

# **CHAPTER – I**

## **INTRODUCTION**

## 1. INTRODUCTION

### 1.1 Kinetics and Reaction Mechanism

Chemical kinetics is a powerful tool for studying reaction mechanism, since it provides a measure of reaction rates and an indication of number and nature of molecules involved in the rate controlling step. The detailed step-by-step description of the pathway by which reactants are converted to products is known as reaction mechanism. This description includes the movements of electrons and which leads to the making and breaking of bonds and the spatial relations of atoms through the transformation. Ideally, a mechanism should account for both the structural and energy changes that occur at every stage of the reaction. Often more than one pathway for a reaction can be conceived of, choose the “most reasonable” mechanism which is consistent with the available experimental data.

### 1.2 Oxidation-Reduction Reaction

The classical definition of oxidation and reduction in terms of gain or loss of oxygen has in modern times been abandoned in favour of concepts of electron loss (oxidation) and electron gain (reduction). Oxidation-reduction reactions are also defined as involving changes in oxidation states or oxidation numbers. The assignment of oxidation number is based on :-

- i) the oxidation number of an atom in an element is zero;
- ii) the oxidation number of monoatomic ion is its charge;
- iii) the oxidation number of each atom in a covalent compound of known structure is the charge remaining on the atom when each shared electron pair is assigned completely to the more electronegative of the two atoms

sharing it. An electron pair shared by like atoms is split between them and

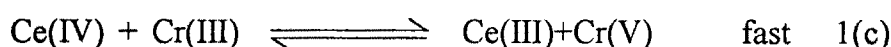
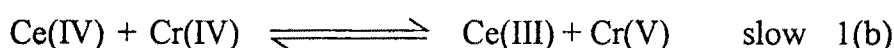
- iv) the oxidation number of an element in a compound of uncertain structure is usually obtained by assigning reasonable oxidation numbers to the other elements in the compound. Generalizations are also made depending on the position of an element in the periodic table.

### 1.3 Unstable Oxidation States

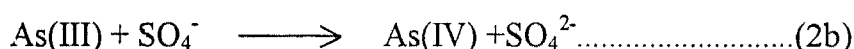
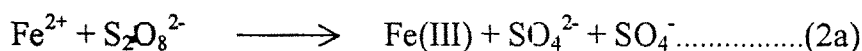
The formation of unstable oxidation states during the course of non complementary reactions has been now anticipated in a number of such reactions with sufficient proofs. The reductions for example of Tl(III) by Fe(II)<sup>1</sup>, V(III) or V(IV)<sup>2</sup> can only be explained through the formation of unstable Tl(II) species. The interconversion between Cr(III) and Cr(IV) always appear to involve the unstable states Cr(IV), and Cr(V). In a classic study, King and Tong<sup>3</sup> have worked out the details of the redox reaction between Ce(IV) and Cr(III) in aqueous sulphuric acid. The rate law was found to be as in (1) which is very reasonably explained by the mechanism,

$$\text{Rate} = \frac{K[\text{Ce(IV)}]^2 [\text{Cr(III)}]}{[\text{Ce(III)}]} \quad (1)$$

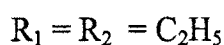
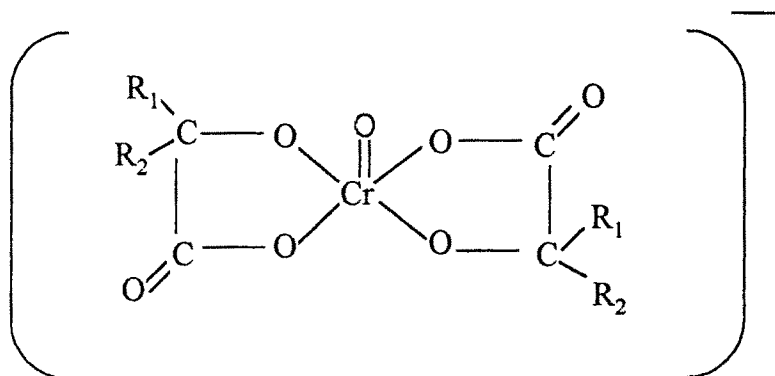
involving steps of 1(a) to 1(c). The first is a rapid equilibrium and the second step,



the interconversion of Cr(IV) and Cr(V) is the rate determining. Excellent support comes from the studies of related reactions such as the oxidation of vanadyl ion by acid chromate ion ( $\text{HCrO}_4^-$ )<sup>4</sup> and the analytically important oxidation of ferrous ion by acid chromate ion<sup>5</sup>. It is significant that in the above example, the change over from Cr(V) to Cr(IV) or vice versa, is a rate determining. This may be related to the likelihood that, at this stage, a change in coordination number from 4 to 6 occurs<sup>3</sup>. The existence of the intermediates, Cr(IV) and Cr(V), is sustained by the observation of induced oxidation. The direct reaction of acid chromate and iodide is slow, but the addition of  $\text{Fe}^{2+}$  or  $\text{VO}^{2+}$  will cause rapid reaction between acid chromate and  $\text{Fe}^{2+}$  or  $\text{VO}^{2+}$  in presence of iodide leads to the conclusion its reaction with Cr(V). A related phenomenon is seen in the oxidation of As(III) by persulphate ion. This slow reaction is accelerated or oxidation is induced by adding Fe(II) and the reaction is postulated to go through the formation of As(IV) from the reaction (2a, 2b)<sup>7</sup>.



While the Cr(V) formed during Cr(VI) oxidations is unstable, water soluble stable carboxylate chromium (V) complexes have been synthesised (I)<sup>8</sup>, the redox reactions and mechanisms involving (I) with various, organic and metal reductants have been reported<sup>9</sup>. The formation of oxochromate (IV) complexes of various porphyrin ligands and some alkoxide complexes of Cr(IV) in non aqueous solvents have been reported<sup>10</sup>. The rapid decomposition in contact with moisture complicates further studies on these systems.



Another feature of these unstable oxidation states is the frequent occurrence of catalysis. A number of studies of the catalysis by Pt of oxidation reactions have been made<sup>11</sup>. The catalysis by Ag(I), Cu(II), Mn(II) and Cr(III) in oxidation reactions are also found to occur through formation of unstable oxidation states<sup>12-14</sup>.

Cr(III) has been utilised as a catalyst for cerimetric analysis of organic and inorganic substances. The catalysis is understood to be due to intermediate oxidation states of Cr(VI). A detailed study of the Cr(III) catalysis of Ce(V) – As(III) reaction emphasized the role of Cr(IV)<sup>15</sup>.

#### 1.4 Catalysis

It has been observed that the rate of a chemical reaction is altered by the presence of a foreign substance, called the catalyst. A catalyst is defined as a substance which accelerates the rate of a reaction and is recovered unchanged in mass and chemical composition at the end of the reaction. The phenomenon of rate acceleration is known as catalysis. Although the catalyst is not consumed, it does enter in to chemical reaction but does not appear in the overall reaction. Thus

a catalyst is used up in a chemical reaction, but is subsequently regenerated and therefore, does not appear in the stoichiometric equation. In most of the cases the rate of reaction is a function of catalyst concentration.

Catalyzed reactions have some general characteristics compared to uncatalyzed reactions and are characterized by following criteria.

- i) A catalyst remains unaltered in amount and chemical composition at the end of the reaction, although its physical form, such as particle size or surface, may be modified.
- ii) A small amount of catalyst is often sufficient to change the rate of a reaction.
- iii) A catalyst cannot initiate a reaction. It can only accelerate or retard the speed of a chemical reaction by changing the mechanism, thereby decreasing energy of activation. It functions as an agent to find an alternative path for the process.
- iv) A catalyst does not displace the position of equilibrium in a reversible reaction.
- v) Every catalyst has specific action. A catalyst which is good for one type of reaction may be ineffective in another.

Traditionally, catalysed reactions are divided into two classes, namely homogeneous and heterogeneous, depending on the physical state of reactants, products and catalyst. Homogeneous type of reactions are those in which the catalyst is in the same phase as the reactants. If the catalyst is in a different phase than that of the reactants, the reactions are called heterogeneous.

In homogeneous catalysis the reaction occurs in one phase and the rate is a function of the catalyst concentration. For example oxidation of isopropanol and acetone by ceric sulphate catalysed by Ir(III)<sup>16</sup>, Ag<sup>+</sup> catalysed oxidation of ethanol, formaldehyde, acetone and acetic acid by ceric nitrate in HNO<sub>3</sub> medium and ceric sulphate in H<sub>2</sub>SO<sub>4</sub> medium<sup>17</sup> and Ru<sup>3+</sup> catalysed oxidation of propanol, ethylene, glycol and mannitol by ceric sulphate.<sup>18</sup>

### 1.5 Michaelis Menten Kinetics

In some types of catalysis, notably by acids and bases, the catalyst is in excess over the substrate or is provided in constant amount by a buffer present in excess. But in others, especially in catalysis by metal ions and by enzymes, the catalyst is a minor constituent of the reaction mixture. In order for a catalyst to function it must interact with the substrate. Typically, the catalysed reaction involves several steps involving the catalyst. These include complexing of catalyst with substrate, reversion of complex to substrate and free catalyst and conversion of substrate-catalyst complex to product(s) and free catalyst.

When the catalyst is a minor constituent, the system is amenable to treatment by means of the steady state approximation. However, the derivation differs from cases to cases, because the reagent present in deficiency (the catalyst) may be complexed to a considerable extent and because the catalyst is regenerated as a byproduct of the reaction. The kinetic expression obtained embraces as a special case the situation in which substrate catalyst interaction is in a mobile equilibrium.

Enzyme catalysed reactions are normally of this character, and the treatment of this type of kinetic situation originated mainly with bio-chemists. The principles are, however, applicable to catalysis by metal ions and in other situations. This is

known as Michaelis-Menten kinetics, after the pioneer investigators<sup>19</sup>, although the approach was originated by Henri<sup>20</sup>.

### 1.6 The Predominant Species :

The rate equation that can be interpreted in terms of mechanistic proposals expresses the rate as a function of the concentrations of the species in their predominant forms. The experimental data, however, are originally formulated in terms of laboratory concentrations referred to as stoichiometric or total concentrations. One case to be considered is when a reactant is converted to an entirely different species by reaction with the solvent or with other substrates. In many instances this is almost trivial situation. The addition of a small concentration of  $\text{NH}_3$  to aqueous mineral acid convert it almost entirely to  $\text{NH}_4^+$  and the real laboratory variables are  $[\text{NH}_4^+]$  and  $[\text{H}^+]$ . The concentration of  $\text{NH}_3$ , being quite small is controlled only directly. Similarly, when  $\text{VCl}_4$  is dissolved in water  $\text{VO}^{2+}$ , is formed and when cyanogen is dissolved in base, it undergoes complete conversion to  $\text{CN}^-$  and  $\text{CNO}^-$ .

The species involved in many overall chemical reactions may be subject to other equilibria, which are maintained rapidly relative to the main reaction. These equilibria serve to reduce the concentration of a reacting species from the value of the formal concentration. For example, the concentration of  $\text{Fe}^{3+}$  in a solution is lowered appreciably by the addition of even small quantities of the HF owing to the formation of the rather stable complex  $\text{FeF}_2^+$  and the partial ionisation of  $\text{H}_3\text{PO}_2$  lowers the added quantity.

To formulate the reaction rate as a function of species concentration, therefore, requires a knowledge of the existence of such equilibria and generally



speaking, the knowledge or determination of one or more equilibrium constants. The distinction between the species and laboratory concentration is particularly critical in the case of partially displaced equilibria, because the rate equations, if expressed in the form of reaction rate as a function of laboratory concentrations, quite often resemble the equations applicable to entirely different mechanisms.

A familiar and frequent incident where pre-equilibrium are important has to do with the pH dependence of a reaction rate. the case where an acid base reaction converts a significant fraction of a reactant into a different form ( which may be more reactive than the original) and the case where only a very small fraction is converted to highly reactive form often lead to the rate laws of the same algebraic form. In general one must be able to evaluate the appropriate equilibrium constants to distinguish the alternatives.

## 1.7 Prior Equilibria

Prior equilibria includes all steps of mechanism that precede the rate limiting step or steps. Prior equilibria affect the overall rate law in various ways. Certain prior equilibria contribute half order factors to the rate law. If the predominant form of a reactant is a dimer but the small amount of monomer in equilibrium with the dimer is what actually reacts the overall rate will be proportional to the one half power of dimer concentration.

A prior equilibrium that transforms most of the reaction(s) introduced into other species affects the rate by changing the effective identity of reactants. An obvious example concerns a reaction in rather strongly alkaline solution ( say pH 13) into which a carboxylic acid is introduced as a reactant. It is of course immediately converted to the corresponding carboxylate ion, which is the effective

substrate in the system. Although such a prior equilibrium introduces no mathematical complications, it is of the greatest chemical significance and must be recognised if the rate law is to be interpreted properly. In some cases, such as that just mentioned, the rapid initial transformation of the reactant introduced is utterly obvious, but in others it is not at all obvious. Indeed, recognition of an unexpected rapid initial transformation represents a considerable stride towards understanding of a reaction mechanism. It was for example, not obvious to early investigators that nitric acid in a concentrated sulphuric acid solution is almost totally converted to nitronium ion or that p-nitro-benzene diazonium ion<sup>21</sup> introduced into 0.1 M methanolic sodium methoxide is within micro-seconds, converted in an adduct, presently cis-p- nitrophenylazomethyl ether<sup>22</sup>.

Because the validity of the interpretation of a rate law is crucially dependent on correct identification of the effective reactants, special efforts to detect any rapid initial transformation of the reactant(s) introduced are recommended. Special monitoring of the reacting system with attention to the spectra of the original reactants, often reveals rapid initial changes that may occur, UV-Vis and NMR spectra are useful for this purpose.

A rapid initial transformation of irreversible character conceivably might go undetected if the overall reaction rate were followed by detection of the ultimate product. On the other hand, it would have the effect of changing the identity of the effective reactant in the phase of the reaction studied kinetically and therefore, must be recognized if the rate law is to be interpreted correctly.

A prior equilibrium that substantially splits a reactant between two forms may cause the rate law to be involved a summation term in the denominator. A

familiar case is an acid-base equilibrium. It often happens that which of the form ( the protonated or the unprotonated ) is reactive and the other not.

If a prior equilibrium substantially splits a reactant between two forms but the equilibrium is unaffected by the concentration of the other species, it will have no effect on the rate law. For example, a reactant may be split between two or more conformations or between forms representing differing degrees of solvation

## 1.8 Stoichiometry

In all studies of mechanism, one of the first and certainly most important pieces of data needed is the stoichiometry of the reaction. There are two ways to interpret this word and both are correct. Stoichiometry refers to the number of particles ( atoms, molecules and ions ) in the balanced chemical equation representing the chemical reaction. In many cases, where more than a single reaction occurs, stoichiometry may refer more broadly to how much reactant(s) goes to what products(s) and to the extent to which the various reactions complete. It is also worth noting that identification of all products of the reactions can be useful in elucidation of mechanism. A single product suggests a single transition state involving atom transfer, whereas multiple products usually occur where the mechanism involves molecular fragmentation and competing transition states.

## 1.9 LITERATURE SURVEY

### 1.9.1 Uncatalysed Reactions

The mechanism of oxidation of alcohols usually proceed through a prior formation of oxidant-alcohol complex<sup>23</sup>. Rangaswamy and Santappa<sup>24</sup> reported the oxidation of n-propyl, n-butyl, isobutyl, isopropyl, sec. amyl, tert butyl, tert amyl and benzyl alcohols and cyclohexanol by ceric perchlorate in perchloric acid medium (0.5 to 2.0 M) in the temperature range 5-30°C. They showed that products of primary alcohols are the corresponding acids and for secondary and tertiary alcohols the corresponding ketones. A mechanism of oxidation of the alcohols based on unimolecular decomposition of complexes ( $\text{Ce}^{4+} + \text{Alcohols}$ ) has been put forward to explain the observed results for all alcohols, except for benzyl alcohol, which shows a different behavior in that it is a second order reaction, first order each in  $[\text{Ce}^{4+}]$  and  $[\text{alcohol}]$ . The rate and equilibrium constants and their thermodynamic parameters for the reactions have been evaluated and discussed.

The reaction between Ce(IV) and ethylene glycol in  $\text{H}_2\text{SO}_4$  medium was investigated by Sant and co-workers<sup>25</sup> and found to be first order with respect to Ce(IV). The results showed that the reaction takes place between an ion and a neutral molecule. Rate is directly proportional to  $[\text{H}^+]$ . At constant ionic strength, addition of  $\text{SO}_4^{2-}$  decreases the rate of the reaction. The values of K at 40, 45 and 50°C were determined. The values for the energy of activation, frequency factor and entropy of activation were calculated. The decomposition of a reversible complex formed between ethylene glycol and Ce(IV) to give free radical explains the above results.

### 1.9.2 Catalysed Reactions

Ir(III) catalysed oxidation of methyl, ethyl, propyl, butyl and isobutyl alcohols by ceric sulphate has been studied by Rao and Saiprakash<sup>26</sup>. The oxidation of these alcohols follows first order kinetics with respect to [Ce(IV)] and fractional order with respect to [Substrate] and [Ir(III)]. A mechanism involving an Ir(III) alcohol complex was proposed. Rate constants, formation constant and relevant thermodynamic parameters were evaluated.

Oxidation of propanol, ethylene glycol and mannitol by ceric sulphate catalysed by Ru(III) were reported<sup>18</sup>. The order with respect to [Ce(IV)] was found to be unity but fractional order both in [Alcohol] and [Catalyst]. They showed formation of complex between Ru(III) and alcohol which reacts with Ce(IV) in the rate determining step.

Singh and others reported oxidation of triethylene glycol and tetraethylene glycol by cerium(IV) sulphate in aqueous H<sub>2</sub>SO<sub>4</sub> medium catalysed by Ru(III) chloride. The reaction was found to be zero order in [Ce(IV)] and first order, both [substrate] and [catalyst]. An inner-sphere mechanism involving hydride ion transfer between organic substrate and RuCl<sub>3</sub> was suggested.

The Ce(IV) oxidation of isobutanol, isoamyl alcohol, isopropyl alcohol, and secondary butanol catalysed by chromium(III) in sulphuric acid and perchloric acid mixture at 30°C have been reported<sup>23</sup> (were studied by G.S. Gokavi and others.) The reaction was found to proceed with the formation of a chromium(IV) intermediate followed by its complexation with alcohol. The complex thus formed decomposed into an aldehyde or ketone by a two electron hydride ion transfer. The formation constants for complexes were determined from Michaelis – Menten plots.

The accelerating effect of  $[H^+]$  on the reaction is attributed to the formation of active species,  $H_2Ce(SO_4)^{3+}$  and  $H_2Alcohol^+$ , of the oxidant and alcohol respectively. The activation parameters were also determined and an isokinetic plot was found to be linear.

Uncatalysed and chromium(III) catalysed oxidations of n-butanol and ethylene glycol by cerium(IV) in mixture of sulphuric acid and perchloric acids at  $30^\circ C$  have been reported. The uncatalysed reactions involve the oxidant alcohol complex formation with the alcohols which decomposes in a rate determining step to produce the respective aldehyde by a two electron hydride ion transfer. The accelerating effect of hydrogen ion concentration in both uncatalysed and catalysed reactions was predicted to be due to promoted oxidant species, the active species of the oxidant was found to be  $H_2Ce(SO_4)^{3+}$ .<sup>29</sup>

Cr(III) catalysed oxidation of Te(IV) by Ce(IV) has also been reported. The micro amount of Cr(III) catalyzes the oxidation of Te(IV) by Ce(IV) in acid medium which proceeds through substrate catalyst complex. The effectiveness of catalyst is maximum in the mixture of acids ( $HClO_4 + H_2SO_4$ ) compared to the individual acids. The active species of Ce(IV), Te(IV) and Cr(III) are understood to be  $H_2Ce(SO_4)^{3+}$ ,  $TeO(OH)^+$  and  $Cr^{+3}$ ,  $SO_4^{2-}$  respectively under the reaction conditions studied<sup>30</sup>.

### 1.10 Present Work :

The uncatalysed and chromium(III) catalysed oxidation of cyclohexanol and selenium dioxide was studied. The experimental results obtained include study of effect of oxidant, alcohol, perchloric acid and temperature on the reaction. Based on the results a probable mechanism is suggested which involves formation of a

complex between cyclohexanol and oxidant in uncatalysed reactions and cyclohexanol and catalyst in catalysed reactions. The complex thus formed will decomposes to give free radicals followed by its oxidation to give products in fast steps.

From the effect of temperature on the reaction various thermodynamic parameters were calculated. The effect of perchloric acid was useful in predicting the nature of the active species of the oxidant.