CHAPTER I

INTRODUCTION
The Co$^{3+}$ ion shows a particular affinity for N donors such as NH$_3$, en, EDTA, -NCS, etc. and complexes are exceedingly numerous. They generally undergo ligand-exchange reactions relatively slowly, like Cr$^{3+}$ and Rh$^{3+}$. Hence, from the days of Werner and Jorgensen, they have been extensively studied. A large part of our knowledge of the isomerism, modes of reaction, and generally properties of octahedral complexes as a class is based on studies of Co(III) complexes.

The reactions of co-ordination compounds have been divided into three main categories: (1) Isomerization and racemisation reactions (2) electron-transfer reactions, and (3) substitution reactions.

Ligand substitution reactions have been divided into four general mechanisms$^{1-2}$: (1) Associative (A), (2) Dissociative (D), (3) Interchange dissociative (I$_d$) and (4) Interchange associative (I$_a$).

The important features of A and D mechanisms are bond-making and bond-breaking respectively, whereas in an interchange process, bond-breaking and bond-making are of comparable importance. In the associative processes, the co-ordination number of the metal ion or of the ligand
increases by one in the transition state:

\[ \text{M - X + Y} \rightarrow \text{Y - - X} \rightarrow \text{M-Y+X} \]

Transition state

The co-ordination number of both the ligand and the metal decrease by one in the rate determining step of the dissociative process.

\[ \text{M-X} \xrightarrow{\text{Slow}} \text{M+X} \]
\[ \text{M+Y} \xrightarrow{\text{Rapid}} \text{M-Y} \]

Among the inert transition metal complexes, the Co(III) and Cr(III) complexes have received maximum attention by researchers interested in mechanistic studies. Co(III) complexes particularly serve as good models in mechanistic studies as their kinetic studies are conveniently performed in laboratories. Substitution involving the replacement of a group by a hydroxide ion is called Base Hydrolysis while as the substitution involving the replacement of a group by a water molecule is termed Aquation or Acid Hydrolysis. The mechanism of the replacement reaction of water (Aquation) is strikingly analogous to the substitution reactions in organic compounds, except that in the case of cobalt the aquo salts are stable when hydrolysed, whereas with organic compounds, in consequence of the more extensive hydrolysis,
the free hydroxy compound (alcohol) is obtained. It has been shown by several workers\textsuperscript{4-6} that aquation reactions follow first order kinetics. There is a first order dependence on the concentration of the complex, and as water is the solvent, this is said to be a pseudo-first-order reaction.

Pearson, Boston and Basolo\textsuperscript{7} have studied the acid hydrolysis of several trans-\([\text{Co(AA)}\text{Cl}_2]^{+}\) cations and have shown that the complex ions containing C-substituted ethylenediamine undergo hydrolysis more rapidly than the corresponding ethylenediamine complex. The fact that increased crowding around the central ion does not decrease the rate would indicate that these reactions do not involve the approach of an incoming group or proceed through a 7-co-ordinated activated complex, i.e., by an \(\text{SN}_2\) mechanism. A more probable interpretation is that a pentacoordinated intermediate is involved or, in other words, the acid hydrolysis reaction proceeds by a dissociation (\(\text{SN}_1\)) process. For the cobalt pentamines, the order of reactivity as far as the leaving group is concerned is \(\text{NO}_3^- > I^- > Br^- > Cl^-\). This is in good agreement with the order expected on the basis of the stability constants of the complexes\textsuperscript{2}. Bosnich and Dwyer\textsuperscript{8} have studied the rates of aquation of a series of homoisomeric cations \(-[\text{Co X en. dien}]^{2+}\) (\(X=\text{Cl, Br, I}\) and
observed that the rates follow the order $I > Br > Cl$.
Although rates of acid hydrolysis are for the most part independent of ionic strength, Garrick\(^6\) has shown that the rate with $[\text{Co(NH}_3\text{)}_5 \text{Cl}\text{]}^{2+}$ is definitely accelerated in the presence of nitrate or sulphate ions. However, it is doubtful that the molecularity of an acid hydrolysis reaction could be ascertained solely on the basis of the ionic strength effect.

Basolo, Bergmann and Pearson\(^9\) studied the rates of reactions of analogous complex ions which vary in the amount of steric hindrance in the complex. In the first of these studies the rates of both acid and base hydrolysis were determined for some C-substituted acetatopentammine cobalt (III) ions. The rates of reaction were found to vary with the acidity of the corresponding substituted acetic acid. There was no indication that different steric requirements had any influence on the rates. Lamb and Marden\(^4\) have shown that the rate of acid hydrolysis of ammine complexes in an acid medium (ph $\sim 0.5$ to 3) is independent of the hydrogen-ion concentration. However, the rate of aquation of an acidoaquo-ammine complex varies inversely with the concentration of hydrogen ion\(^5\). The effect of chelation on the rate of acid hydrolysis of Co(III) complexes has been investigated by several workers.\(^{10-12}\) The increase in aquation rate of cobalt(III)
complexes on expansion of chelate ring has been observed by many workers. The rate of aquation is considerably enhanced by the addition of halide abstractors e.g., Hg$^{2+}$, Tl$^{3+}$ or Ag$^+$ to the acidic solution of the halogeno complexes. These are not technically catalysts, as the initial and final states of the added reagent are different but the term has crept into the literature. The term 'assisted' has, therefore, been coined. The rate of aquation of $\left[\text{Co(NH}_3\text{)}_5\text{X}\right]^{2+}$ and similar complexes is accelerated by the presence of cations that can complex with the ligand group X. Thus the presence of 0.1M silver ion speeds up the aquation of $\left[\text{CrCl(H}_2\text{O)}_5\right]^{2+}$ by a factor of $10^5$. Bronsted and Livingston studied the mercuric ion catalysed aquation of $\left[\text{Co(NH}_3\text{)}_5\text{Br}\right]^{2+}$ and observed that the reaction occurs with measurable speed and goes practically to completion under ordinary conditions.

Tobe and his students have carefully studied the stereochemistry of some substitution reactions of Co(en)$_2$ L$^{X^{n+}}$ systems and suggested that the leaving group X exerts an influence on the position of attack of the entering water molecule. The sterochemical studies by Loeliger and Taube support the view that the departing X may have an effect on the steric course of aquation reactions in these systems. For example, the spontaneous aquation of trans-$\left[\text{Co(en)}_2\text{Cl}_2\right]^+$ yields 35% cis- and 65%
trans-$[\text{Co}(\text{en})_2\text{H}_2\text{O}\text{Cl}]^{2+}$, whereas the induced aquation with the addition of Hg$^{2+}$ yields 28% cis- and 72% trans-$[\text{Co}(\text{en})_2\text{H}_2\text{O}\text{Cl}]^{2+}$. Also, the rapid reaction of trans-$[\text{Co}(\text{en})_2\text{N}_3\text{Cl}]^{2+}$ with $\text{HNO}_2$ to liberate $\text{N}_2$ and $\text{N}_2\text{O}$ in aqueous solution yields$[\text{Co}(\text{en})_2\text{H}_2\text{O}\text{Cl}]^{2+}$ in the same isomeric quantities as for the induced aquation with added Hg$^{2+}$. Since these two different rapid reactions give the same products, it is assumed that the products are formed from the same 5-coordinated intermediate.$^{21}$

Isotopic studies on the aquation of $[\text{Co(\text{NH}_3)}_5\text{X}]^{2+}$ in the presence of Hg$^{2+}$ also agree with the formation of a 5-coordinated intermediate in the induced aquation reactions. In kinetic studies Bronsted and Teeter$^{22}$ have established that Hg$^{2+}$ catalysed hydrolysis reactions are sensitive to variation in ionic strength and this has been confirmed by later workers. T.K.Huan$^{23}$ et.al. have reported that the addition of Hg$^{2+}$ to solutions of the Co.en.dien. Cl$^{2+}$ isomers causes the rapid formation of aquo ions.

Their data indicate that the rates of acid hydrolysis are rather insensitive to geometry within a group of isomers and similar remarks apply to the Hg$^{2+}$ assisted aquations. Banerjee and Banerjee$^{24}$ have reported the metal ion catalysed dissociation of tris-biguanide complexes of chromium (III) and cobalt (III), using bivalent metal
ions e.g., Mn, Co, Ni, Zn and Cu as catalysing ions. A.C. Dash and R.K. Nanda studied the aquation of cis-Oxalatoammine bis(en) cobalt(III) complex in the presence of Mn(II), Ni(II), Cu(II), Zn(II), Al(III), Ga(III) and Fe(III) ions, and observed that oxalate bridged nuclear complexes act as the catalytically active. M.L. Tobe and C.K. Williams have studied the mercuric ion catalysed aquation of cis-chlorocyanobis(en) cobalt(III) cations and explained the kinetics in terms of the formation of an adduct between the mercury and the substrate. Reynolds et al. have concluded from their studies of the assisted aquations of Mn$^{2+}$ and of M(O$_2$CNH$_2$)$_2$ by nitrous acid and M$^{3+}$(M$^{3+} = \text{Co(NH}_3)_5^{3+}$, $X = \text{Cl}^-$, Br$^-$, I$^-$) by Hg$^{2+}$ that a common 5-coordinated intermediate was formed in all these reactions. The structure-reactivity patterns of isomeric Co Cl(N$_5$)$_{2+}$ systems (where N$_5$ is a bidentate-tridentate or bis (monodentate)-tridentate polyamine ligand combination) have been studied by a number of authors. The synthesis and reaction kinetics of some isomeric Co Cl(AA)-(dien)$_{2+}$ (AA = Phen, bipy) complexes has been reported by A.R. Gainsford and D.A. House. The kinetic parameters for the Hg$^{2+}$-assisted chloride release from these complexes were compared with those obtained for analogous Co Cl(AA)-(dien)$_{2+}$ complexes.
A comparative study on the kinetics and mechanism of silver and mercurous ion catalysed aquation of chloro and bromo(ethylenediamine) (diethylenetriamine) cobalt(III) cations has been reported by K.P. Dubey and M.L. Bhat. The kinetics of Ag⁺ and Tl⁺ catalysed aquation of \([\text{Co(en)}(\text{dien})X]\) \(X_2\) \((X = \text{Cl}, \text{Br})\) has been studied spectro-photometrically over a range of temperatures at constant pH and ionic strength. Activation parameters have been determined and a reaction mechanism suggested. The Ag⁺ and Tl⁺ kinetics has been explained in terms of the formation of an activated complex between the catalyst, \(M(M=\text{Ag}^+, \text{Tl}^+)\) and the substrate, such that \(\frac{[\text{activated complex}]}{[\text{Substrate}][M]} = K\). The activated complex has been reported to be a halogen-bridged adduct which facilitates the breaking of the original Co-X bond, thereby favouring an essentially \(S_N^1\) type of substitution. Foong, Kipling and Sykes carried the kinetics of Tl(III) and Mercury (II) - catalysed aquations of the chloropentaammine cobalt(III) and cis- and trans-Dichlorobis (ethylenediamine) cobalt(III) complexes and it was found that Tl(III)-catalysed aquations of Co(NH₃)₅Cl²⁺ and cis- and trans-Co(en)₂Cl₂ (first chloride) show a first order dependence on Tl(III) over a wide range. There is no evidence in the case of the cis-complex for the formation of a stable binuclear adduct as in the corresponding mercury(II) - catalysed aquation.
Studies of the substitution of octahedral cobaltamine complexes in non-aqueous solution have indicated some ambiguity in the interpretation of the role of the solvent. Brown and Ingold have investigated the kinetics of substitution of a chloro group in cis-Co(en)$_2$Cl$^+$ by several anions in the solvent methyl alcohol, using polarimetric, spectroscopic, chemical and radiochemical methods and reported that their results were a good evidence of SN$^1$ dissociation mechanism. However, Basolo and Pearson argue that substitution could be equally in agreement with an SN$^2$ mechanism involving the solvent methanol as the nucleophilic reagent. On the other hand, Wells has suggested that the two mechanistic categories are expected to show such markedly different changes in reactivity that solvent effects have been suggested as diagnostic of mechanism. Correlations of rate constants with solvent Y-values have been particularly useful. C.H. Langford used a similar approach for Co(III) complexes and reported two correlations of rates with solvent Y-values for trans-[Co(en)$_2$Cl$^+$] and trans-[Co(en)$_2$(NO$_2$)Br$^+$] in methanol-water mixtures. Burgess and Price reported the rates for spontaneous aquation of [Co(NH$_3$)$_5$Cl]$^{2+}$ and trans-[Co(en)$_2$Cl$^+$] and of Hg(II) - assisted aquation of [Co(NH$_3$)$_5$Cl]$^{2+}$ and [Rh(NH$_3$)$_5$Cl]$^{2+}$ in a range of binary mixed solvents,
including methanol-, ethanol-, dioxane-, acetic acid-, acetone- and t-butyl- water mixtures. These results and previously published results on similar complexes were discussed in terms of the Grunwald-Winstein treatment of solvolysis in mixed solvents. Reynolds, Glavas and Dzelilovic\textsuperscript{56} reported the assisted aquation of chloropentaamine Cobalt(III) ion in different media. The product ratios from competition reactions accompanying the Hg\textsuperscript{2+} - assisted removal of Cl\textsuperscript{-} from \(\text{Co(NH}_3\text{)}_5\text{Cl}^{2+}\) in aqueous solutions of NaNO\textsubscript{3}, NaH\textsubscript{2}SO\textsubscript{4}, H\textsubscript{3}PO\textsubscript{4} and CH\textsubscript{3}CO\textsubscript{2}H and in three water + nonaqueous solvent mixtures were determined at 0, 25 and 55°C. An \(\text{Id}\) interchange of leaving and incoming ligands was postulated which adequately explains the observed data. In mixtures of water with one of the nonaqueous solvents dimethyl sulfoxide, N,N-dimethylformamide, or acetonitrile the product ratios were equal for equal bulk mole fraction of nonaqueous solvent. This result was interpreted to mean that, at equal bulk mole fraction, the three nonaqueous solvents were equally available in the solvation shell of the encounter complex preceding the formation of products and that complete, preferential solvation by one solvent component did occur in some solvent mixtures but not in others. Dubey and Bhat\textsuperscript{57} studied the kinetics of spontaneous and mercurous ion assisted aquation of three complexes viz., \([\text{Co.en.dien.Cl}^{2+}]\).
\[ \text{Co.en.dien.Br}^{2+} \text{ and Co.en.dpt.Cl}^{2+} \]\text{ spectrophotometrically at constant pH and ionic strength in methanol- and ethanol-water mixtures containing between 0 to 30% by volume of the non-aqueous component. Good correlations were observed between logarithms of rate constants and solvent Y-values.}

**Literature Review and Present Work:**

Detailed kinetic studies of metal-ion catalysed aquation reactions of cobalt (III) complexes are of interest for two reasons. First, they provide information as to the nature of the activated complex in acid hydrolysis (i.e. aquation) reactions of Cobalt(III) - amine complexes. Secondly the activated complexes resemble those obtained for inner-sphere electron-transfer reactions, and might, therefore, provide information which is relevant to such processes. The mercury(II) -catalysed aquations of Chloride from the inner-Co-ordination sphere of Cobalt(III) complexes have been fairly extensively studied. A review of the literature on aquation studies of halogencpentamine Co(III) complexes reveals that the kinetics have been mostly restricted to spontaneous reactions. Scattered investigations on Ag\(^+\) and Tl\(^{3+}\) catalysed aquations have also been reported. A review of literature further shows
that there have been few investigations on catalysed behaviour of metal ions like Tl\(^+\), Hg\(^{2+}\) and Ag\(^+\) which have strong affinity for halogens specially because of low solubility of their halides. Hence, it was thought desirable to investigate the metal ion assisted aquations of halogeno mixed diamine-triamine Co(III) complexes using Tl\(^+\), Ag\(^+\) and Hg\(^{2+}\). In the present Thesis, spectrophotometric technique was used to study the halogen abstractor ion assisted aquation of \([\text{Co(AA)(ABA)}X]^2+\) in aqueous and binary mixed solvents at a range of temperatures. The diamine ligands chosen were 2,2'-bipyridyl, 1,10-phenanthroline and propylenediamine. The triamine ligand was Diethylene-triamine. The studies were undertaken in order to have a further insight of the assisted aquation reactions and to investigate the effect of leaving group (X = Cl, Br), chelation and solvent composition on these aquation reactions, and to establish the underlying mechanism.

Metal ions and hydrogen ion are acids of the same type. However, metal ions may have many advantages over hydrogen ion. Metal ions usually have a positive charge greater than one, can readily form metal chelates, and may be considered as super acids that can exist in neutral solution.

Hg\(^{2+}\) ion has formally a d\(^{10}\) s\(^1\) non-bonding
configuration, but actually exists as the diatomic Hg$^{2+}_2$ cation in which both the electrons in 6s orbital are in fact being used for bonding purposes one in forming the Hg-Hg covalent bond and the other in ionisation. As a result, the metal atom attains the stable d$^{10}$ configuration. Mercurous Chloride and bromide are insoluble, which thus precludes the possibilities of hydrolysis or disproportionation to give Hg$^{2+}_2$ halide complexes. Hg$^{2+}_2$ ion is a soft acid.

Tl$^+$ ion has the ground state electronic configuration 6s$^2$ and the first excited state has 6 s$^1$ p$^1$. The effect of heavy metal-like properties of thallium on its behaviour as a univalent cation is of considerable interest. Tl$^+$ has a considerably greater molecular polarisability than alkali metals and hence Tl$^+$ is a class (b) or soft acid. The Tl$^+$ ion is only very weakly hydrated in solution. For Tl$^+$ halides the stability constants give an order F < Cl < Br < I for increasing strength of complex formation. For Cl and Br ligands, the stability constants ($K_1$) are 0.79 and 2.1 respectively.

Ag$^+$ ion (4 d$^{10}$) is solvated in aqueous solution. There is an appreciable covalent character in the Ag $\cdots$ X(X=Cl,Br) interactions. For monodentate ligands, the complex ions, AgL$^+$, AgL$_2^+$, AgL$_3^+$ & AgL$_4^+$ exist. The constants
$K_1$ and $K_2$ are usually high whereas $K_3$ and $K_4$ are relatively small. The main species are hence, $AgL_2^+$. The stability constants sequence for halogeno complexes is $I > Br > Cl > F$. For Cl and Br ligands, the stability constants are 3.08 and 4.3 respectively. Like $Tl^+$ ion, $Ag^+$ ion is also a soft acid.

The solubility product constants of the halides of $Tl^+$, $Ag^+$ and $Hg^{2+}$ are:

$$
TlCl = 1.9 \times 10^{-4} \quad AgCl = 1.7 \times 10^{-10} \quad Hg_2Cl_2 = 1.1 \times 10^{-18}
$$

$$
TlBr = 3.6 \times 10^{-6} \quad AgBr = 3.3 \times 10^{-13} \quad Hg_2Br_2 = 1.3 \times 10^{-21}
$$

In binary mixed solvents, the percentage of the non-aqueous component was varied from 0 to 30 only, in order to avoid the possibility of ion pair formation and to maintain aquation as the sole reaction.

The spectrophotometric method of measuring reaction rates has many advantages over the chemical methods. The advantages here are; (i) Measurements are made without arresting the reaction; (ii) A continuous record of the rate of reaction may be obtained; (iii) The measurements can easily be automatically recorded; and (iv) For relatively slow reactions, samples can be withdrawn from the thermostated reaction mixture for measurements.
Applications of Metal Ion Assisted Aquations In Analysis

Based on the metal ion catalysed (assisted) aquation reactions, various kinetic and equilibrium methods have been developed for trace analysis of catalyst/s either singly or in mixture. The advantages and analytical potential of such reactions are being recognised and utilised. However, as early as 1954, Asperger and Murati developed a method for determining small amounts of mercury in the atmosphere by making use of its catalytic effect on the aquation of potassium ferrocyanide. The reaction progress was monitored by the color developed on addition of nitrosobenzene, which quickly develops an intense violet color with the aquation product. When the nitrosobenzene concentration is $> 1.4 \times 10^{-3} \text{M}$, the rate of color development becomes independent of this (non-limiting) species and the color intensity at a fixed reaction time is a direct measure of the $[\text{Hg}^{2+}]$ in the solution. Concentrations of $\text{Hg}^{2+}$ as low as $5 \times 10^{-7} \text{M}$ were analysed. 2,2'-Dipyridyl and O-Phenanthroline have also been used instead of nitrosobenzene for color development. Further, $\text{Fe(CN)}_5(\text{NH}_3)_3^{3-}$ may be used instead of $\text{Fe(CN)}_6^{4-}$. 


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