ACID HYDROLYSIS OR AQUATION –

The ligand substitution reaction occuring 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

$$MA_5L + H_2O \longrightarrow MA_5(H_2O) + L$$

is and acid hydrolysis reaction. In this 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 pi-donor or pi-acceptor. Letus consider the acid hydrolysis of MA_5L complex in which ~~As~~ ligands A are inert. None of these ligands ~~is~~ are either pi-donor or pi-acceptor. So,

$$MA_5L + H_2O \longrightarrow MA_5(H_2O) + L$$

S_N^1 Mechanism $\longrightarrow$ The reaction proceeds

through the following two steps which are based on S_N^1 mechanism.

$$\underset{C.N=6}{MA_5L} \xrightarrow[\text{slow } k]{-L} \underset{C.N=5}{MA_5} + L$$

$$\downarrow \text{fast } +H_2O$$

$$\underset{C.N=6}{MA_5(H_2O)}$$

Rate of reaction $= k\,[MA_5L]$

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

S_N^2 mechanism – Hydrolysis reaction may also proceeds through the following two steps of S_N^2 mechanism

$$\underset{C.N=6}{MA_5L} + H_2O \xrightarrow[\text{slow } k]{\text{Association } +H_2O} \underset{C.N=7}{MA_5L(H_2O)}$$

$$\downarrow \text{fast Dissociation } -L$$

$$MA_5(H_2O) + L$$

Rate of reaction $= k\,[\text{Complex}]\,[H_2O]$
$= k\,[\text{Complex}]$
$= k\,[MA_5L]$

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

$$\underset{(I)\ (Charge +1)}{cis[Co^{3+}(en)_2Cl_2]^+} + H_2O \xrightarrow{fast} cis[Co(en)_2Cl(H_2O)]^{2+} + Cl^-$$

$$\underset{II,\ (Charge +2)}{cis[Co^{3+}(en)_2Cl(H_2O)]^{2+}} + H_2O \xrightarrow{slow} cis[Co(en)_2(H_2O)_2]^{3+} + Cl^-$$

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~~ If the hydrolysis is supposed

to proceeds through S_N^2 mechanism, the rate of hydrolysis would remain unchanged with 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:

$$CF_3COO^- < CCl_3COO^- < CHCl_2COO^- < CH_2ClCOO^- < CH_3CH_2COO^-$$

Rate of hydrolysis decreases as:

$$CF_3COO^- > CCl_3COO^- > CHCl_2COO^- > CH_2ClCOO^-$$

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~~ through S_N^1 mechanism.

(3) Inductive effect of the inert group —

$$[Co(en)_2(A\text{-}Py)Cl]^{2+} + H_2O \rightarrow [Co(en)_2(A\text{-}Py)(H_2O)]^{3+} + Cl^-$$

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 confirm the fact that the acid hydrolysis reaction given below occurs through dissociative S_N1 mechanism.

4) Steric effects :— Due to the increase in the bulk bulk of the ligand the steric hindrance of the ligand round the central metal ion Co^{3+} also increases, so the another ligand cannot be taken up by the complex, so there is no possibity of S_N2 mechanism. On the contrary the removal of a ligand will reduce the overcrowding of the ligand round the central metal ion. This gives the evidence of S_N1 mechanism.

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

AA = $NH_2-CH_2-CH_2-NH_2$, $NH_2-CH_2-C(CH_3)-C(CH_3)-NH_2$, $NH_2-CH_2-CH(CH_3)-NH_2$,

$NH_2-CH_2-CH(CH_3)-CH(CH_3)-NH_2$, $NH_2-CH_2(CH_3)_2-NH_2$ etc.

Complexes with these are chelalated/ octahedral complexes producing 5 and 6 membered chelated ring the value of k for the equation g_1 ~~[illegible]~~ 6 membered ring than 5-membered ring through S_N1 mechanism.

Teacher's Signature