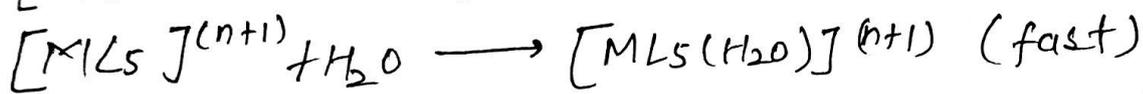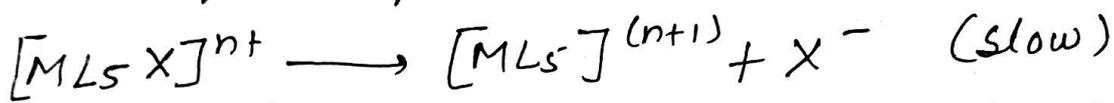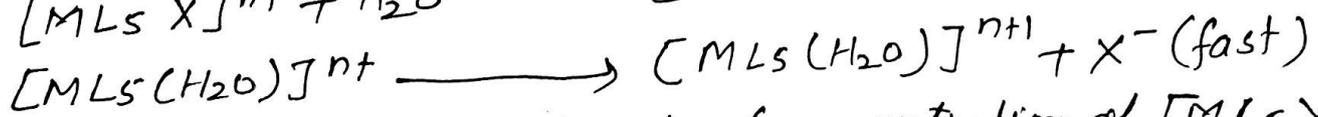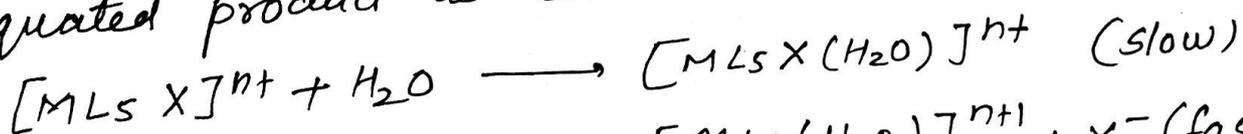# Acid Hydrolysis

A. Mechanism of Acid Hydrolysis when no inert ligand in the complex is a pi donor or pi-acceptor

- In S_N1 (dissociative) mechanism of acid hydrolysis, the rate determining step is the one in which the bond M-X dissociates to produce a 5-coordinate intermediate complex which then immediately reacts with water to form the aquated product as below.

$$[ML_5X]^{nt} \longrightarrow [ML_5]^{(n+1)} + X^- \quad (slow)$$

$$[ML_5]^{(n+1)} + H_2O \longrightarrow [ML_5(H_2O)]^{(n+1)} \quad (fast)$$

Rate of acid hydrolysis = K_1 (concentration of $[ML_5X]^{nt}$

- In S_N2 (associative) mechanism of acid hydrolysis, the rate determining step is the one in which a seven coordinate intermediate complex is formed which then releases the leaving group X' to yield the aquated product as below.

$$[ML_5X]^{nt} + H_2O \longrightarrow [ML_5X(H_2O)]^{nt} \quad (slow)$$

$$[ML_5(H_2O)]^{nt} \longrightarrow [ML_5(H_2O)]^{n+1} + X^- \quad (fast)$$

Rate of acid hydrolysis = K_2 (concentration of $[ML_5X]^{nt}$ and H_2O)

Since H_2O is present in large amount in all reactions. It's concentration can be taken as constant hence Rate of acid hydrolysis = K_2 (concentration of $[ML_5X]^{nt}$ x constant)

Rate of acid hydrolysis = K_2 (concentration of $[ML_5X]^{nt}$

So, As we find that in first case
rate of acid hydrolysis (for S_N1) = K_1 (concentration of $[ML_5X]^{nt}$)

and rate of acid hydrolysis (for S_N2) = K_2 (concentration of $[ML_5X]^{nt}$)

since both in SN^1 and SN^2 pathways, the rate of acid hydrolysis depends on the concentration of the comple $[ML_5X]^{nt}$, therefore. it will be difficult to determine whether acid hydrolysis takes place through SN^1 or SN^2 pathway.

- Therefore following factors would be used to determine the pathway of acid hydrolysis.

1) Charge on substrate
2) Strength of $M-X$ bond
3) Inductive effect of inert ligand
4) Solvation effect

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 SN^1 or SN^2 mechanism
- On the basis of the above, the aquation process occurring through dissociative SN^2 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 SN^2 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 SN^2 mechanism.

Hence the probability of occurence of the aquation reaction through SN^2 mechanism.

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

Rate Constants for the Acid Hydrolysis of $[Co(NH_3)_5 X]^{2+}$

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

Leaving Group X⁻	Dissociation constant for X⁻ (k_d)	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.
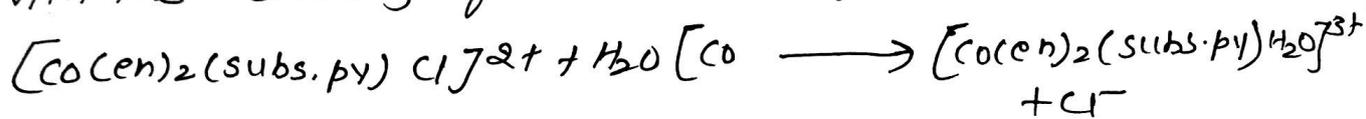
Basicity = Electron donating power of inert ligand.
- Strength of the M—X bond is directly proportional to the basicity of the leaving group x, therefore as basicity increases, M—X bond strength increases and aquation decreases.

- Hence it clearly indicates that the aquation reaction[4] of octahedral complexes follows a dissociative $S_N 1$ mechanism.

3 Inductive Effect of Inert Ligand

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

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

- 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 $S_N 1$ mechanism.
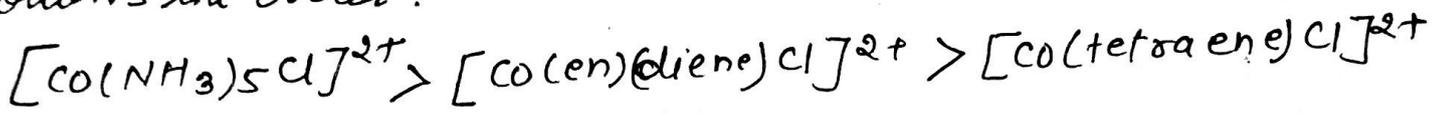
ACID Hydrolysis

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.

4 Solvation Effect

- The rate of aquation of the following complexes follows the order :

$$[Co(NH_3)_5Cl]^{2+} > [Co(en)(diene)Cl]^{2+} > [Co(tetra ene)Cl]^{2+}$$

where   en = ethylenediamine
diene = diethylene triamine
tetraene = tetraethylenepentamine.

- The rate of aquation goes on decreasing with the increase in the extent of chelation. (chelates are much more stable than straight chain complexes).

- The solvation theory helps to explain the above phenomenon which is explained as.

1. The reacting species, the intermediate state and the final product are all   in the form of hydrated species.

2. Hydration of any species decreases its energy and thus causes its stabilization. Therefore greater the hydration of a given species, greater will be its stability.

3. Greater the charge and smaller the size of the species greater will be its hydration hence greater will be its stability.

- The five coordinate intermediate state formed by dissociative S_N1 mechanism would be smaller in size as compared to seven co-ordinate intermediate state formed by associative S_N2 mechanism.

- Since the five coordinate intermediate state is smaller in size, it would undergo greater extent of hydrogen hence would become more stable than the seven co-ordinate intermediate.

- Hence the aquation of octahedral complexes would prefer to follow dissociative S_N1 mechanism rather than associative S_N2 mechanism.

* The presence of complicated ligands like en, diene, tetra ene etc. in place of simple unidentate ligands increases the size of the complex hence causing lesser hydration and affecting the stability of the complex accordingly.
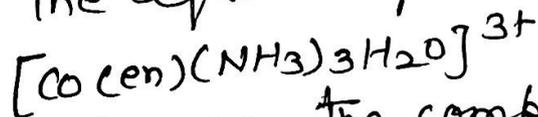
For example

- Consider the aquation of $[Co(NH_3)_5Cl]^{2+}$ and $[Co(en)(NH_3)_3Cl]^{2+}$
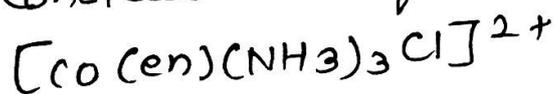
- Then the aquation product of $[Co(NH_3)_5Cl]^{2+}$ is $[Co(NH_3)_5H_2O]^{3+}$ and
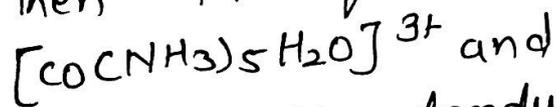
- The aquation product of $[Co(en)(NH_3)_3Cl]^{2+}$ is $[Co(en)(NH_3)_3H_2O]^{3+}$

In this case the complex $[Co(en)(NH_3)_3H_2O]^{3+}$ is a chelate complex. it is larger in size hence will undergo lesser hydration and hence will be lesser stabilized as compared to $[Co(NH_3)_5H_2O]^{2+}$

- Hence the aquation of $[Co(NH_3)_5Cl]^{2+}$ will take place at a great pace than the aquation of $[Co(en)(NH_3)_3Cl]^{2+}$