}{k_2\ k_4\ \left[OH^-\right]\ +\ (k_2 + k_3)\ \left[Mn^{VII}\right]\ k_5}$$

If the equilibrium between enol and enolate ion to be maintained, $k_4 \left[HO^-\right] \gg k_5 \left[Mn^{VII}\right]$ under these conditions, the rate expression reduces to

$$-\frac{d}{dt}\left[Mn^{VII}\right] = \frac{k_1\ k_3\ k_5}{k_2\ k_4}\left[\text{Acetone}\right]\left[Mn^{VII}\right]$$

Here no base dependence is noted on the other hand, if $k_5 \left[Mn^{VII}\right] \gg k_4 \left[OH^-\right]$.

The rate expression would become

$$-\frac{d}{dt}\left[Mn^{VII}\right] = \frac{k_1\ k_3}{(k_2 + k_3)}\left[\text{Acetone}\right]\left[OH^-\right]$$

and the reaction rate would be zero order with respect to permanganate concentration. The similar rate law is also obeyed in case of oxidation of studied amides by permanganate in alkaline condition.

Mechanistic path of the reaction :

In order to discuss the probable mechanism for the oxidation of amides by permanganate, it is necessary to summarise the results obtained. The results are given below :

1) The oxidation of nicotinamide and iso-nicotinamide is first order with respect to amide, first order with respect to alkali and zero order with respect to permanganate.

2) Oxidation exhibits large negative values of entropy.

3) The values of frequency factor are much smaller than 10^{13}, suggesting complex mechanism.

4) The final products corresponding acids of amides are identified.

5) The salt effect is positive.

On the basis of the experimental results, the mechanism by permanganate may be formulated as follows :

Experimental rate law suggests that

$$-\frac{d}{dt}\left[MnO_4^-\right] \propto \left[Amide\right]\left[OH^-\right]$$

Applying steady state conditions to the reaction scheme the above experimental rate law has been verified as described under the title "Probable Reaction Mechanism and the Rate Law".

<u>The effect of substituents on the rate of oxidation</u> :

It is observed from Table that the order of reactivity is

a) $HCONH_2 > CH_3(CH_2)_2CONH_2 > ClCH_2CONH_2 > CH_3\ CH_2\ CONH_2 > CH_3CONH_2$

b) o-chlorobenzamide $>$ Benzamide

Generally, it has been observed that the electron donating groups accelerate the rate of oxidation reactions.[11]

c) iso-Nicotinamide $>$ Nicotinamide $\simeq$ Benzamide.

1) Thus, due to the electron donating effect of alkyl group the rate of oxidations increases from acetamide to butaramide.

2) The rate of o-chlorobenzamide is found to be greater than benzamide. This may be attributed to the electromeric effect.

3) Formamide is found to be very reactive indicating the formation of an unstable formic acid intermediate which undergoes further decomposition to CO_2 and H_2O, thus removing the product from the reaction mixture in favouring the forward reaction.

For the above interpretation of the results chloroacetamide is an exceptional case. The general effect of substitution is evidently quite complex and it is not surprising that the structural changes affect the value of E and A to different extents, and hence give different sequences of ease of oxidation according to the nature of substituents.[11]

4) The rate of oxidation of nicotinamide is found to be comparable with benzamide, but iso-nicotinamide is found to undergo fast oxidation this can be explained on the basis of electromeric effect.

REFERENCES

1 Arrhenius, S., Z. Physik. Chem., 4, 226 (1889).

2 Polanyi, M. and Evans, M.G., Trans. Far. Soc., 31, 875 (1935); 33, 448 (1937).

3 Eyring, H., J. Chem. Phys., 3, 107 (1935).

4 Haber, F. and Wiess, J., Proc. Roy. Soc., A-147, 332(1934).

5 Bronsted, J.N., Z. Physik. Chem., 102, 169 (1922); 115, 337 (1925).

6 Hughes, S.A., "The Kinetics of Reactions in Solution", The Clarendon Press, Oxford, 2nd Ed. (1947).

7 Frost, A.A. and Pearson, R.G., "Kinetics and Mechanism" John Wiley & Sons, Inc., New York (1953).

8 Frost, A.A. and Pearson, R.G., "Kinetics and Mechanism", John Wiley & Sons., Inc. New York (1953).

9 Amis, S.S., "Solvent Effects on Reaction Rates & Mechanisms", Acad. Press, New York & London (1966).

10 Wiberg, K.B. and Geer, R.D., J. Am. Chem. Soc., 87, 5202 (1965).

11 Cullis, R.C.F. and Ladburg, J.W., J. Am. Chem. Soc., 1407 (1955).