PG. Semister I

Core Course-I, INORGANIC CHEMISTRY

UNIT-IV - Reaction Mechanisms of Transition metal complexes

Factors which are used to determine the pathway of Acid Hydrolysis reaction when no Inert Ligand in the complex is pi donor or pi acceptor.

1 Charge on Substrate

- It has been observed that if the positive charge on the reacting complex ion increases, its rate of aquation decreases. eg.

$$cis[Co(en)_2Cl_2]^+ + H_2O \longrightarrow cis[Co(en)_2Cl(H_2O)]^{2+} + Cl^-$$

$$cis[Co(en)_2Cl(H_2O)]^{2+} + H_2O \longrightarrow cis[Co(en)_2(H_2O)_2]^{3+} + Cl^-$$

- The rate of aquation of the first reaction is about 100 times faster than the second reaction.
- The above aquation reaction may occur through S_N1 or S_N2 mechanism
- On the basis of the above, the aquation process occurring through dissociative S_N2 mechanism would be very slow process because as the charge on the substrate increases, the dissociation of the leaving group 'M' from the CMI would become more and more difficult. Hence the formation of a 5-coordinate intermediate would not occur easily.
- If the reaction would proceed through S_N2 mechanism the increase in charge on the substrate would make difference because as the charge on the ion increases, the incoming H_2O Ligand would greatly attracted towards the reacting complex hence promoting the feasibility of formation of a 7 co-ordinate intermediate hence S_N2 mechanism.

Hence the probability of occurence of the aquation reaction through S_N2 mechanism.

2. Strength of M-X bond (where 'X' = Leaving group).

Rate Constants for the Acid Hydrolysis of $[Co(NH_3)_5X]^{2+}$

$[CoCNH_3)_5X]^{2+} + H_2O \longrightarrow [Co(NH_3)_5(H_2O)]^{3+} + X^-$

Leaving Group X^-	Dissociation constant for X- (Kd)	Kaquation.
CF_3COO^-	2.0×10^{-14}	5.5×10^{-3}
CCl_3COO^-	5.0×10^{-14}	5.4×10^{-3}
$CH_2Cl_2COO^-$	2.0×10^{-13}	1.6×10^{-3}
CH_2ClCOO^-	7.1×10^{-12}	0.6×10^{-3}
$CH_3CH_2COO^-$	6.6×10^{-10}	0.3×10^{-3}

Rate of aquation depends on the basicity of the leaving group.

- It is clear from the data that as the basicity of the leaving group X^- increases ; the rate of aquation (removal) of the outgoing ligand and addition of water ligand) goes on decreasing.

Basicity = Electron donating power of inert ligand.

- Strength of the M-X bond is directly proportional to the basicity of the leaving group X, therefore as basicity increases, M-X bond strength increases and aquation decreases.

- Hence it clearly indicates that the aquation reaction of octahedral complexes follows a dissociative S_N1 mechanism.

3 Inductive Effect of Inert Ligand

- The rate of the following aquation reaction varies with the basicity of the inert ligand.

$$[Co(en)_2(subs.py)Cl]^{2+} + H_2O \longrightarrow [Co(en)_2(subs.py)H_2O]^{3+} + Cl^-$$

- As the basicity of the inert ligand increases, it's electron cloud gets shifted towards the metal ion increasing its charge density, hence the heterolytic dissociation of Co-Cl bond would become easier.
- This indicates that the above mentioned reaction would proceed through dissociative S_N1 mechanism.