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.

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

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

Rate of acid hydrolysis = K_1 (concentration of $[ML_5X]^{n+}$)

- 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.

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

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

Rate of acid hydrolysis = K_2 (concentration of $[ML_5X]^{n+}$ 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 $[ML_5X]^{n+}$ x constant)

Rate of acid hydrolysis = K_2 (concentration of $[ML_5X]^{n+}$)

So, As we find that in first case

rate of acid hydrolysis (for S_N1) = K_1(concentration of $[ML_5X]^{n+}$)

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

since both in SN^1 and SN^2 pathways, the rate of acid hydrolysis depends on the concentration of the complex $[ML_5X]^{n+}$, 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