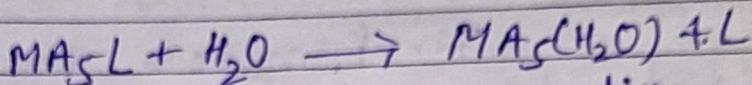


ACID HYDROLYSIS OR AQUATION -

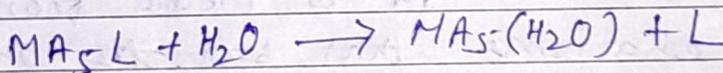
The ligand substitution reaction occurring in aqueous medium in which a ligand present in the coordination sphere of a complex species is replaced by H_2O molecule is called acid hydrolysis or aquation, of the complex. For example, the reaction



is an acid hydrolysis reaction. In this reaction L is the leaving ligand and H_2O is the entering group. The ligand A is called inert ligand, since the ligand remains attached in the product, $MA_5(H_2O)$ also.

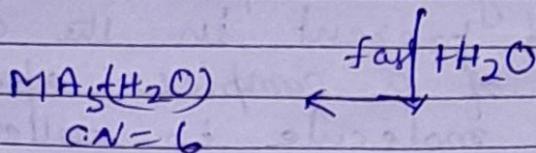
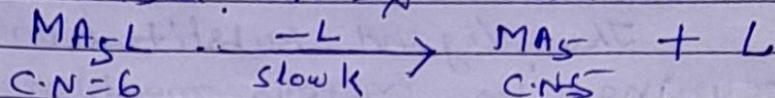
Mechanism of Acid hydrolysis or aquation of different types of octahedral complexes.

- 1) Octahedral complexes in which none of the inert ligand is a π -donor or π -acceptor. Let us consider the acid hydrolysis of MA_5L complex in which A_5 ligands A are inert. None of these ligands are either π -donor or π -acceptor. So,



S_N1 Mechanism \longrightarrow The reaction proceeds

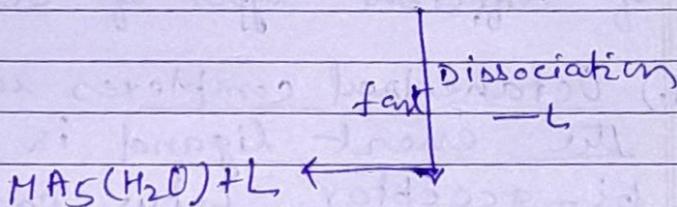
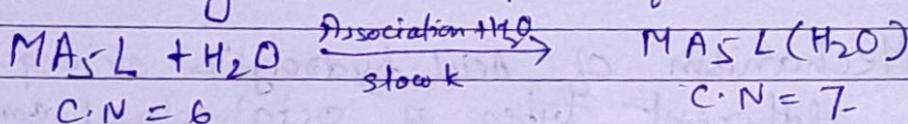
through the following two steps which are based on S_N1 mechanism.



$$\text{Rate of reaction} = k [\text{MA}_5\text{L}]$$

First order reaction because rate depends only on the reactant complex (MA_5L)

S_N2 mechanism - Hydrolysis reaction may also proceed through the following two steps of S_N2 mechanism.



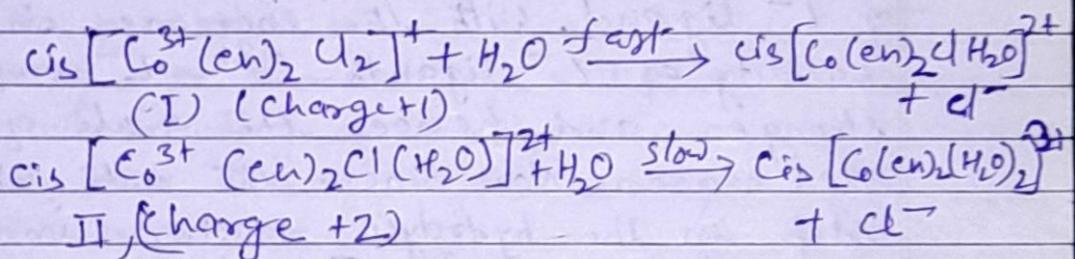
$$\begin{aligned} \text{Rate of reaction} &= k [\text{Complex}] [\text{H}_2\text{O}] \\ &= k [\text{Complex}] \\ &= k [\text{MA}_5\text{L}] \end{aligned}$$

It is clear from above two mechanisms that both the mechanisms rate of hydrolysis reaction is dependent only on the concentration

of the complex MA_5L . So rate of hydrolysis reaction is not able to decide whether the hydrolysis reaction proceeds through S_N1 mechanism or through S_N2 mechanism. So we will have to look to some other factors to decide the type of mechanism. These factors are given below:

1. Charge on the complexes: - It has been observed during the hydrolysis of several octahedral complexes of $Co(III)$ and other metal ions that the rate of hydrolysis of a complex decreases with the increase in the charge on the complex.

Example — The rate of hydrolysis of $cis [Co(en)_2Cl_2]^+$ (I) is hundred times faster than that of $[Co(en)_2Cl(H_2O)]^{2+}$ (II). Thus the hydrolysis of (I) is fast and that of (II) is slow as shown below



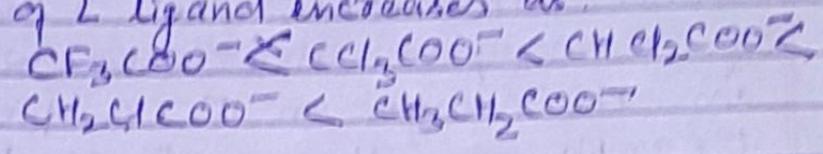
The above observation can be explained S_N1 mechanism of hydrolysis reaction, since the increase in the positive charge on the complex makes the dissociation of the leaving group (Cl^- ion) from the metal ion (Co^{3+}) more difficult and hence the rate hydrolysis becomes slow.

If of the hydrolysis is supposed

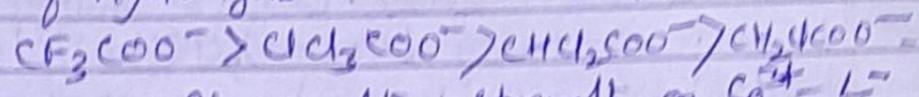
to proceed through S_N^2 mechanism, the rate of hydrolysis would remain unchanged with the increase or decrease in the charge on the complex.

2. Basicity of leaving group L^- — The rate of hydrolysis of complexes, $[Co(NH_3)_5L]^{2+}$ which contain L^- ligands, the rate of hydrolysis of these complexes decreases with the increase of the basicity of L^- ligands.

For example — the rate of hydrolysis of complex $[Co(NH_3)_5L]^{2+}$ Basicity of L^- ligand increases as:



Rate of hydrolysis decreases as:



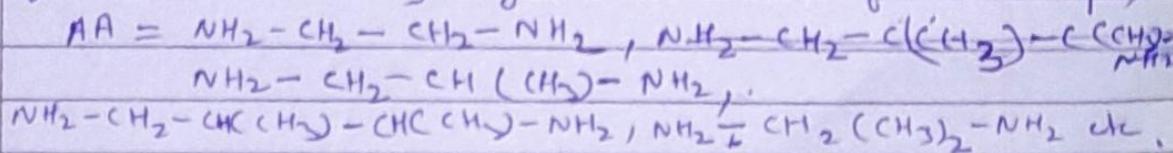
Since the strength of $Co^{3+}-L^-$ bond is directly proportional to the basicity of L^- ligand, with the increase in the basicity of L^- ligands $Co^{3+}-L^-$ bond becomes stronger and hence the rate of hydrolysis decreases. Now since the rate determining step in the hydrolysis reaction involves dissociation of $Co^{3+}-L^-$ bond the hydrolysis reaction proceeds through S_N^1 mechanism.

(3) Inductive effect of the inert group — $[Co(en)_2(A-P)Cl]^{2+} + H_2O \rightarrow [Co(en)_2(A-P)(H_2O)]^{2+} + Cl^-$
 In this reaction rate constants of acid hydrolysis reaction increases

with CH_3 substitution in pyridine. In this reaction A-Py stands for various derivatives of pyridine which are obtained by removing one of the H-atoms of pyridine by CH_3 group. A-Py is an inert ligand since it remains co-ordinated to metal in the complex. The increase in rate constant is due to the inductive effect caused by the increasing CH_3 substitution which results in distorting density towards Co-atom and thus helps the dissociation of Cl^- ion. This again confirms the fact that the acid hydrolysis reaction given below occurs through dissociative S_N mechanism.

4) Steric effects: → Due to the increase in the bulk of the ligand the steric hindrance of the ligand around the central metal ion Co^{3+} also increases, so ~~the~~ another ligand cannot be taken up by the complex, so there is no possibility of $\text{S}_\text{N}2$ mechanism. On the contrary the removal of a ligand will reduce the overcrowding of the ligand around the central metal ion. This gives the evidence of $\text{S}_\text{N}1$ mechanism.

The increase in the bulk of ligand (AA) also increases the value of rate constant for the acid hydrolysis reaction of the complex



Complexes with these are chelated/ octahedral complexes producing 5 and 6 membered chelated ring the value of k for the aquation of 6 membered ring is higher than 5-membered ring through $\text{S}_\text{N}1$ mechanism.