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Topic: Mechanism of Acid Hydrolysis

Reaction Mechanism in Transition Metal Complexes

ACID HYDROLYSIS

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Substitution Reaction in Octahedral Complexes

- Most of the kinetic studies on substitution reactions have been carried out in aqueous medium…

- Consider the following reaction where the ligand **'X'** has to be replaced with the ligand **'Y'** in the coordination sphere.

- Since water is in abundance, the replacement of **'X'** with water will first take place followed by inclusion of **'Y'**. This is called **Aquation** of the complex.

$$[MA_5X]^{n+} + H_2O \longrightarrow [MA_5(H_2O)]^{(n+1)+} + X^-$$

$$[MA_5(H_20)]^{(n+1)+} + Y^- \longrightarrow [MA_5Y]^{n+} + H_20$$

Substitution Reaction in Octahedral Complexes

- The reaction in aqueous medium in which a *water molecule replaces a coordinated ligand from the complex species* is termed as **Aquation reaction or Acid Hydrolysis reaction.**

$$[MA_5X]^{n+} + H_2O \longrightarrow [MA_5(H_2O)]^{(n+1)+} + X^-$$

- However, the reaction in aqueous medium in which the *anion of water molecule i.e. OH^- ion replaces a coordinated ligand from the complex species* is known as **Base Hydrolysis**.

$$[MA_5X]^{n+} + OH^- \longrightarrow [MA_5OH]^{n+} + X^-$$

Acid Hydrolysis

A. Mechanism of Acid Hydrolysis when no Inert Ligand in the complex is a pi donor or pi acceptor

B. Mechanism of Acid Hydrolysis when the inert ligand is a pi donor

C. Mechanism of Acid Hydrolysis when the inert ligand is a pi acceptor

  i. Mechanism when inert pi acceptor ligand is Trans to the leaving group

  ii. Mechanism when inert pi acceptor ligand is Cis to the leaving group

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 Aquation**, 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:

$$[MA_5X]^{n+} \xrightarrow{\qquad\qquad} [MA_5]^{(n+1)+} + X^- \quad \textit{(slow)}$$

$$[MA_5]^{(n+1)+} + H_2O \xrightarrow{\qquad\qquad} [MA_5(H_2O)]^{(n+1)+} \quad \textit{(fast)}$$

Rate of Aquation = k_1 *(concentration of* $[MA_5X]^{n+}$)

Acid Hydrolysis

A. Mechanism of Acid Hydrolysis when no Inert Ligand in the complex is a pi donor or pi acceptor

- In **S_N2** (associative) **mechanism of aquation**, 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

$$\mathbf{[MA_5X]^{n+} + H_2O \longrightarrow [MA_5X(H_2O)]^{n+} \quad \textit{(slow)}}$$

$$\mathbf{[MA_5X(H_2O)]^{n+} \longrightarrow [MA_5(H_2O)]^{(n+1)+} + X^- \quad \textit{(fast)}}$$

Rate of aquation = k_2 (concentration of $[MA_5X]^{n+}$ 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 aquation = k_2 (concentration of $[MA_5X]^{n+}$ x constant)

Rate of aquation = k_2 (concentration of $[MA_5X]^{n+}$)

Acid Hydrolysis

A. Mechanism of Acid Hydrolysis when no Inert Ligand in the complex is a pi donor or pi acceptor

- **S_N1 Rate of Aquation** = k_1 *(concentration of* $[MA_5X]^{n+}$)
- **S_N2 Rate of aquation** = k_2 (concentration of $[MA_5X]^{n+}$)

- Since both in S_N1 and S_N2 pathways, the rate of aquation depends on the concentration of the complex $[MA_5X]^{n+}$, therefore it will be difficult to determine whether aquation would take place through S_N1 and S_N2 pathway.

- Therefore the following factors would be used to determine the above:

1. Charge on Substrate

- It has been observed that if the positive charge on the reacting complex ion increases, it’s 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_N1 mechanism would be a 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.

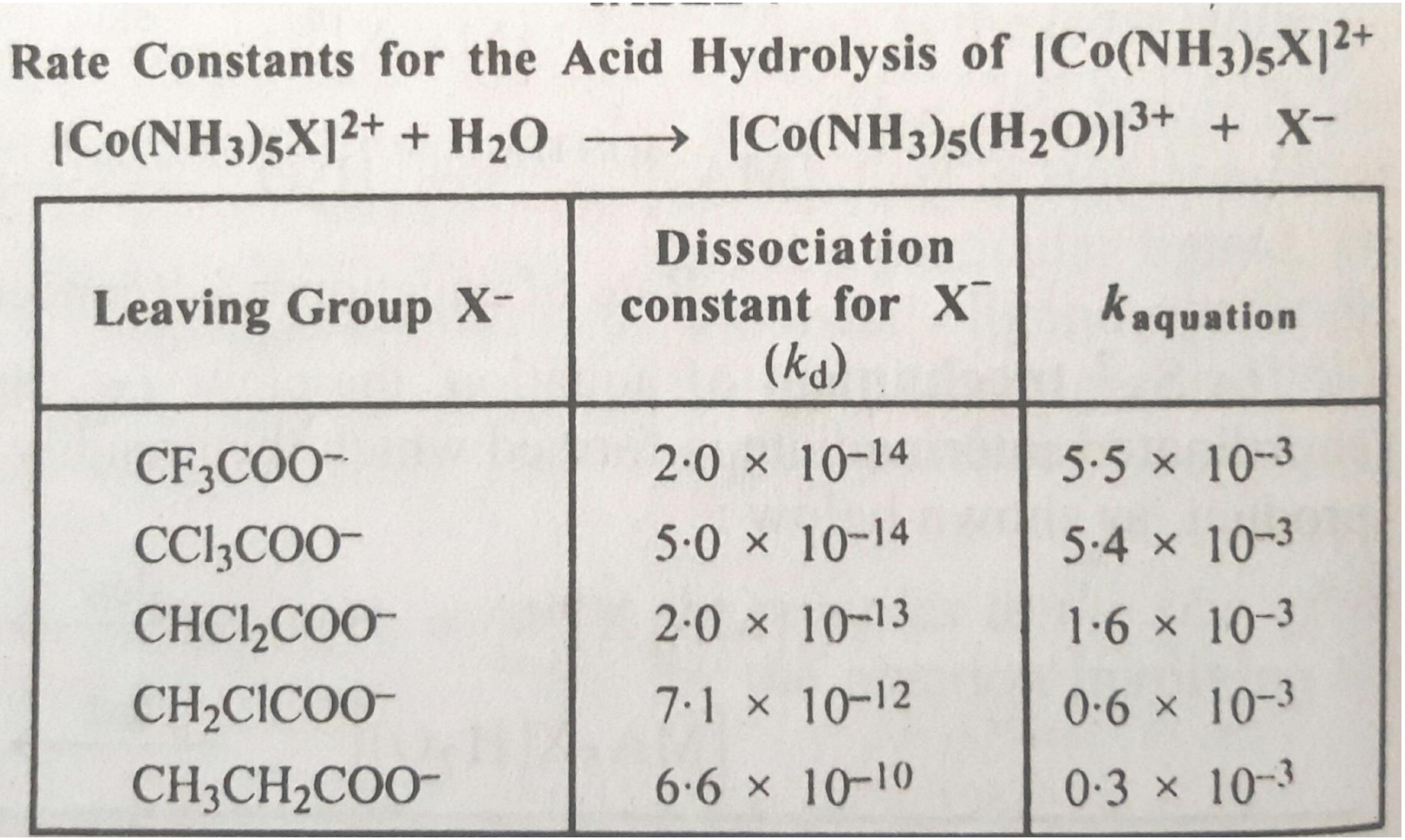
1. Charge on Substrate Contd….

- If the reaction would proceed through **S_N^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 be greatly attracted towards the reacting complex hence promoting the feasibility of formation of a 7 coordinate intermediate hence S_N^2 mechanism.

Hence the probability of occurrence of the aquation reaction through S_N^2 mechanism.

2. Strength of M – X bond

(Where ‘X’ = Leaving group)



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

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

Leaving Group X^-	Dissociation constant for X^- (k_d)	$k_{aquation}$
CF_3COO^-	$2{\cdot}0 \times 10^{-14}$	$5{\cdot}5 \times 10^{-3}$
CCl_3COO^-	$5{\cdot}0 \times 10^{-14}$	$5{\cdot}4 \times 10^{-3}$
$CHCl_2COO^-$	$2{\cdot}0 \times 10^{-13}$	$1{\cdot}6 \times 10^{-3}$
CH_2ClCOO^-	$7{\cdot}1 \times 10^{-12}$	$0{\cdot}6 \times 10^{-3}$
$CH_3CH_2COO^-$	$6{\cdot}6 \times 10^{-10}$	$0{\cdot}3 \times 10^{-3}$

Rate of aquation depends on the basicity of the leaving group X^-

2. Strength of M – X bond Contd…

- 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 the 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.

$$\textbf{[Co(en)}_2\textbf{(subs.py)Cl]}^{2+} + \mathbf{H_2O} \xrightarrow{\hspace{3cm}} \textbf{[Co(en)}_2\textbf{(subs.py)H}_2\textbf{O]}^{3+} + \mathbf{Cl^-}$$

- 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.**

4. Solvation Effect

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

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

  en = ethylenediammine; diene = diethylenetriammine; 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.

4. Solvation Effect contd…

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.

4. Solvation Effect contd…

- The **five coordinate** intermediate state formed by dissociative S_N^1 mechanism would be **smaller in size** as compared to the seven coordinate intermediate state formed by associative S_N^2 mechanism.

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

- Hence the aquation of octahedral complexes would prefer to follow dissociative S_N^1 mechanism rather than associative S_N^2 mechanism.

- **NOTE:** The presence of complicated ligands like en, diene, tetraene, 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.

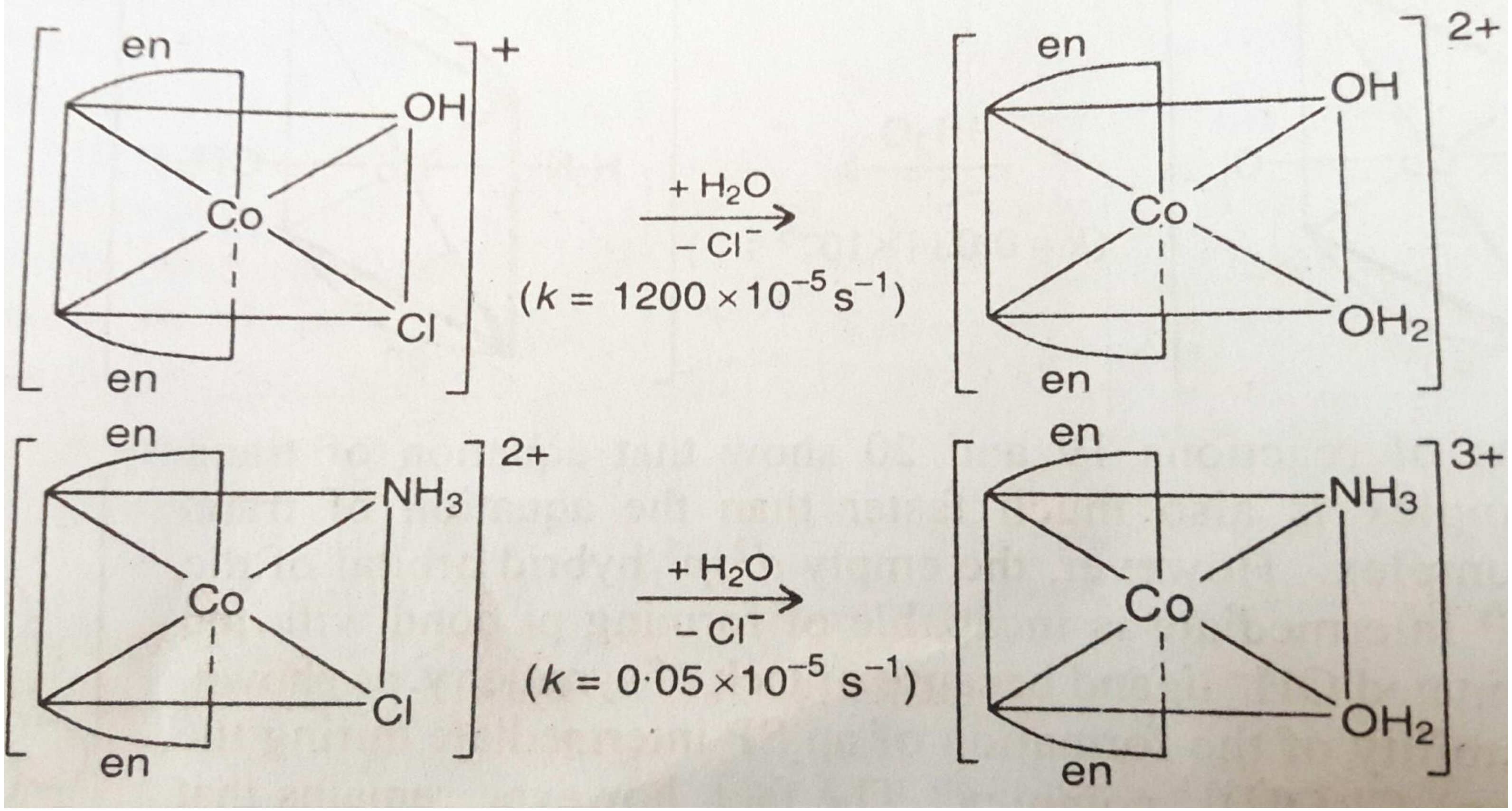
4. Solvation Effect contd…

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

Acid Hydrolysis

B. Mechanism of Acid Hydrolysis when the Inert Ligand is a pi Donor

Let us consider the aquation reactions of **cis complexes** $[Co(en)_2(OH)Cl]^+$ and $[Co(en)_2(NH_3)Cl]^{2+}$ as mentioned below. The rate of aquation of reaction 1 is much greater than that of reaction 2.



Acid Hydrolysis

B. Mechanism of Acid Hydrolysis when the Inert Ligand is a pi Donor

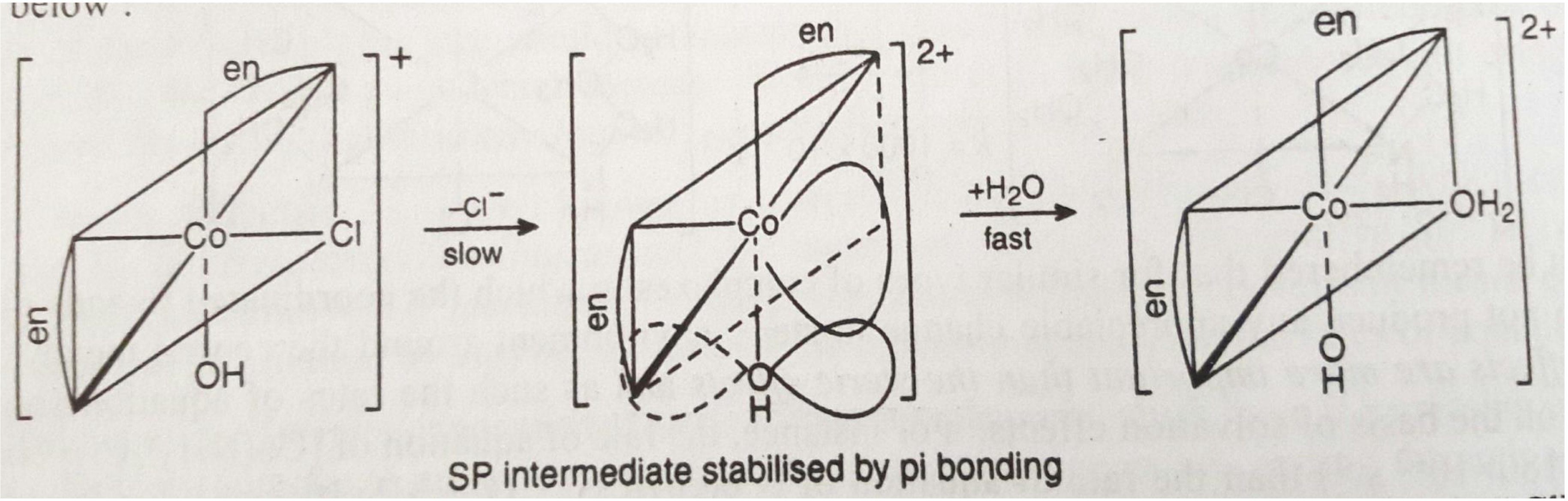
- The difference in the rate of aquation can be explained by taking into consideration, the pi bonding capacity of the OH^- ligand.

- The coordinated **OH^- ligand has filled *p* orbitals** which are capable of forming pi bond with the empty orbitals of the central metal ion. However, in case of **NH_3, no such orbitals are present**, the only lone pair of electron is already used in attaching to the central metal ion through formation of coordinate bond.

- The **Square Pyramidal** (SP) intermediate formed during the aquation of ***cis*** $[Co(en)_2(OH)Cl]^+$ has an ***empty d^2sp^3 hybrid orbital which overlaps with the filled p orbital of coordinated OH^- ligand*** forming a pi bond thus stabilizing the SP intermediate as shown below.

Acid Hydrolysis

B. Mechanism of Acid Hydrolysis when the Inert Ligand is a pi Donor



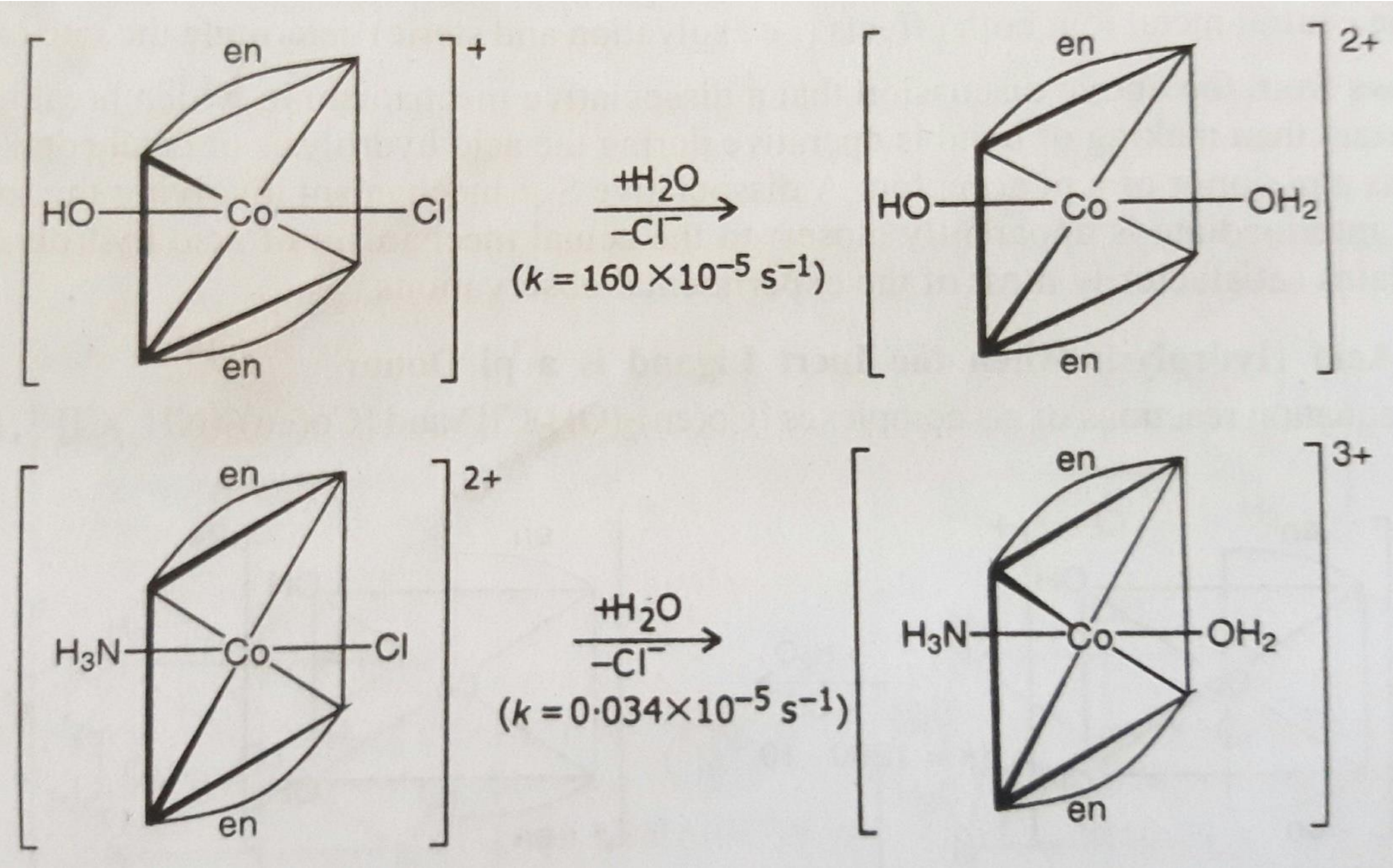
SP intermediate stabilised by pi bonding

- Because of the stabilization of the SP intermediate, the aquation of $[Co(en)_2(OH)Cl]^{2+}$ complex occurs with much greater ease than the aquation of $[Co(en)_2(NH_3)Cl]^{2+}$ complex whose SP intermediate cannot be stabilized because of the absence of pi bond formation between coordinated ligand (NH_3) and central metal ion.

Acid Hydrolysis

B. Mechanism of Acid Hydrolysis when the Inert Ligand is a pi Donor

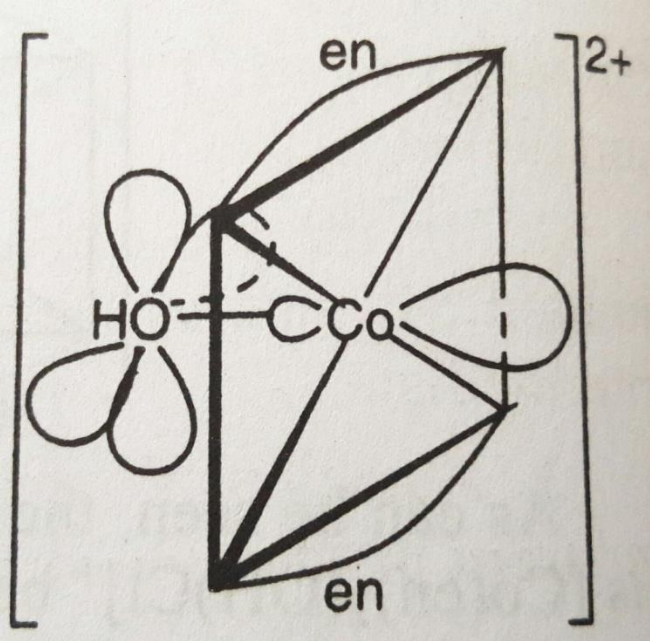
Now let us consider the aquation reactions of **Trans complexes** $[Co(en)_2(OH)Cl]^+$ and $[Co(en)_2(NH_3)Cl]^+$ as mentioned below. The rate of aquation of the two complexes is as follows:



Acid Hydrolysis

B. Mechanism of Acid Hydrolysis when the Inert Ligand is a pi Donor

- The rate constants shows that the aquation of $[Co(en)_2(OH)Cl]^+$ is much faster then the aquation of $[Co(en)_2(NH_3)Cl]^+$.
- ***The empty d^2sp^3 hybrid orbitals of the central metal ion in SP intermediate is incapable of forming pi bond with the filled p orbital of the coordinated OH^- ligand because of <u>lack of symmetry</u>.***



Therefore the aquation of trans complex cannot take place through formation of SP Intermediate Complex species

Acid Hydrolysis

B. Mechanism of Acid Hydrolysis when the Inert Ligand is a pi Donor

- It has been noticed that aquation of such **trans complexes** takes place through formation of **Trigonal Bipyramidal** (TBP) intermediate which can be stabilized by pi bond formation.

- TBP intermediate is stabilized by ***pi bond formed by the overlapping of the empty d orbital of the central metal ion with the filled p orbital of the coordinated OH^- ligand in the TBP intermediate species***.

- This process follows through **S_N1 mechanism** involving the formation of a TBP intermediate. ***(1 equitorial bond breaks changing square base to triangular base)***

- The formation of TBP intermediate from SP intermediate requires some energy since some bond angles have to change from 180^0 to 120^0. However, this increase of energy is more than compensated by the energy released as a result of pi bond formation.

Acid Hydrolysis

B. Mechanism of Acid Hydrolysis when the Inert Ligand is a pi Donor

- Thus in the aquation of **trans** $[Co(en)_2(OH)Cl]^+$ a more stable TBP intermediate is formed rather than a less stable SP intermediate.

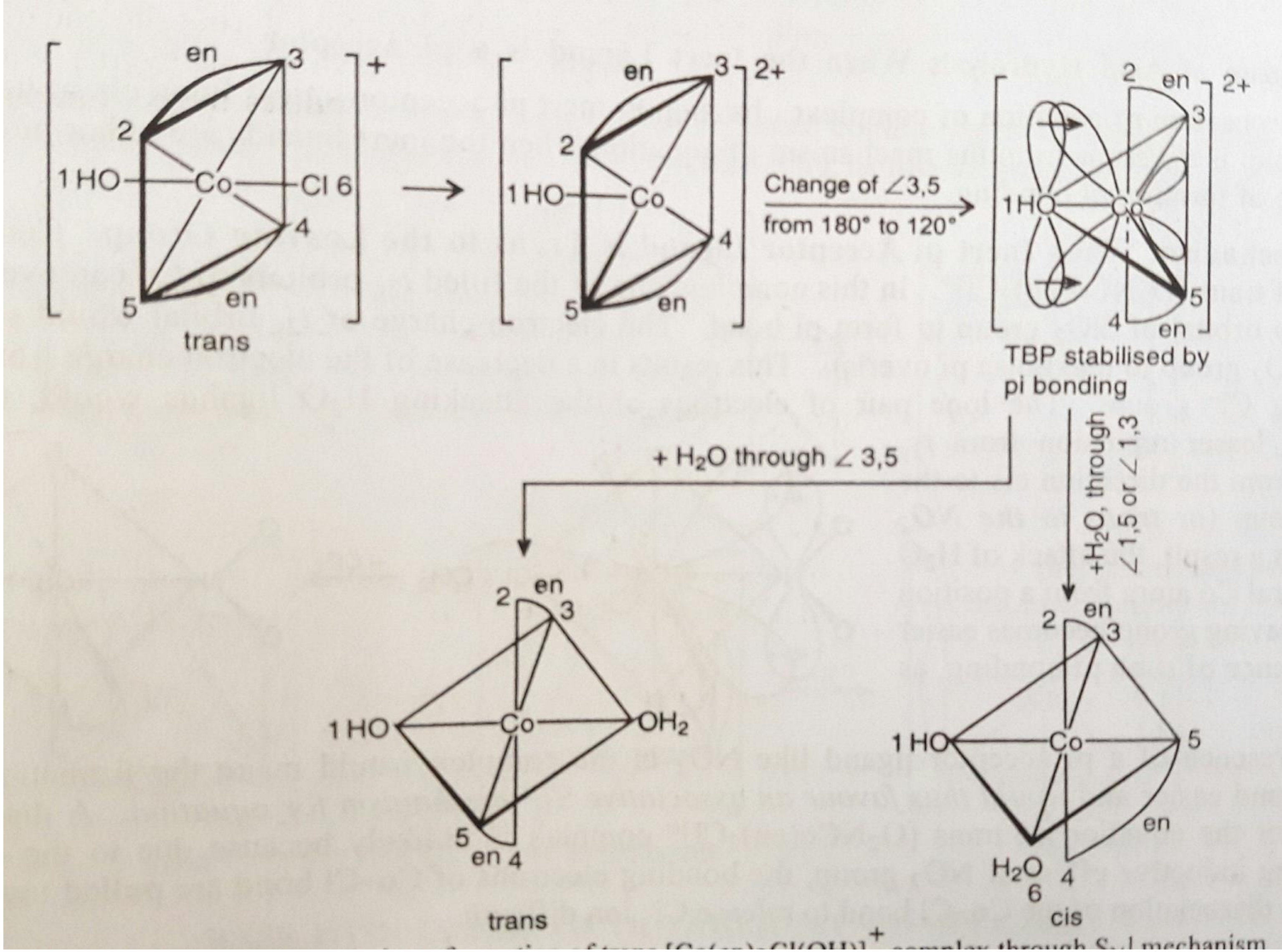
- Depending upon the direction of attack of water molecule, the aquation product of $[Co(en)_2(OH)Cl]^+$ can be a mixture of **cis & trans** isomers.

- If water ligand attacks through angles 3,5; **trans** form is formed. However, if water ligand attacks through angles 1,3 or 1,5, **cis** isomer is formed.

- In all cases, aquation proceeds through a dissociative S_N1 mechanism and not associative S_N2 mechanism.

Acid Hydrolysis

B. Mechanism of Acid Hydrolysis when the Inert Ligand is a pi Donor

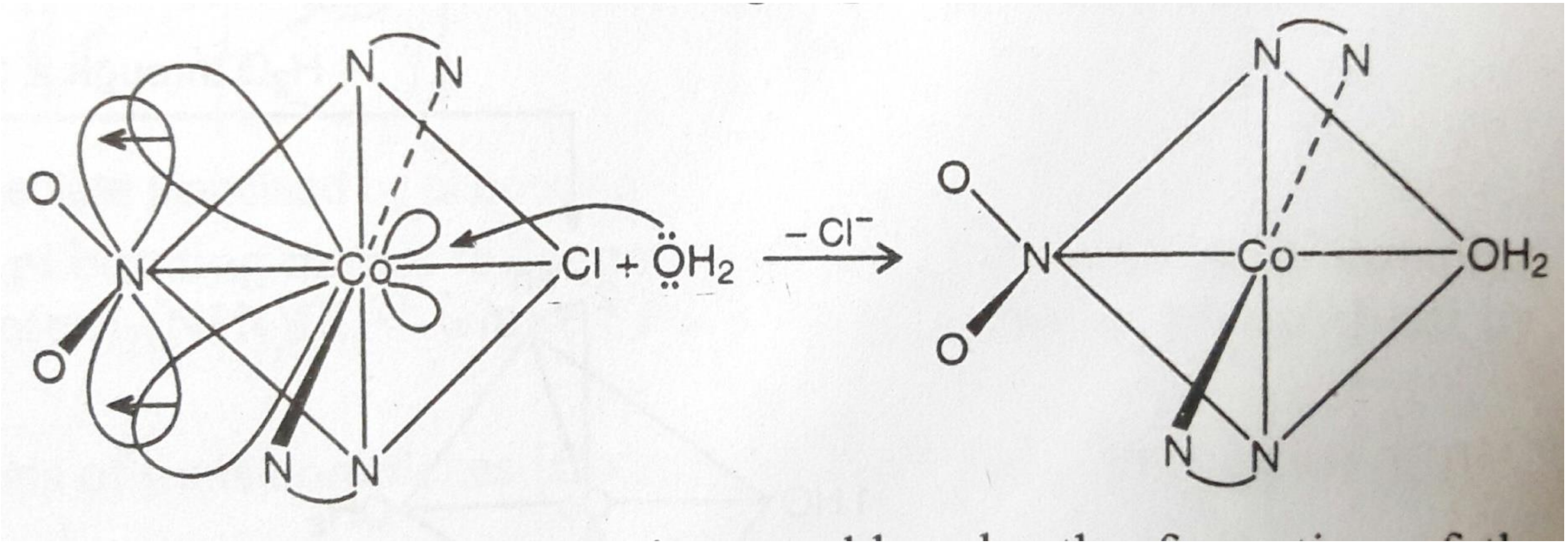


Acid Hydrolysis

B. Mechanism of Acid Hydrolysis when the Inert Ligand is a pi Acceptor

1. Mechanism when inert pi acceptor ligand is trans to the leaving group

Consider the aquation of **trans $[O_2NCo(en)_2Cl]^+$**.



NO_2 is the inert ligand, Cl^- is the leaving group and Co is the CMI.

Acid Hydrolysis

B. Mechanism of Acid Hydrolysis when the Inert Ligand is a pi Acceptor

- One of the filled orbitals of Co CMI overlaps with the vacant p orbital of NO_2 group (inert ligand) forming a pi bond.
- The electron charge shifts towards the NO_2 group to make the pi bond more effective as a result there is decrease in the electron charge from around the Cl^- leaving group hence Cl^- group can leave easily.
- The lone pair of electron of the incoming H_2O ligand would experience lesser repulsion from the electrons of Co from the direction **cis to the leaving group or trans to the inert group**.

Acid Hydrolysis

B. Mechanism of Acid Hydrolysis when the Inert Ligand is a pi Acceptor

- As a result, the attack of H_2O ligand on the Co CMI from a position cis to the leaving group becomes easier in the presence of such pi bonding *(since there would be lesser repulsion between the electrons of Co CMI and lone pair of H_2O ligand)*.

- Therefore the presence of pi acceptor ligands such as NO_2 in the complex would make the formation of the Co – H_2O bond easier and would thus favour an **associative $S_N{}^2$ mechanism for aquation**.

Acid Hydrolysis

B. Mechanism of Acid Hydrolysis when the Inert Ligand is a pi Acceptor

2. Mechanism when inert pi acceptor ligand is cis to the leaving group

- The extent of pi overlap when the inert NO_2 ligand is cis to the leaving group is **much less** as compared to when the inert NO_2 ligand is trans to the leaving group ***(there would be greater repulsion between electrons of Co and incoming ligand)***.

- This would result in less withdrawal of the electrons from the Co CMI hence formation of Co – H_2O bond would not be so easy.

- As a result, the aquation of complex in which the inert pi acceptor ligand is **trans** to the leaving group is **faster and easier** than when the inert pi acceptor ligand is **cis** to the leaving group.

- Consequently aquation of cis $[O_2NCo(en)_2Cl]^+$ is slower than aquation of trans $[O_2NCo(en)_2Cl]^+$.

- However, this aquation would still be faster than the aquation of cis or trans isomer of $[H_3NCo(en)_2Cl]^+$ in which the inert ligand (NH_3) is not a pi acceptor ligand.

Acid Hydrolysis

B. Mechanism of Acid Hydrolysis when the Inert Ligand is a pi Acceptor

Intermediates formed during aquation of complexes containing inert pi acceptor ligands.

- It has been noticed that aquation of cis $[ACo(en)_2X]^{n+}$ always yields 100% cis $[ACo(en)_2H_2O]^{(n+1)+}$ while aquation of trans $[ACo(en)_2X]^{n+}$ always yields 100% trans $[ACo(en)_2H_2O]^{(n+1)+}$.

- A = Inert pi acceptor ligands viz. NO_2, CO, CN^-, etc.
- X = Leaving group viz. Cl^-, etc.

- If the H_2O ligand attacks the Co CMI from a position cis to the leaving group and trans to the inert ligand, it would result in the formation of a **Pentagonal Bipyramidal (PBP) intermediate.**

- The formation of such intermediate is **energetically unfavorable** since in the process of accommodating H_2O ligand, structure changes from SP to PBP, which will cause shifting (decrease in bond angle from 90^0 to 72^0) of four metal – ligand bonds which will cause structural instability.

Acid Hydrolysis

B. Mechanism of Acid Hydrolysis when the Inert Ligand is a pi Acceptor

Intermediates formed during aquation of complexes containing inert pi acceptor ligands.

However if the H_2O ligand and leaving groups are kept at equivalent positions in the complex, an alternate **Octahedral Wedge intermediate** is formed which is energetically more stable and cis and trans aquation products are always obtained.