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LABILE AND INERT COMPLEXES

❖ **A complex which reacts rapidly is called a labile complex. A complex which reacts slowly is an inert complex (or) non-labile complex.**

❖ **These two terms, labile and inert refers to the rates of reactions and not related to the stability or instability of complexes which refer to the thermodynamic character of the complexes to exist under equilibrium.**

❖ **For example, $[Hg(CN)_4]^{2-}$ is thermodynamically very stable, because its formation constant is very high ($\beta = 1 \times 10^{42}$) . But it can react fast with some reagents. i.e., kinetically labile.**

$$[Hg(CN)_4]^{2-} + *CN^- \longrightarrow [Hg(CN)_3(*CN)]^{2-} + CN^- \quad t_{1/2} < 1 \, min$$

❖ **On the other hand, $[Co(NH_3)_6]^{3+}$ is thermodynamically highly unstable (low β value).**

$$Co^{3+} + 6\,NH_3 \rightleftharpoons \left[Co\,(NH_3)_6\right]^{3+} \qquad \beta = 1 \times 10^{-25}$$

❖ **However, this complex can be stored in aqueous solution containing some acid in the lab for several days without any noticeable change. This is possible, because its reaction with water in acid medium is very slow due to high E_a value for the reaction. i.e., this complex is kinetically inert.**

$$\left[Co\,(NH_3)_6\right]^{3+} + 6\,H_3O^+ \longrightarrow \left[Co\,(H_2O)_6\right]^{3+} + NH_4^+ \quad \text{(very slow)}$$

❖ **But, the complex, $[Fe(CN)_6]^{4-}$ ion is thermodynamically stable and also kinetically inert.**

❖ **Complexes of 0.1M that react completely within about one minute should be considered as 'labile' and those that take longer time should be considered as 'inert' –Taube definition**

VBT – Explanation of Lability and Inertness

❖ **According to VBT, the octahedral complexes are of two types, namely, (i) Outer orbital complexes which are formed by using sp^3d^2 hybridization and (ii) Inner orbital complexes which are formed by using d^2sp^3 hybridization.**

❖ **All the Outer-outer complexes are generally labile. This lability is correlated with the weakness of the metal-ligand bond.**

❖ **Thus all the high spin (outer-orbital) complexes of $Cr^{2+}(d^4)$, $Mn^{2+}(d^5)$, $Fe^{2+}(d^6)$ and $Co^{2+}(d^7)$ exchange their ligands rapidly and hence they are labile.**

❖ **But all the inner-orbital complexes are not inert. In the inner-orbital complexes, if all the three t_{2g} levels are filled either singly or doubly, then they are kinetically inert. If it contains at least one vacant orbital, they are kinetically labile.**

❖ **For example, $[V(H_2O)_6]^{3+}(d^2)$ contains 2 e⁻ns in the t_{2g} set and one t_{2g} orbital is vacant. This vacant t_{2g} orbital can be used to accept the e⁻ pair donated by the incoming ligand to form a 7-coordinated intermediate which expels one of the original ligand to get stabilized substituted product. i.e., $[V(H_2O)_6]^{3+}$ is labile.**

$V^{3+}(d^2)$

3d					4S	4p		
↑	↑							

vacant

d^2sp^3-hybridisation
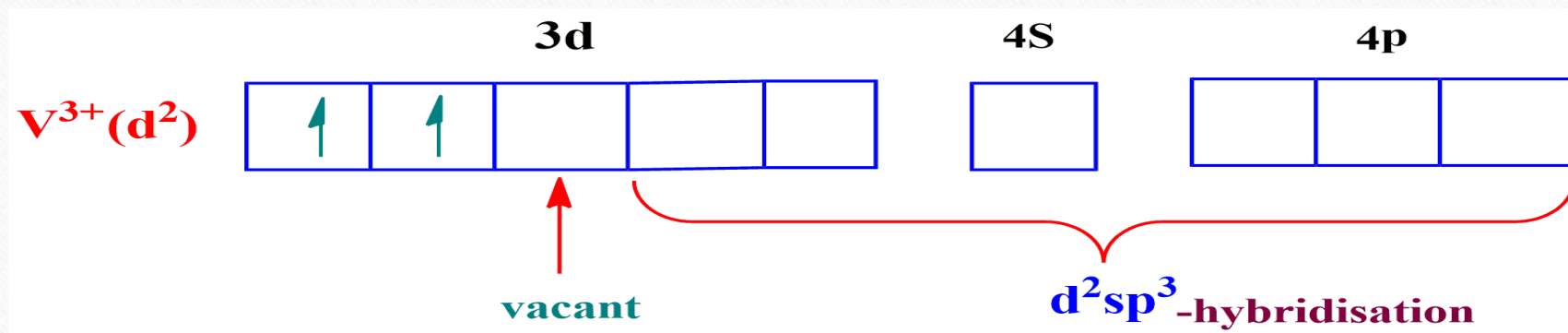
❖ **But in $[Cr(H_2O)_6]^{3+}$ (d^3) there is no d-level vacant to accept an e⁻n pair donated by the incoming ligand, hence this complex is inert.**

Taube's explanation of Lability and Inertness

❖ **According to Taube, the degree of lability or inertness of a transition metal complex can be correlated with d-electronic configuration of the metal ion.**

❖ **If a complex contains e⁻ns in the antibonding e_g^* orbitals, the ligands are expected to be weakly bound and can be easily displaced, hence it is labile. E.g. $[Cr(H_2O)_6]^{2+}$ (d⁴) $t_{2g}^3 e_g^1$ - labile.**

❖ **If the metal contains an empty t_{2g} orbital, it is labile. Because, the four lobes of that vacant orbital corresponds to four directions from which an incoming ligand can approach the complex with little electrostatic repulsion.**

❖ **Therefore it may be concluded that a complex with one or more e_g^* e⁻ns or with fewer than three d- e⁻ns should be labile and that a complex with any other e.c should be relatively inert.**

Table: The Taube's classification of labile and inert complexes

Complex	d-level electronic Configuration	Labile/Inert
$[Sc(H_2O)_6]^{3+}$	d^0	Labile
$[Ti(H_2O)_6]^{3+}$	d^1	Labile
$[V(o\text{-}phen)]^{3+}$	d^2	Labile
$[V(H_2O)_6]^{2+}$	d^3	Inert
$[\overset{..}{Cr}(H_2O)_6]^{2+}$	$d^4 (HS)\ t_{2g}^3 e_g^1$	Labile
$[\overset{..}{Cr}(CN)_6]^{4-}$	$d^4 (LS)\ t_{2g}^4 e_g^0$	Inert
$[\overset{..}{Mn}(H_2O)_6]^{2+}$	$d^5 (HS)\ t_{2g}^3 e_g^2$	Labile
$[\overset{..}{Fe}(CN)_6]^{3-}$	$d^5 (LS)\ t_{2g}^5 e_g^0$	Inert

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$[Fe^{II}(H_2O)_6]^{2+}$	d^6 (HS) $\quad t_{2g}^4 e_g^2$	Labile
$[Fe^{II}(CN)_6]^{4-}$	d^6 (LS) $\quad t_{2g}^6 e_g^0$	Inert
$[Co^{II}(NH_3)_6]^{2+}$	d^7 (HS) $\quad t_{2g}^5 e_g^2$	Labile
$[Co^{III}(NH_3)_6]^{3+}$	d^6 (LS) $\quad t_{2g}^6 e_g^0$	Inert
$[Co^{II}(CN)_6]^{4-}$	d^7 (LS) $\quad t_{2g}^6 e_g^1$	Labile
$[Ni^{II}(H_2O)_6]^{2+}$	d^8 (weak field) $t_{2g}^6 e_g^2$	Moderately labile
$[Ni^{II}(CN)_4]^{2-}$	d^8 (Strong field)	Inert
$[Cu^{II}(H_2O)_6]^{2+}$	$d^9 - t_{2g}^6 e_g^3$	Labile
$[Zn^{II}(H_2O)_6]^{2+}$	$d^{10} - t_{2g}^6 e_g^4$	Labile

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Factors affecting the lability of complexes

1. The type of hybridization of central metal ion (VBT).

2. Electronic configuration of d-orbitals of metal ion.

3. Principal quantum number of d-orbital of metal ion.

4. Charge of the metal ion.

5. Crystal field activation energy (CFAE).

1. The type of hybridization of central metal ion (VBT).

❖ According to **VBT**, the outer orbital complexes which are formed by sp^3d^2 hybridization are generally **labile** due to the **weakness** of the M-L bonds.

(e.g.) High spin complexes of $Cr^{2+}(d^4)$, $Mn^{2+}(d^5)$, $Fe^{2+}(d^6)$ and $Co^{2+}(d^7)$

❖ According to **VBT**, among the Inner orbital complexes which are formed by using d^2sp^3 hybridization, if all the three t_{2g} orbitals are filled singly or doubly, they are inert and if it contains at least one t_{2g} orbital vacant, it is labile. (e.g.) $V^{3+}(d^2)$ –labile; Cr^{3+} (d^3)-inert.

2. Electronic configuration of d-orbitals of metal ion. (Taube explanation)

❖ According to Taube, the degree of lability or inertness of a transition metal complex depends upon the d-electronic configuration of the metal ion.

❖ If a complex contains e⁻ns in the antibonding e_g^* orbitals, then that complex will be labile due to the weakness of M-L bonds. E.g. $[Cr(H_2O)_6]^{2+}$ - d^4 (HS)- $t_{2g}^3 e_g^1$ -labile complex. If the metal in the complex contains an empty t_{2g} orbital, it is labile. (e.g.) $[V(H_2O)_6]^{3+}(d^2)$ -$t_{2g}^2 e_g^0$- one vacant t_{2g} orbital-labile. A complex with any other electronic configuration should be relatively inert. (e.g.) $[Cr(H_2O)_6]^{3+}$ - d^3 -$t_{2g}^3 e_g^0$- inert; $[Fe(CN)_6]^{4-}$ -d^6 (LS)- -$t_{2g}^6 e_g^0$- inert.

3. Principal quantum number of d-orbital of metal ion.

❖ **It is generally observed that lability decreases within a group as the principle quantum number of the d-orbital increases because, the loss of Crystal field stabilization energy (CFSE) increases in the order. (e.g.)** Ni^{2+} - $3d^8$ -labile; Pt^{2+} - $5d^8$-inert.

4. Charge of the metal ion.

❖ **As the positive charge of the metal ion increases, the M-L bond strengthening increases and hence lability decreases. Thus Fe(III) complex is less labile than Fe(II) complex. In non-transition metal complexes also, the same trend is followed. The lability decreases as the oxidation state of the central metal ion increases. (e.g.)**

$$\overset{III}{[AlF_6]^{3-}} > \overset{IV}{[SiF_6]^{2-}} > \overset{V}{[PF_6]^-} > \overset{VI}{[SF_6]} \text{ (Highly inert)}$$

5. Crystal field activation energy (CFAE).

The difference of crystal field stabilization energy of intermediate and reactant is called crystal field activation energy. Crystal field activation energy is one of the important factor that can decide activation barrier of the reaction. Since, activation barrier is directly related to rate of reaction, CFAE can be treated as a deciding factor behind lability and inertness of the complexes.

CFAE = CFSE of the intermediate – CFSE of the reactant complex

According to CFT, if the calculated CFAE is negative or zero, the reacting complex would require less energy for the formation of intermediate and the complexes are more labile. If the if the calculated CFAE is high positive value, the reacting complex would require more energy for its transformation into the intermediate and the complexes are inert.

| d electronic configuration	CFSE for O_h (in Dq)	CFSE for S.P. (in Dq)	CFAE (in Dq)	Labile/ Inert
d^1	-4.0	-4.5	-0.5	Labile
d^2	-8.0	-9.0	-1.0	Labile
d^3	-12.0	-9.9	+2.1	Inert
d^4	-16.0	-14.4	+1.6	Inert

Types of Intermediates formed during S_N1 and S_N2

1. S_N1 Mechanism

Considering the substitution reaction of octahedral complexes,

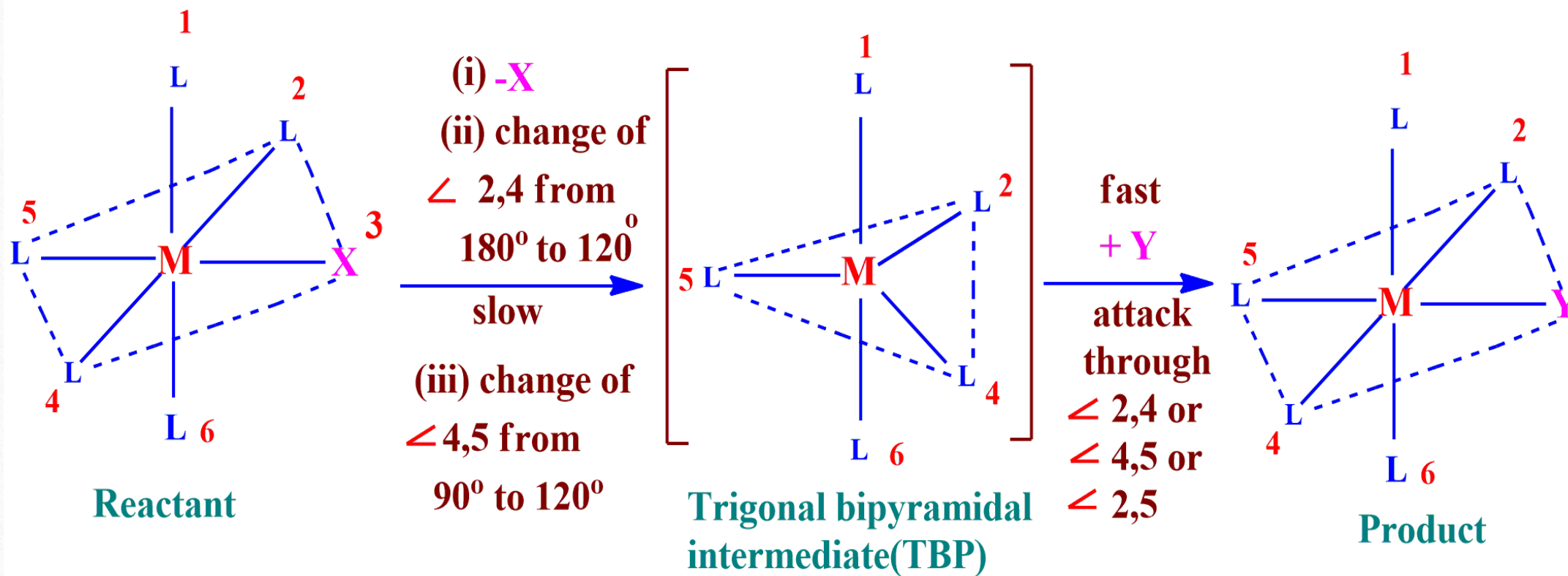$$[ML_5X] + Y \longrightarrow [ML_5Y] + X$$

If the reaction proceeds through dissociative S_N1 mechanism, two types of intermediates are formed.
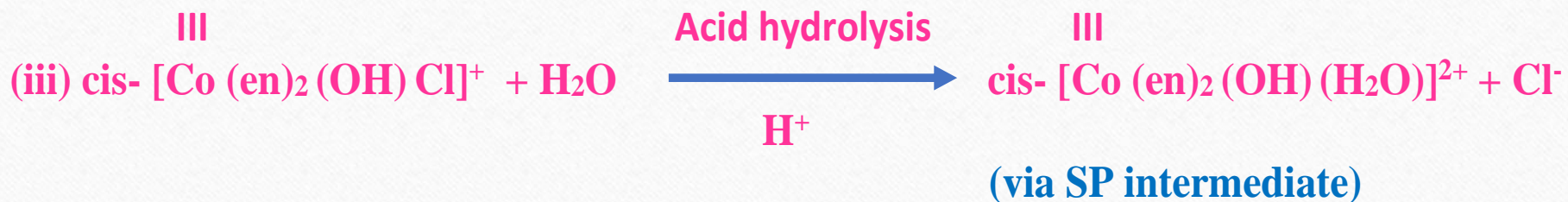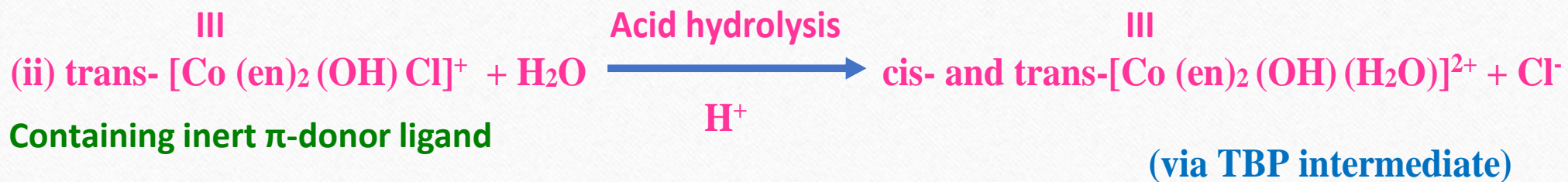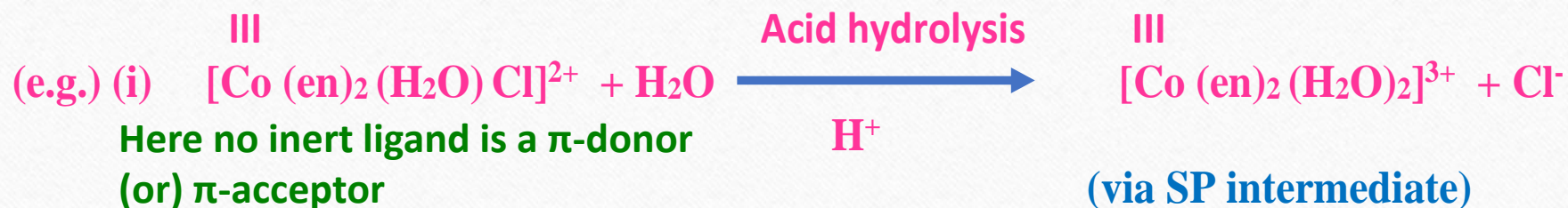
(i) In the first type, the bond M-X dissociates causing least disturbance to the remaining intermediate $[ML_5]$ which has Square pyramidal geometry. This intermediate is then attacked by the nucleophile, Y to produce $[ML_5Y]$ product.
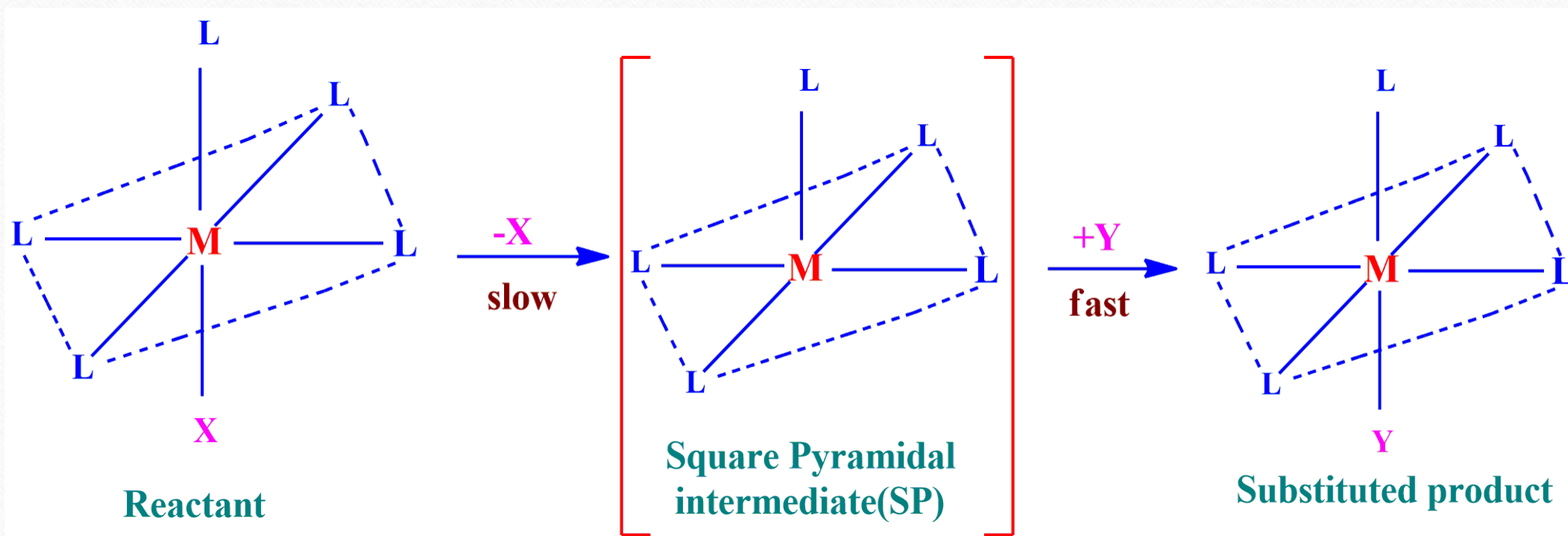
(ii) In the **second type**, the bond **M-X** dissociates and the **remaining intermediate** **[ML$_5$]** immediately **adjusts the bond angles** to produce a **trigonal bipyramidal intermediate** which is then attacked by **Y** to produce **[ML$_5$Y]** product as given below.

(i) **-X**
(ii) change of ∠ 2,4 from 180° to 120°
slow
(iii) change of ∠4,5 from 90° to 120°

fast
+ Y
attack through
∠ 2,4 or
∠ 4,5 or
∠ 2,5

Reactant

Trigonal bipyramidal intermediate(TBP)

Product

❖ It is evident that the **formation of TBP** intermediate involves the **movement of at least two M-L bonds** whereas **no such movement is required** during the formation of **a SP intermediate.**

❖ So, the **S_N1 reactions** proceed normally through the **more stable SP** intermediate unless a **TBP** intermediate is so much **stabilized by** L➙M **π–bonding** that it becomes more stable than the **SP** intermediate. In that case only, **S_N1 reaction** proceeds through a **TBP intermediate.**

$$\text{(e.g.) (i)} \quad [\overset{III}{Co} (en)_2 (H_2O) Cl]^{2+} + H_2O \xrightarrow[\quad H^+ \quad]{\text{Acid hydrolysis}} [\overset{III}{Co} (en)_2 (H_2O)_2]^{3+} + Cl^-$$

Here no inert ligand is a π-donor (or) π-acceptor

(via SP intermediate)

$$\text{(ii) trans-} [\overset{III}{Co} (en)_2 (OH) Cl]^+ + H_2O \xrightarrow[\quad H^+ \quad]{\text{Acid hydrolysis}} \text{cis- and trans-}[\overset{III}{Co} (en)_2 (OH) (H_2O)]^{2+} + Cl^-$$

Containing inert π-donor ligand

(via TBP intermediate)

$$\text{(iii) cis-} [\overset{III}{Co} (en)_2 (OH) Cl]^+ + H_2O \xrightarrow[\quad H^+ \quad]{\text{Acid hydrolysis}} \text{cis-} [\overset{III}{Co} (en)_2 (OH) (H_2O)]^{2+} + Cl^-$$

(via SP intermediate)

2. S$_N$2 Mechanism

❖ **If the substitution reaction proceeds through an associative S$_N$2 mechanism, there are again two types of intermediates are possible.**

(i) The first type of intermediate is formed if the nucleophile Y attacks through one of the edges of the octahedron which leads to the formation of a Pentagonal bipyramidal(PBP) intermediate.
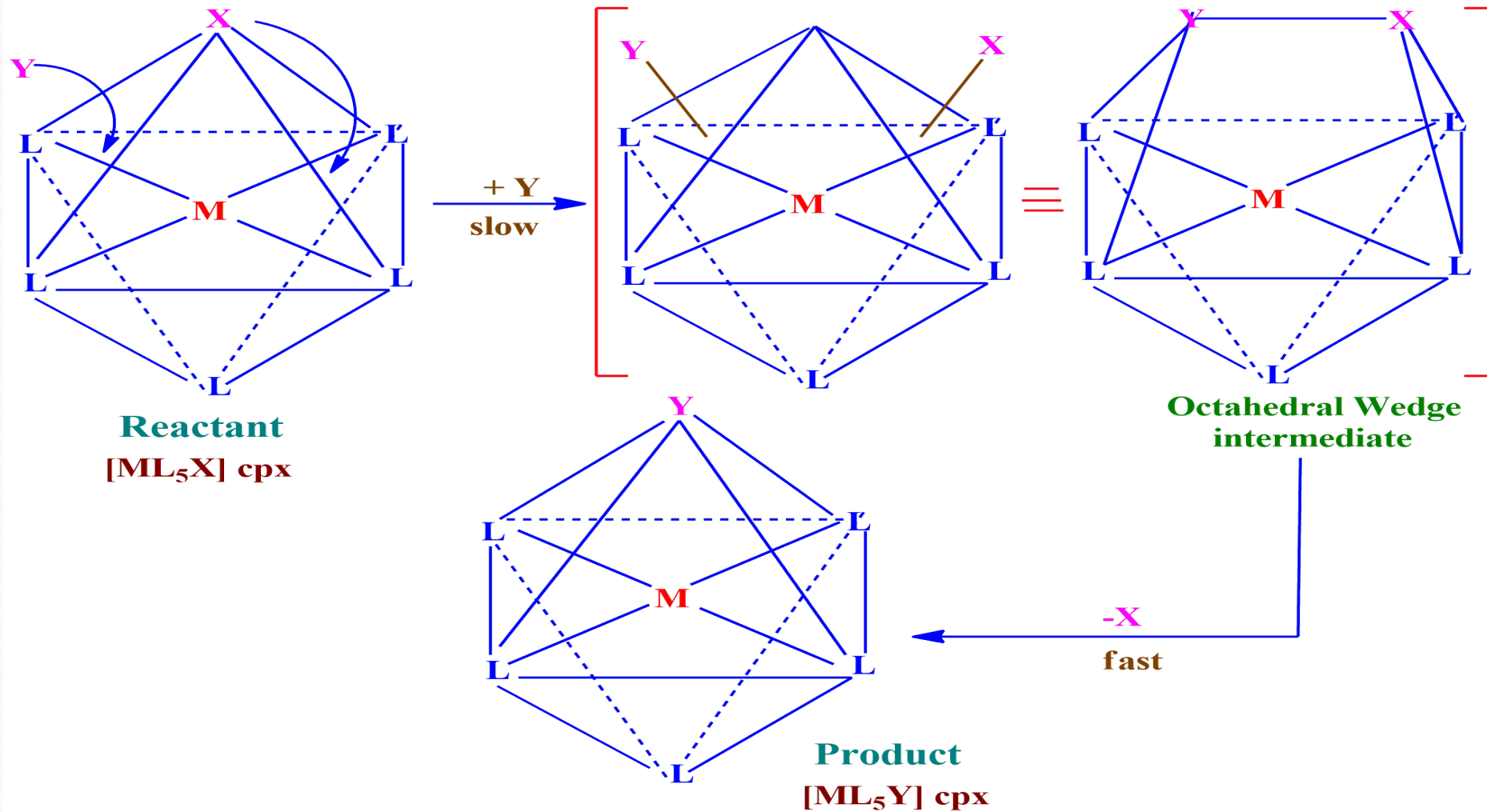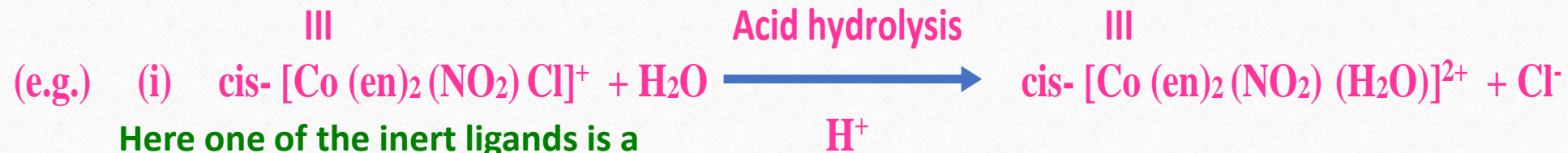

Reactant
[ML$_5$X] cpx

Pentagonal bipyramidal
intermediate

Product
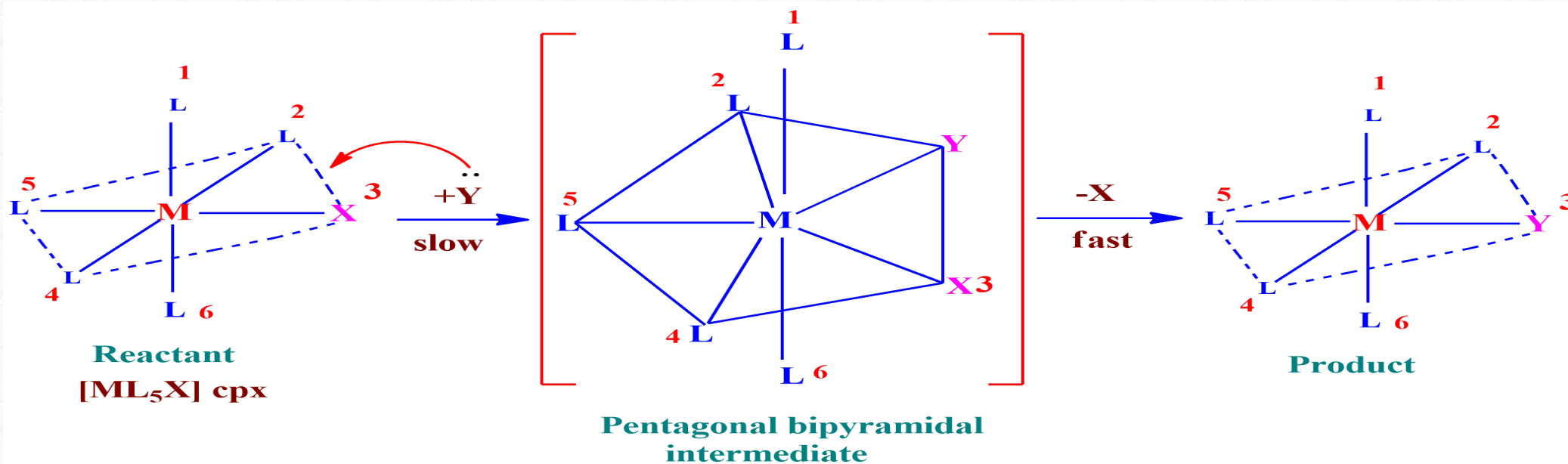
❖ **The formation of PBP intermediate requires the movement of at least four ligands to adjust the nucleophile, Y. The ligand-ligand repulsions also increase the energy of PBP intermediate because, the decrease in L-M-L bond angles (from 90° to 72°) brings the electron pairs of M-L bonds nearer to one another in this intermediate. So, energetically, the formation of PBP intermediate is unfavourable.**

    (ii)   The second type of intermediate is formed if the nucleophile Y attacks through the middle of one of the triangular faces of the octahedron. As soon as Y starts approaching M, the outgoing ligand X starts moving towards the middle of opposite triangular face so that the 'octahedral Wedge'(OW) intermediate formed has both X and Y ligands in equivalent positions.
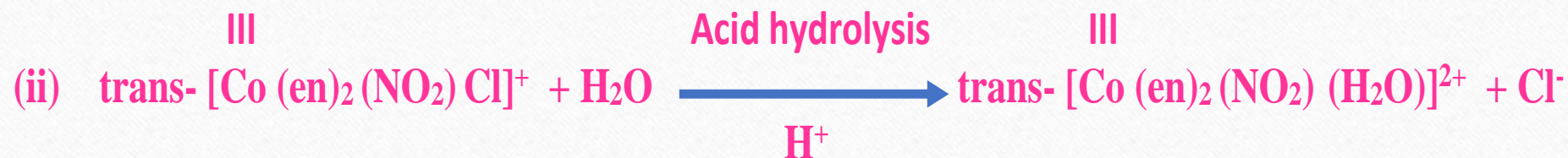
❖ **The formation of an OW intermediate requires minimum movement of ligands and the ligand-ligand repulsions are less than that in PBP intermediate. Thus, the OW intermediate require less energy for its formation than the PBP intermediate.**

❖ **Hence, S$_N$2 reactions proceed through OW intermediate than a PBP intermediate. The formation of OW intermediate is shown below.**

Reactant
[ML$_5$X] cpx

Octahedral Wedge intermediate

Product
[ML$_5$Y] cpx

(e.g.) (i) cis- $[\overset{III}{Co} (en)_2 (NO_2) Cl]^+ + H_2O$ $\xrightarrow[H^+]{\text{Acid hydrolysis}}$ cis- $[\overset{III}{Co} (en)_2 (NO_2) (H_2O)]^{2+} + Cl^-$

Here one of the inert ligands is a π-acceptor ligand

(ii) trans- $[\overset{III}{Co} (en)_2 (NO_2) Cl]^+ + H_2O$ $\xrightarrow[H^+]{\text{Acid hydrolysis}}$ trans- $[\overset{III}{Co} (en)_2 (NO_2) (H_2O)]^{2+} + Cl^-$

(Both the S_N2 reactions proceed through OW intermediate)

Substitution reactions of octahedral complexes

❖ **Because of the inertness of Co(III) (d^6 -t_{2g}^6 e_g^0) and Cr(III) (d^3 -t_{2g}^3 e_g^0) complexes, the majority of kinetic studies has been done with these complexes. They undergo substitution reactions at convenient rates(measurable speed).**
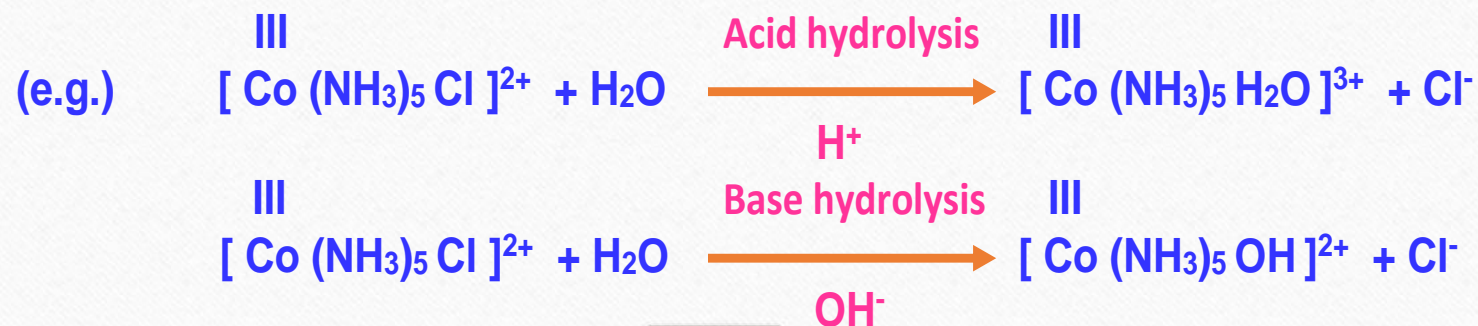
❖ **Studies on substitution reactions of octahedral complexes have been largely limited to two types of reactions.**

(i) Replacement of coordinated water by anions (X^-)- Anation reaction:

$$\text{(e.g.)} \quad [\overset{III}{\text{Co}}(NH_3)_5(H_2O)]^{3+} + Br^- \longrightarrow [\overset{III}{\text{Co}}(NH_3)_5Br]^{2+} + H_2O$$
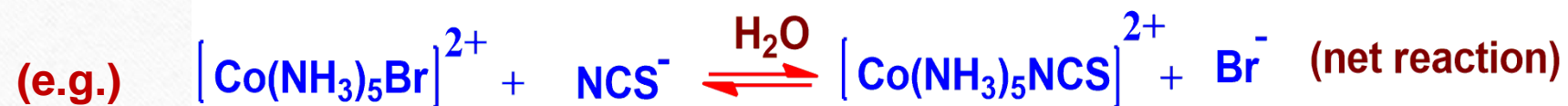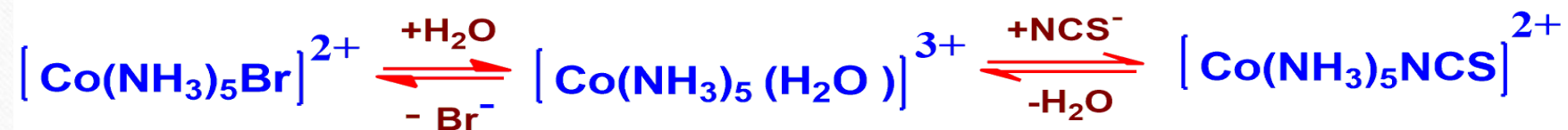
(ii) Solvolysis (Hydrolysis)

❖ **Since majority of octahedral substitution reactions have been carried out in aqueous solution, hydrolysis is a more appropriate term. Hydrolysis reactions have been done under both acidic and basic conditions.**

$$\text{(e.g.)} \quad [\overset{III}{\text{Co}}(NH_3)_5Cl]^{2+} + H_2O \xrightarrow[\quad H^+ \quad]{\text{Acid hydrolysis}} [\overset{III}{\text{Co}}(NH_3)_5H_2O]^{3+} + Cl^-$$

$$[\overset{III}{\text{Co}}(NH_3)_5Cl]^{2+} + H_2O \xrightarrow[\quad OH^- \quad]{\text{Base hydrolysis}} [\overset{III}{\text{Co}}(NH_3)_5OH]^{2+} + Cl^-$$

❖ **Octahedral substitution reactions involving direct exchange of two anions is uncommon (common in square planar complexes). Instead, an Octahedral complex first loose a coordinated anion by H_2O molecule (hydrolysis reaction) and then replace the newly coordinated H_2O (solvent) molecule by the other anion (Anation reaction)**

(e.g.) $$[Co(NH_3)_5Br]^{2+} + NCS^- \overset{H_2O}{\underset{}{\rightleftharpoons}} [Co(NH_3)_5NCS]^{2+} + Br^- \quad \text{(net reaction)}$$

❖ **The above substitution reaction takes place in two stages in aqueous solution.**

$$[Co(NH_3)_5Br]^{2+} \overset{+H_2O}{\underset{-Br^-}{\rightleftharpoons}} [Co(NH_3)_5(H_2O)]^{3+} \overset{+NCS^-}{\underset{-H_2O}{\rightleftharpoons}} [Co(NH_3)_5NCS]^{2+}$$
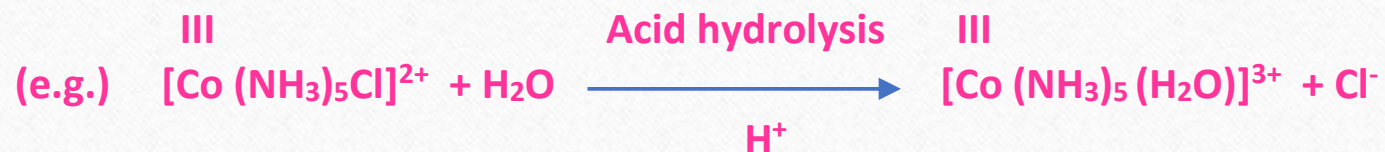
❖ **Both the steps occur by dissociative (I_d) mechanism.**

ACID HYDROLYSIS (or) AQUATION REACTIONS OF OCTAHEDRAL Co(III) AMMINE COMPLEXES

❖ **The reaction in aqueous medium in which a water molecule replaces a coordinated ligand from the reacting complex is termed as aquation reaction or acid hydrolysis.**

Mechanism of acid hydrolysis when no inert ligand in the complex is a π-donor or a π-acceptor

$$\text{(e.g.)} \quad \overset{III}{[Co\,(NH_3)_5Cl]^{2+}} + H_2O \xrightarrow[H^+]{\text{Acid hydrolysis}} \overset{III}{[Co\,(NH_3)_5\,(H_2O)]^{3+}} + Cl^-$$

If the above aquation reaction takes place through dissociative mechanism (D or I_d), the mechanism and rate equation is:

$$[Co\ (NH_3)_5\ Cl]^{2+} \xrightarrow{\text{Slow}} [Co\ (NH_3)_5]^{3+} + Cl^-$$

Five coordinated intermediate

$$[Co\ (NH_3)_5]^{3+} + H_2O \xrightarrow{\text{Fast}} [Co\ (NH_3)_5\ (H_2O)]^{3+}$$

Rate of aquation = $k_1 [Co\ (NH_3)_5\ Cl]^{2+}$ where k_1 is the first order rate constant

If the above aquation reaction takes place through **associative mechanism** (**A or I$_a$**), the mechanism and rate equation is:

$$[Co\ (NH_3)_5\ Cl]^{2+} + H_2O \xrightarrow{\text{Slow}} [Co\ (NH_3)_5\ Cl\ (H_2O)]^{2+}$$

Seven coordinated intermediate

$$[Co\ (NH_3)_5\ Cl\ (H_2O)]^{2+} \xrightarrow{\text{Fast}} [Co\ (NH_3)_5\ (H_2O)]^{3+} + Cl^-$$

Rate of aquation = $k_2 [Co\ (NH_3)_5\ Cl]^{2+} [H_2O]$ since H_2O is present in large excess

$$r = k_2 [Co\ (NH_3)_5\ Cl]^{2+} \cdot \text{constant} = k_2' [Co\ (NH_3)_5\ Cl]^{2+}$$

where k_2' is the pseudo first order rate constant

❖ **Thus, both dissociative and associative path ways of aquation predict that the rate of the reaction would be dependent only on the concentration of the reactant complex. So, kinetic studies(rate laws) cannot predict the mechanism of aquation reactions.**

❖ **However, many other factors that affect the rate of aquation reactions suggest a dissociative S_N1 mechanism for aquation reactions. These factors are,**

(i) Effect of charge on the reactant complex

❖ **It has been observed that increase in positive charge on the reacting species decreases its rate of aquation. For example, the rate of aquation of $[\overset{III}{Co}(NH_3)_4\,Cl_2]^+$ is about 100 times faster than that of $[\overset{III}{Co}(NH_3)_5\,Cl]^{2+}$**

$$[\overset{III}{Co}(NH_3)_4\,Cl_2]^+ + H_2O \xrightarrow[H^+]{fast} [\overset{III}{Co}(NH_3)_4\,Cl_2\,(H_2O)]^{2+} + Cl^- \text{ (100 times faster)}$$

$$[\overset{III}{Co}(NH_3)_5\,Cl]^{2+} + H_2O \xrightarrow[H^+]{slow} [\overset{III}{Co}(NH_3)_5\,(H_2O)]^{3+} + Cl^-$$
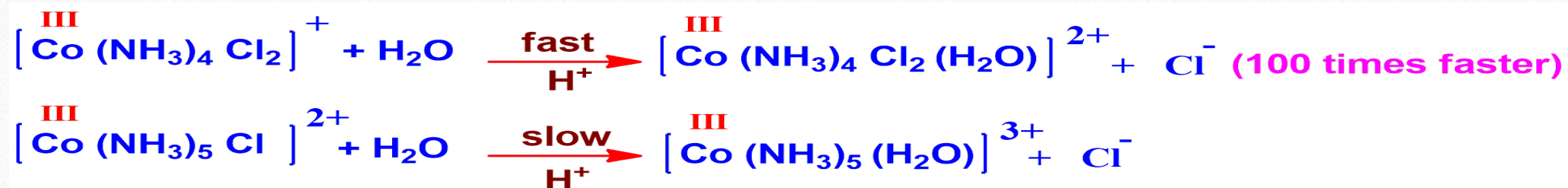
❖ **The above observations favour a dissociative S_N1 path since the increase in positive charge results in the larger electrostatic attraction between the positive metal ion and the negative leaving ligand which makes the dissociation of leaving group from metal ion more difficult in the rate determining step. Thus, resulting in the slower reaction rate by this mechanism.**

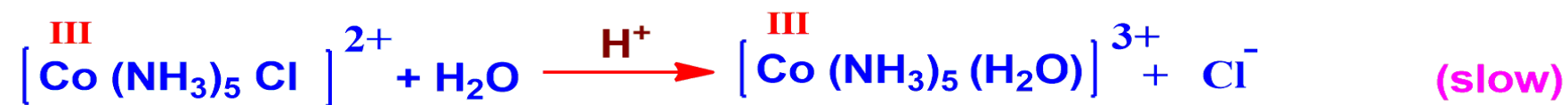## (ii) Effect of M-X bond strength (Effect of leaving group)

The observed rate constants for the acid hydrolysis of $[Co(NH_3)X]^{2+}$ is,

Leaving group, X^-	$k_{aquation}$
CF_3COO^-	5.5×10^{-3}
CCl_3COO^-	5.4×10^{-3}
$CHCl_2COO^-$	1.6×10^{-3}
CH_2ClCOO^-	0.6×10^{-3}
$CH_3CH_2ClCOO^-$	0.3×10^{-3}

❖ **It is evident from the data that the rate of aquation goes on decreasing with increase in the basicity of the leaving group.**

❖ **Since the strength of M-X bond is directly proportional to the basicity of the group, X^-, it can be inferred that the rate determining step involves the dissociation of M-X bond which clearly supports a dissociative S_N1 mechanism for the aquation of octahedral complex.**

(iii) Steric effects of inert ligands:

❖ **Steric crowding** on the reactant complex **increases the rate** of aquation reaction. For example, the rate of the reaction in which water replaces Cl^- in $[Co(MeNH_2)_5 Cl]^{2+}$ takes place **22 times faster** than the same reaction for $[Co(NH_3)_5 Cl]^{2+}$

$$[\overset{III}{Co} (NH_3)_5 Cl]^{2+} + H_2O \xrightarrow{H^+} [\overset{III}{Co} (NH_3)_5 (H_2O)]^{3+} + Cl^- \quad \text{(slow)}$$

$$[\overset{III}{Co} (MeNH_2)_5 Cl]^{2+} + H_2O \xrightarrow{H^+} [\overset{III}{Co} (MeNH_2)_5 (H_2O)]^{3+} + Cl^- \quad \text{(22 times faster)}$$

❖ **The greater steric crowding of methylamine ligand favour the dissociation of the Cl^- ligand easier in the rate determining step. Thus steric effects supports dissociative mechanism for aquation of octahedral complexes.**

❖ **On the other hand, if the reaction proceeded by an associative mechanism, the order of rates would be opposite; because the increased steric crowding retards the approach of incoming ligand in the rate determining step and slow down the reaction.**

(iv) Inductive effect of inert ligands :

❖ It has been found that rate of aquation increases with basicity of inert ligands. This is because, greater the basicity or electron donating power(+I) of the inert ligand, greater would be the accumulation of negative charge on the central metal ion which result in easier heterolytic dissociation of M-X bond. This in turn supports a dissociative mechanism.
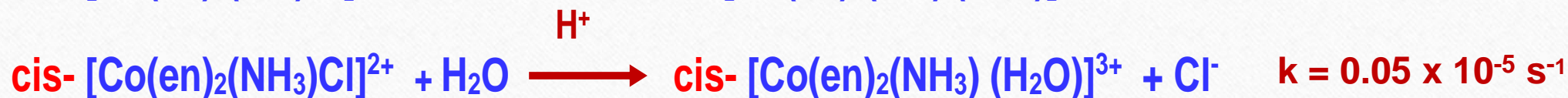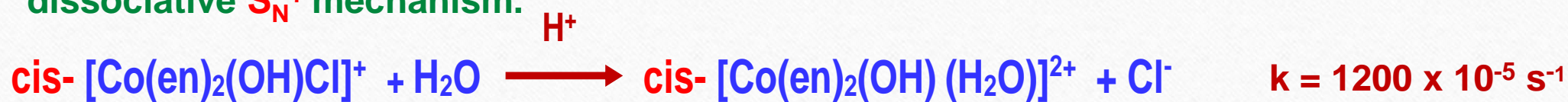
Rate constants of acid hydrolysis of $[Co(en)_2(x\text{-}py)Cl]^{2+}$ at 50°C	
x-py	k (s^{-1})
pyridine	1.1×10^{-1}
3-methyl pyridine	1.3×10^{-1}
4-methyl pyridine	1.4×10^{-1}
4-methoxy pyridine	1.5×10^{-1}

❖ **Thus,** a dissociative (D or I_d) mechanism involving square pyramidal intermediate is proposed for the acid hydrolysis of octahedral Co(III) complexes when no inert ligand is a π-donor or π-acceptor.

Mechanism of acid hydrolysis when the inert ligand in the complex is a π-donor.

❖ **When inert ligands,** such as NH_2^-, OH^-, Cl^-, Br^-, SCN^-, etc., which contains filled p-orbitals are present in the reactant complex, the rates of hydrolysis of such complexes are directly related to the L ➝ M π-bonding capability of the inert ligand.

(i) For example, the rate constants for the aquation reactions of cis- $[Co(en)_2(OH)Cl]^+$ and cis- $[Co(en)_2(NH_3)Cl]^{2+}$ are as follows: This acid hydrolysis reactions undergoes by dissociative S_N1 mechanism.

$$\text{cis- }[Co(en)_2(OH)Cl]^+ + H_2O \xrightarrow{H^+} \text{cis- }[Co(en)_2(OH)(H_2O)]^{2+} + Cl^- \qquad k = 1200 \times 10^{-5} \text{ s}^{-1}$$

$$\text{cis- }[Co(en)_2(NH_3)Cl]^{2+} + H_2O \xrightarrow{H^+} \text{cis- }[Co(en)_2(NH_3)(H_2O)]^{3+} + Cl^- \qquad k = 0.05 \times 10^{-5} \text{ s}^{-1}$$

❖ **The rate of aquation of cis- [Co(en)$_2$(OH)Cl]$^+$ is being much faster (24000 times) than that of cis- [Co(en)$_2$(NH$_3$)Cl]$^{2+}$. This wide difference in rate constants cannot be accounted by the difference in basicities of OH$^-$ and NH$_3$ ligands and the difference in the charges of the complexes alone.**

❖ **The coordinated OH$^-$ ligand has filled p orbitals which are capable of forming π-bond (L→M) with empty orbitals of the central metal ion in the five coordinated SP transition state. The coordinated NH$_3$ ligand has no such orbital; the only lone pair in NH$_3$ is already used up in (L $\xrightarrow{\sigma}$ M) coordination.**

❖ **The square pyramidal intermediate formed during the aquation of cis- [Co(en)$_2$(OH)Cl]$^+$ has an empty d^{2}sp^3 hybrid orbital of the central metal ion which can overlap laterally with a filled p orbital of the inert OH$^-$ ligand, forming a π- bond (L→M), that stabilizes the SP intermediate.**

Cis-reactant complex

slow
- Cl⁻

**Square pyramidal intermediate
stabilized by L→M pi bonding**

fast
+ H₂O

Cis-product complex
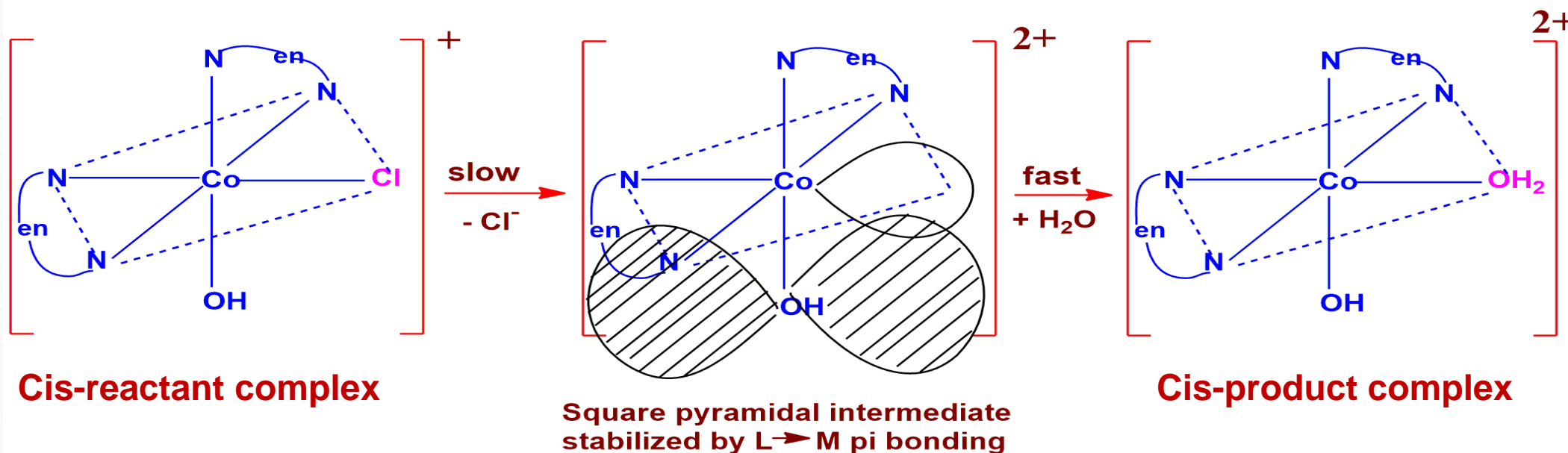
❖ **Thus the stabilization of SP intermediate through π- bonding makes the aquation of cis-[Co(en)₂(OH)Cl]⁺ complex much easier than that of cis- [Co(en)₂(NH₃)Cl]²⁺ .**

(ii) Now considering the aquation reactions of trans complexes of [Co(en)₂(OH)Cl]⁺ and [Co(en)₂(NH₃)Cl]²⁺, the rates are as follows:

trans- $[Co(en)_2(OH)Cl]^+$ + H_2O $\xrightarrow{H^+}$ cis- & trans- $[Co(en)_2(OH)(H_2O)]^{2+}$ + Cl^- k = 160 x 10^{-5} s^{-1}

trans- $[Co(en)_2(NH_3)Cl]^{2+}$ + H_2O $\xrightarrow{H^+}$ trans - $[Co(en)_2(NH_3)(H_2O)]^{3+}$ + Cl^- k = 0.034 x 10^{-5} s^{-1}
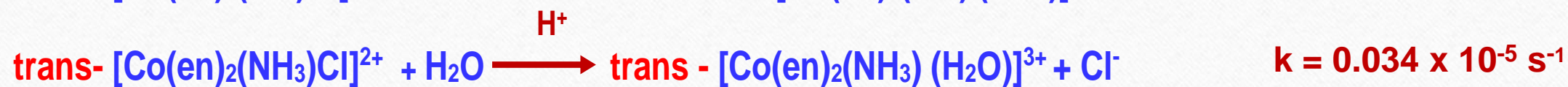
❖ **The above rate constants shows that aquation of trans- $[Co(en)_2(OH)Cl]^+$ is much faster than that of trans- $[Co(en)_2(NH_3)Cl]^{2+}$. This acid hydrolysis reactions undergoes by dissociative S_N1 mechanism.**

❖ **In the case of trans complexes, the formation of a stable SP intermediate is ruled out due to the lack of symmetry to form L→M π-bond. However, a TBP intermediate can be stabilized by L→ M π-bonding involving the overlapping of empty d orbital of the metal with filled p orbital of the coordinated OH⁻ ligand.**
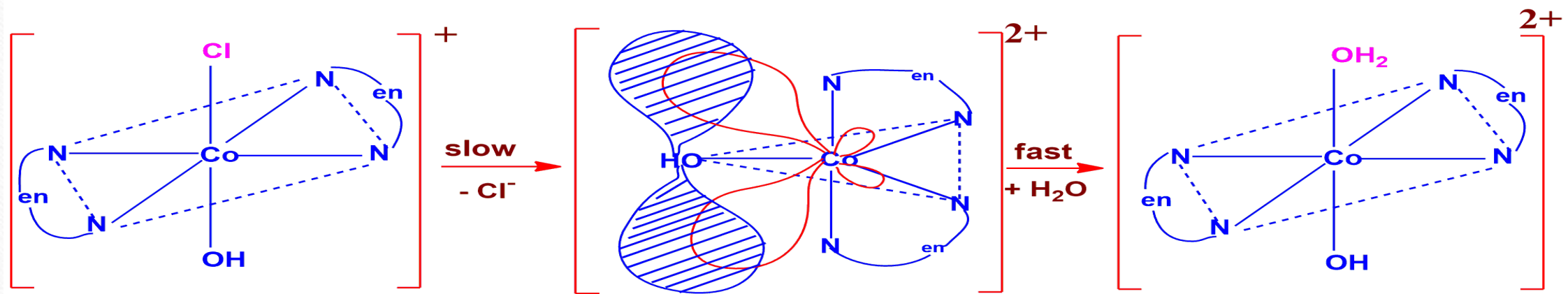
Trans reactant

slow
- Cl⁻

Trigonal bipyramidal
intermediate stabilized
by L→M pi bonding

fast
+ H₂O

Trans product

Cis product

❖ **The formation of a TBP requires some energy since some bond angles have to change from 90⁰ to 120⁰. The extra energy required is more than compensated by the energy released as a result of pi bonding. The TBP intermediate can explain the formation of mixture of cis and trans products during the aquation of trans complexes.**
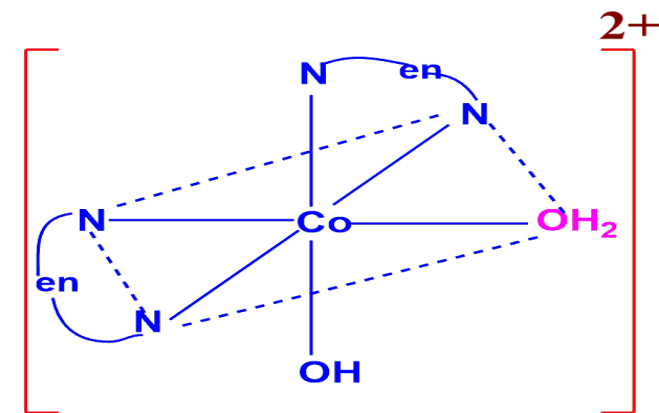
❖ Thus a π-bonded **TBP** intermediate formed during the aquation of **trans-[Co(en)$_2$(OH)Cl]$^+$**, explains the faster rate compared to that of **trans-[Co(en)$_2$(NH$_3$)Cl]$^{2+}$**, which is incapable of forming M ⟶ L π-bonding.

❖ The formation of TBP intermediate requires more energy than SP intermediate. That is why the rate of hydrolysis of cis-complex is more than that of trans complex.

Mechanism of acid hydrolysis when the inert ligand in the complex is a π-acceptor.

Rate of aquation of complexes containing π-acceptor inert ligands such as NO$_2^-$, CN$^-$, CO, etc.

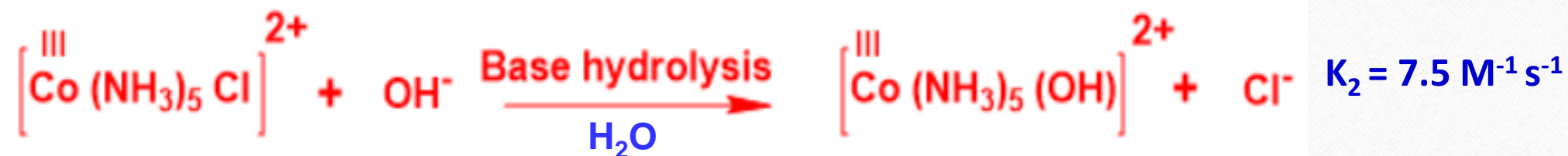| Complex	Rate constant		
trans-[Co(en)$_2$(NO$_2$)Cl]$^+$	98 X 10^{-5}	⟹	100% trans product
cis-[Co(en)$_2$(NO$_2$)Cl]$^+$	11 X 10^{-5}	⟹	100% cis product

❖ **In the presence of a π-acceptor ligand like NO_2^- in the complex, it withdraws electron density from the filled t_{2g} orbital of Co(III) through M→L π –bonding (i.e. by the lateral overlap of filled t_{2g} orbital of Co(III) with an empty p orbital of NO_2^- group), which results in a decrease of the electron charge from around the leaving Cl^- group. This makes the dissociation of Co-Cl bond to release Cl^- difficult.**

❖ **So, the dissociative S_N^1 path is ruled out. But, this situation facilitates the formation of the Co- OH_2 bond easier and thus favour an associative S_N^2 mechanism for aquation.**

❖ **The decrease of the electron density around the leaving Cl^- group also facilitates the attacking of the incoming nucleophile from the side of Cl^- group. So, aquation of cis-complex always yields 100% cis-product and aquation of trans-complex always yields 100% trans-product**

❖ **This type of aquation reactions proceeds through Octahedral Wedge(OW) intermediate.**

Dr. S.K

❖ **The extent of M → L π-overlap when NO₂⁻ group is cis to the leaving group is less than when it is trans to the leaving group. Consequently, the aquation of cis isomers would be slower than the trans complex.**


Trans complex
M → L pi bonding

Octahedral Wedge
intermediate

100% Trans product
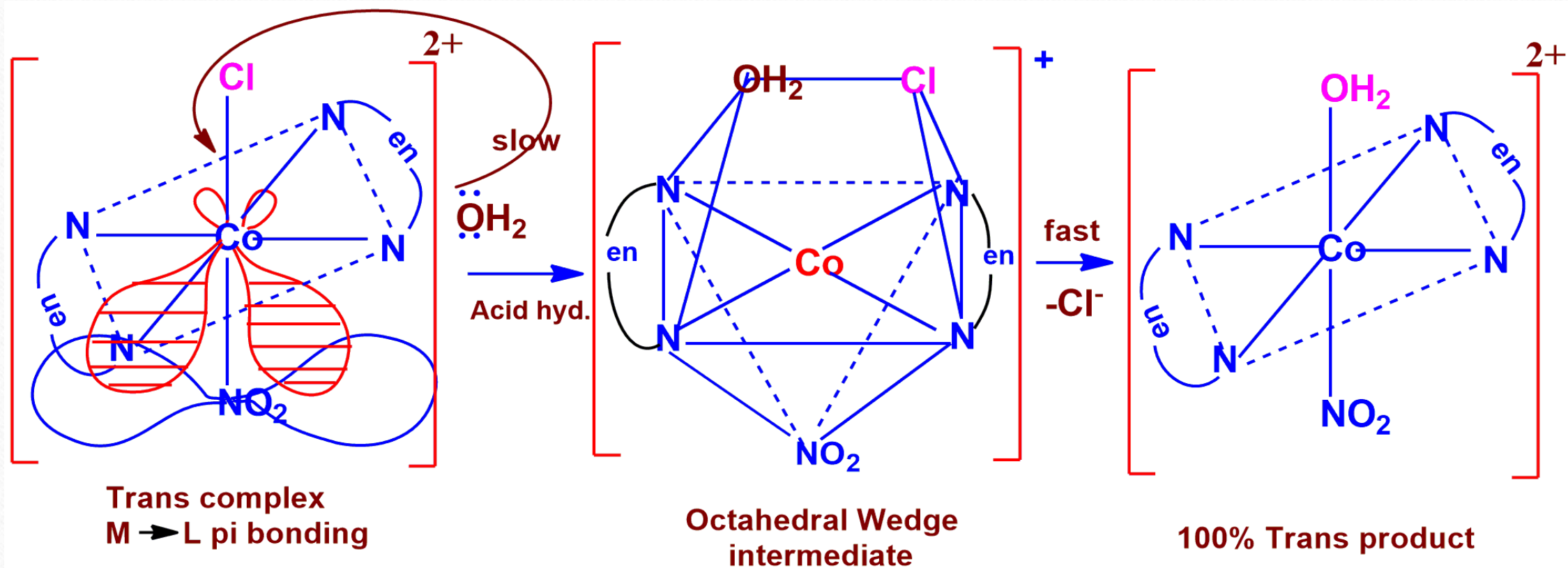
MECHANISM OF BASE HYDROLYSIS OF OCTAHEDRAL SUSTITUTION REACTIONS – SN_1CB MECHANISM
(SUBSTITUTION NUCLEOPHILIC UNIMOLECULAR CONJUGATE BASE MECHANISM)

❖ **The reactions in which a hydroxo complex is formed by the replacement of a ligand by OH⁻ group are called base hydrolysis. Hydrolysis of Octahedral complexes can be greatly accelerated by OH⁻ ions when the coordinated inert ligands possess acidic protons(e.g. NH_3). For example,**
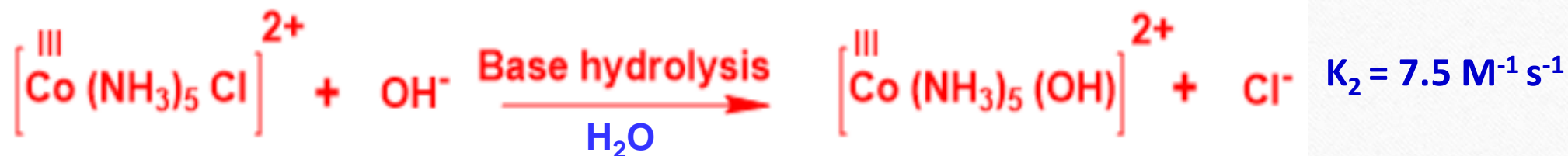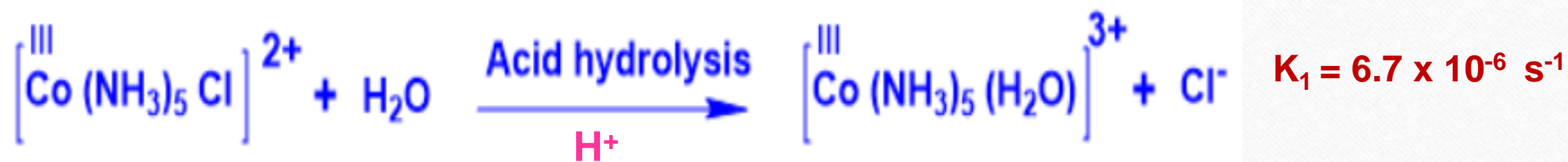
$$[\overset{III}{Co}(NH_3)_5\,Cl]^{2+} + OH^- \xrightarrow[\text{H}_2\text{O}]{\text{Base hydrolysis}} [\overset{III}{Co}(NH_3)_5\,(OH)]^{2+} + Cl^- \qquad K_2 = 7.5\ M^{-1}\,s^{-1}$$

Two important observations of base hydrolysis are:

(i) Kinetic studies have shown that the rate law is overall second order with

$$\text{Rate} = k \left[\overset{\text{III}}{Co}(NH_3)_5 Cl \right]^{2+} \left[OH^- \right]$$
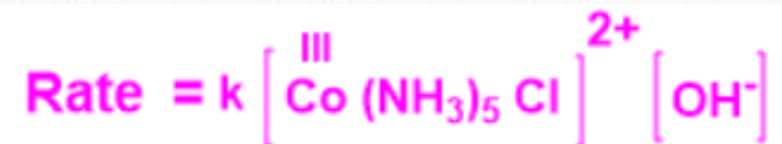
(ii) The rate constant for the hydrolysis of $[Co(NH_3)_5Cl]^{2+}$ in basic solution is

million times more faster than that in acidic solution.

$$\left[\overset{\text{III}}{Co}(NH_3)_5 Cl \right]^{2+} + H_2O \xrightarrow[\text{H}^+]{\text{Acid hydrolysis}} \left[\overset{\text{III}}{Co}(NH_3)_5 (H_2O) \right]^{3+} + Cl^- \qquad K_1 = 6.7 \times 10^{-6} \ s^{-1}$$

$$\left[\overset{\text{III}}{Co}(NH_3)_5 Cl \right]^{2+} + OH^- \xrightarrow[\text{H}_2\text{O}]{\text{Base hydrolysis}} \left[\overset{\text{III}}{Co}(NH_3)_5 (OH) \right]^{2+} + Cl^- \qquad K_2 = 7.5 \ M^{-1} s^{-1}$$

SN$_1$CB Mechanism of base-catalyzed hydrolysis

Step: 1 $[\overset{III}{Co}(NH_3)_5\,Cl]^{2+} + OH^-$ ⇌ (Fast) $[\overset{III}{Co}(NH_3)_4\,(NH_2)\,Cl]^+ + H_2O$

Ammine cpx.   Base   Conjugate base of ammine cpx.(CB)

Step: 2 $[\overset{III}{Co}(NH_3)_4\,(NH_2)\,Cl]^+$ → (Slow) $[\overset{III}{Co}(NH_3)_4\,(NH_2)]^{2+} + Cl^-$

CB of ammine cpx.   Five coordinate intermediate

Step: 3 $[\overset{III}{Co}(NH_3)_4\,(NH_2)]^{2+} + H_2O$ → (Fast) $[\overset{III}{Co}(NH_3)_5\,(OH)]^{2+}$

Five coordinate intermediate   Product

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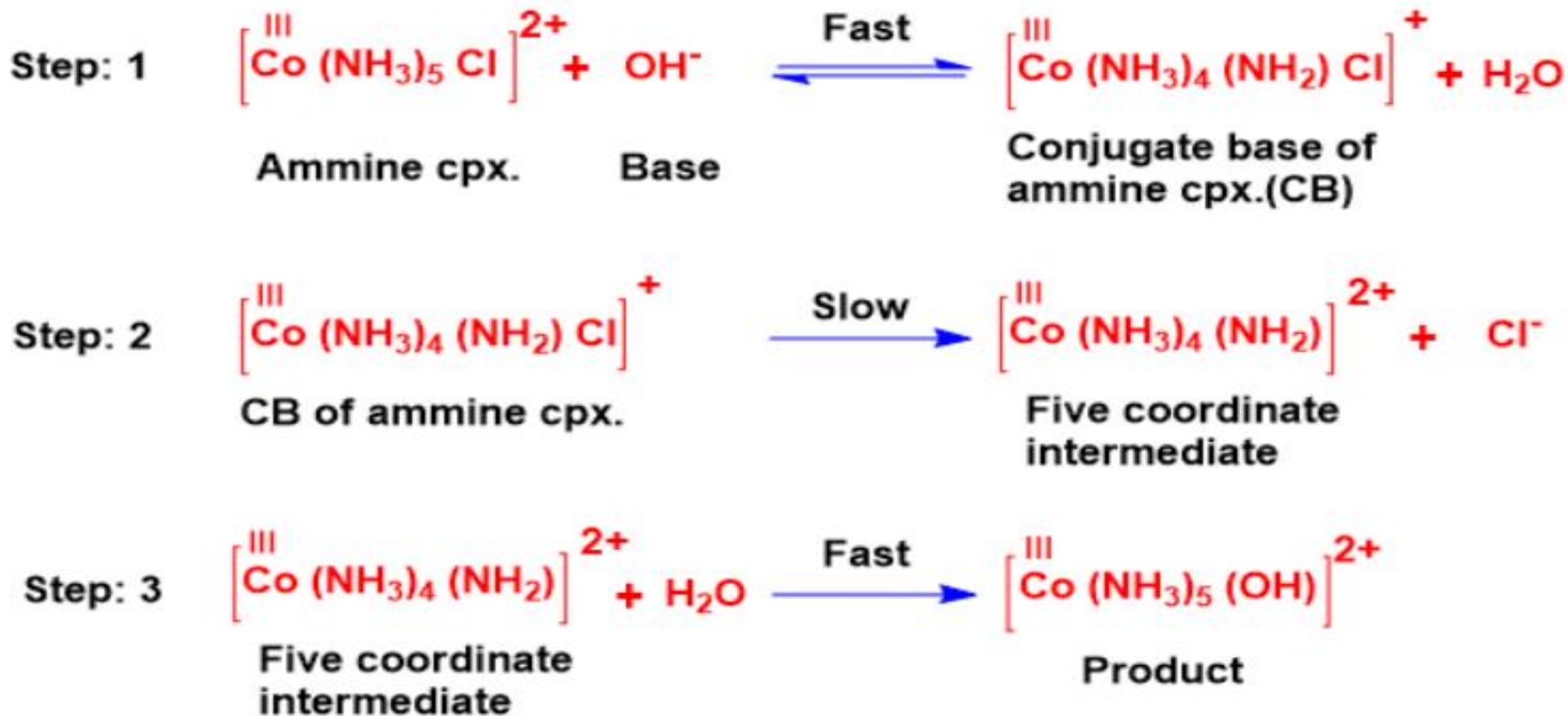
❖ **In the first step,** since the **ammine inert ligand have removable acidic proton, the OH⁻ ions abstract a proton from NH_3,** resulting in the formation of a conjugate base(CB), the NH_2^- ion, as a ligand. The hydroxide ion rapidly sets up an equilibrium between the reactant complex and the amido complex(CB)

❖ **In the second step,** which is **rate determining,** the **CB dissociates** and releasing the leaving ligand **(Cl⁻)** to form the five-coordinated intermediate.

❖ This mechanism is called **unimolecular,** because, **in the slow step only one molecule(CB) is involved.** But, the concentration of the **CB** complex depends on the concentration and the reactant complex and **OH⁻** ion **through equilibrium.** So the rate = k [Co(NH₃)₅Cl]²⁺ [OH⁻]. So, kinetics is second order.

❖ **In the third step, the five-coordinated intermediate $[Co(NH_3)_4(NH_2)]^{2+}$ quickly reacts with water to give the final product of hydration, the hydroxo complex.**

Reason for the high rate of Base hydrolysis:

① **In the rate determining step, the deprotonated form of the ammine complex(CB) has a lower positive charge, it will be able to lose a Cl^- ion more readily than the protonated form (in acid hydrolysis) and thus accelerating the base hydrolysis.**

② **According to SN_1CB mechanism, loss of proton from an NH_3 ligand changes it from a pure σ–donor ligand to a strong σ–donor and a strong π–donor(as NH_2^-) and so helps to stabilize the five-coordinated intermediate(TBP) by a L ⟶ M π–bonding and thus accelerating the loss of Cl^- ion. This is the reason for the million fold increase in the rate of base hydrolysis over acid hydrolysis.**

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Evidences in favour of SN₁CB mechanism for base hydrolysis

(i) <u>The hydroxide ion is unique in its million fold increase in rate over acid hydrolysis.</u>

❖ The anions such as NO_2^-, SCN^-, N_3^-, F^- are as strong nucleophiles as OH^-, but do not increase the rate of hydrolysis of ammine complexes.

❖ Although the anions (NO_2^-, SCN^-, N_3^-, F^-) are as strong nucleophiles as OH^-, yet they are not as strong bases as OH^-, i.e., these anions are incapable of abstracting protons from the ammine complex to yield a conjugate base of the complex in the first step. In the absence of the formation of a conjugate base (CB), the hydrolysis of the complex cannot proceed through SN₁CB mechanism, it may be proceeded by conventional associative or dissociative mechanism.

(ii) A complex having inert ligand with no acidic proton undergoes base hydrolysis very slowly.

$$[\overset{III}{Co}(CN)_5\,Cl]^{3-} + OH^- \xrightarrow[\;H_2O\;]{Base\ hydrolysis} [\overset{III}{Co}(CN)_5\,(OH)]^{3-} + Cl^-$$
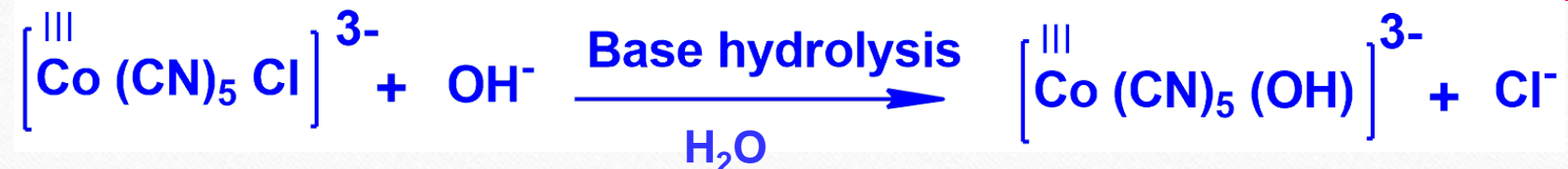
❖ **The rate of the above base hydrolysis reaction is very slow and its rate is independent of OH^- concentration indicating that its hydrolysis do not proceed through SN_1CB mechanism because the inert ligands do not contain any acidic hydrogen.**

(iii) Addition of H_2O_2 actually decreases the rate of base hydrolysis of $[Co(NH_3)_5\,Cl]^{2+}$

❖ **When H_2O_2 is added to OH^- ion solution, the following equilibrium reaction takes place:**

$$H_2O_2 + OH^- \underset{}{\overset{K}{\rightleftharpoons}} H_2O + HO_2^- \left(K > 150 \right)$$
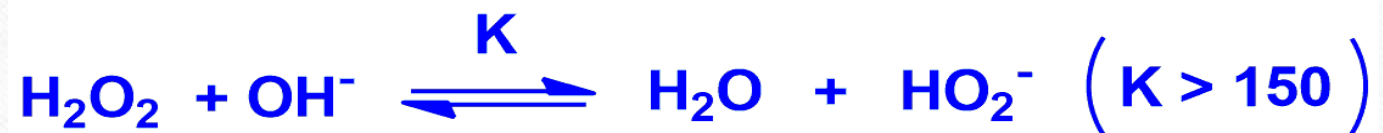
❖ **If the base hydrolysis occurs through normal S_N^2 path, the anion, HO_2^- produced in the reaction is a better nucleophile but weaker base than OH^-, should increase the reaction rate, but, actually the rate decreases. Because, the presence of OH^- ion is a must for SN_1CB mechanism which proves that base hydrolysis occurs through SN_1CB mechanism.**

(iv) **The study of the O^{18}/O^{16} isotope distribution in the product $[Co(NH_3)_5(OH)]^{2+}$ strongly supports SN_1CB mechanism for base hydrolysis.**

❖ **It is known that the O^{18}/O^{16} isotope ratio differs between H_2O and OH^- at equilibrium.**

❖ The O^{18}/O^{16} isotope ratio in the product **matches** that of H_2O not that for the OH^- ions, proving that it is a H_2O molecule is the entering group and not the OH^- ion.

❖ In **SN₁CB** mechanism, **H_2O** is the entering group where as in **S_N^2** mechanism, **OH^-** ion is the entering group. So the above isotope studies **proves SN₁CB** mechanism for base hydrolysis.

Stereochemistry of Intermediates of Base hydrolysis

Two questions arise:

(1) What is the **exact site** from which the **proton is removed** in the first step of SN₁CB mechanism?

(2) What is the **shape** of the intermediate?

Isomers of $\left[\overset{III}{Co}\,(tren)\,(NH_3)\,Cl\right]^{2+}$

(i) **Red Isomer**

(10⁴ times more reactive) — $(10^4 \text{ times more reactive})$
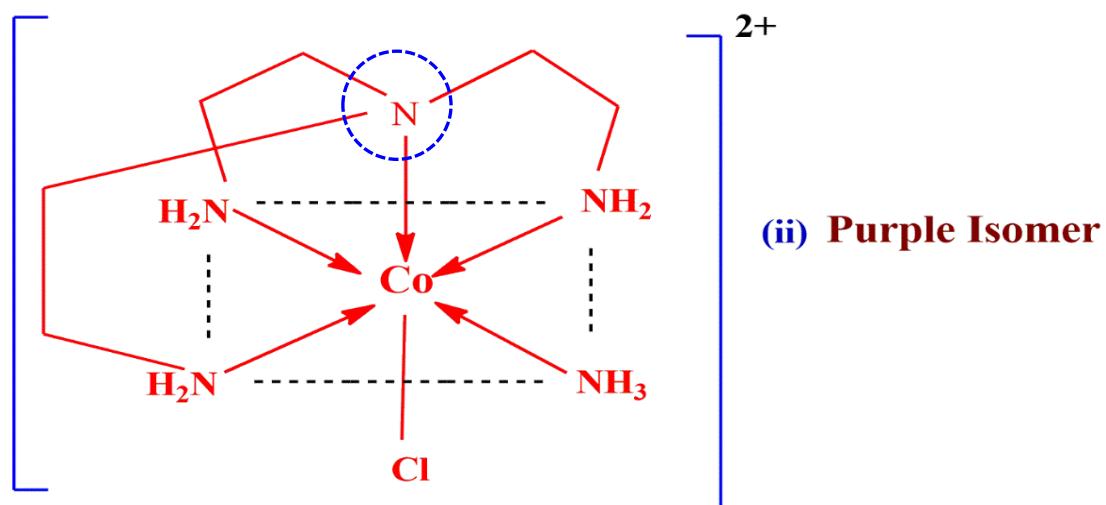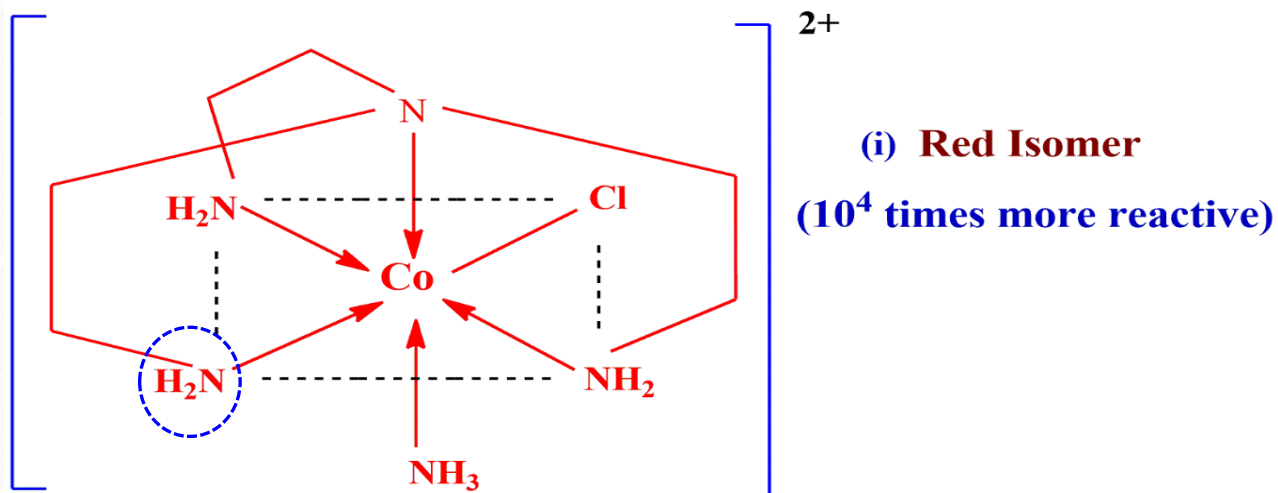
(ii) **Purple Isomer**

Answer to Q.No.(1): The position **trans** to the leaving group is the deprotonation site for a conjugate base mechanism.

❖ Base hydrolysis of red isomer of $[Co(tren)(NH_3)_5Cl]^{2+}$ is hydrolysed much more rapidly than the purple isomer of $[Co(tren)(NH_3)_5Cl]^{2+}$

❖ Because the red isomer only having a removable proton on the nitrogen atom trans to the leaving group.

(tren) = triehyltriamine $N(CH_2-CH_2-NH_2)_3$

Answer to Q.No.(2): The five coordinate intermediate formed during the base hydrolysis of ammine complexes of Co(III) through SN_1CB mechanism is **trigonal bipyramidal**

❖ The five coordinate intermediate formed during the base hydrolysis of ammine complexes of Co(III) contains **π-donor ligands such as NH_2^- or $R\text{-}NH^-$**. Hence, a trigonal bipyramidal intermediate is expected to be more stable than a square pyramidal intermediate because of **L→M π-bonding** when the amido group(NH_2^-) is a part of the trigonal plane of TBP intermediate.

❖ A **TBP** intermediate always gives **a mixture of cis and trans** products irrespective of the geometry of the reactant complex. **Experimental studies revealed that the products of base hydrolysis is a mixture of cis and trans isomers. This observation clearly proves that the five coordinate intermediate is trigonal bipyramidal.**
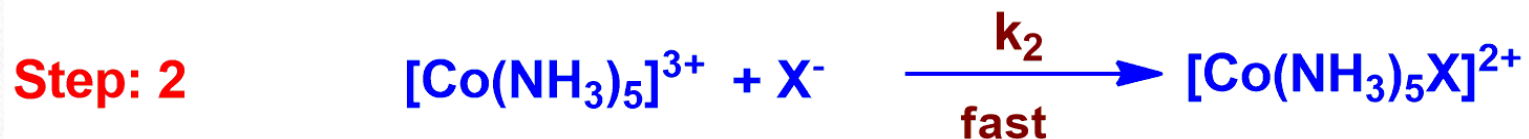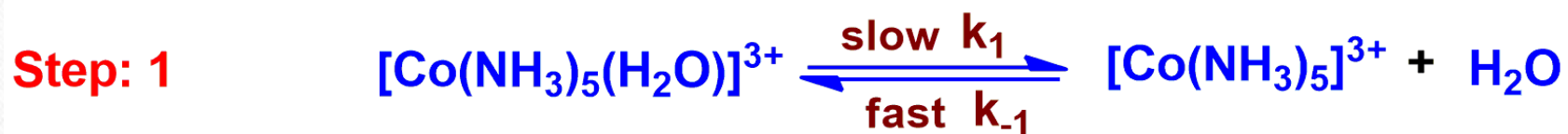
Stereochemistry of Base hydrolysis of Cis-$\left[\overset{III}{Co}\,(en)_2\,A\,X\right]^{n+}$
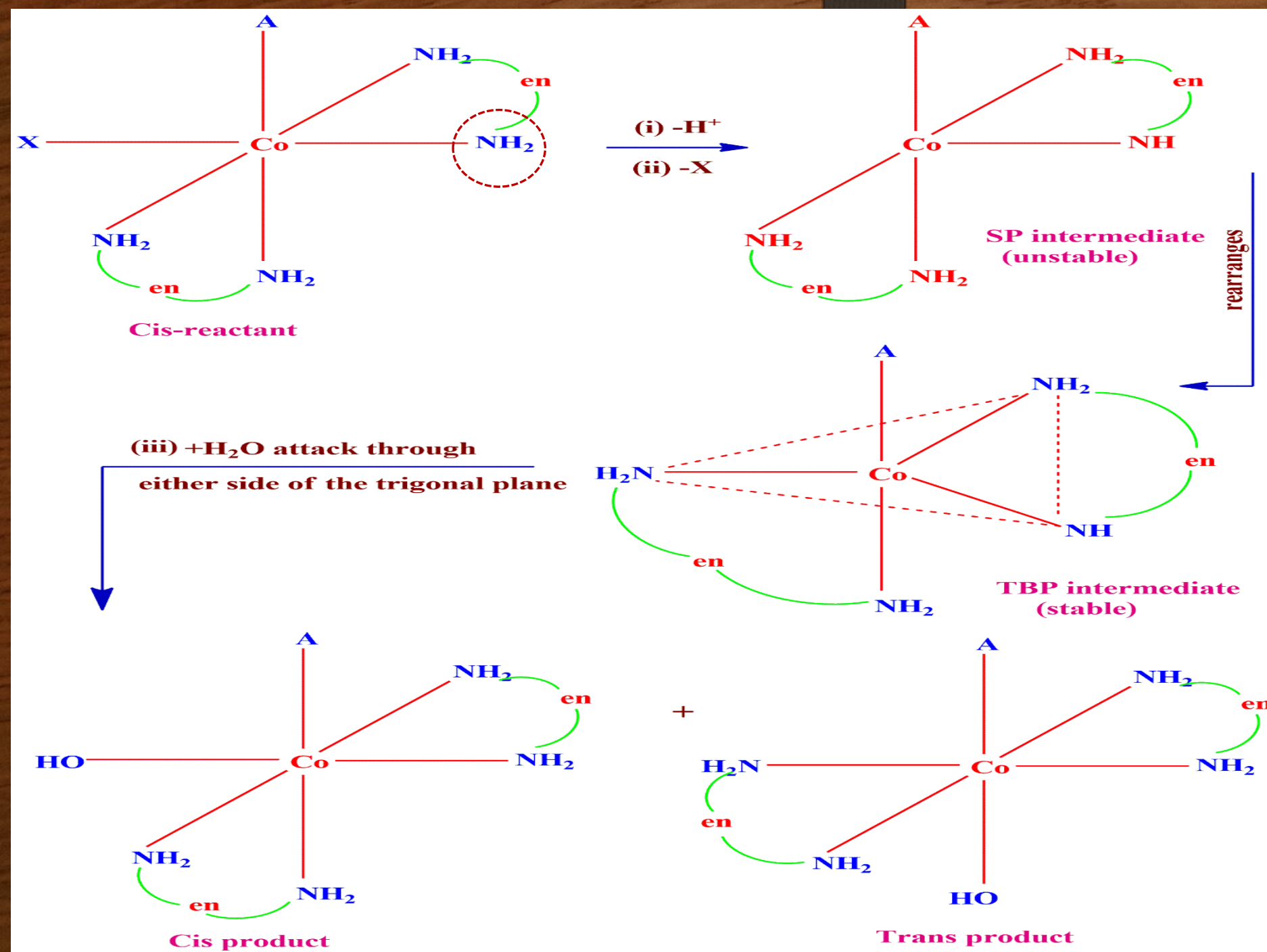
Anation Reactions

❖ Replacement of coordinated water **from an aquo complex** by an anionic group **(X^-) is called** Anation reaction. **This reaction is reverse of an acid hydrolysis** reaction. An example of anation reaction is

(e.g.) $\overset{III}{[Co\,(NH_3)_5\,(H_2O)\,]^{3+}} + Br^- \longrightarrow \overset{III}{[Co\,(NH_3)_5\,Br\,]^{2+}} + H_2O$

❖ From **kinetic studies** of these reactions in aqueous solutions, it is found that these are **bimolecular** with a rate dependent on the concentration of the reactant complex and X^- (**second order kinetics**). However, this information alone is **not sufficient** to prove that these reactions are bimolecular and associative mechanism.

Mechanism of Anation reaction

❖ Although some anation reactions are second order, yet this **does not indicate an associative** mechanism. However, the **dissociative mechanism is more likely:**
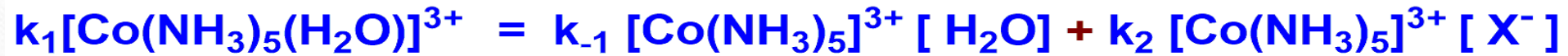
Step: 1 $[Co(NH_3)_5(H_2O)]^{3+} \xrightleftharpoons[\text{fast } k_{-1}]{\text{slow } k_1} [Co(NH_3)_5]^{3+} + H_2O$

Step: 2 $[Co(NH_3)_5]^{3+} + X^- \xrightarrow[\text{fast}]{k_2} [Co(NH_3)_5X]^{2+}$

❖ **The rate law obtained from these reactions shows a dependence on $[X^-]$, even though it is derived for a dissociative mechanism.**

$$\text{rate} = \frac{-\, d\,[Co(NH_3)_5(H_2O)]^{3+}}{dt} = \frac{+\, d\,[Co(NH_3)_5X]^{2+}}{dt}$$

$$\text{rate} = k_2\,[Co(NH_3)_5]^{3+}\,[\,X^-\,] \quad \text{-------- (i)}$$

❖ **Since the intermediate $[Co(NH_3)_5]^{3+}$ is short lived, we can apply steady state principle to these reactions to get the concentration of the intermediate.**

Rate of formation of intermediate = Rate of disappearance of intermediate

$$k_1[Co(NH_3)_5(H_2O)]^{3+} = k_{-1}[Co(NH_3)_5]^{3+}[H_2O] + k_2[Co(NH_3)_5]^{3+}[X^-]$$

$$k_1[Co(NH_3)_5(H_2O)]^{3+} = [Co(NH_3)_5]^{3+}\left[k_{-1}[H_2O] + k_2[X^-]\right]$$

$$[Co(NH_3)_5]^{3+} = \frac{k_1[Co(NH_3)_5(H_2O)]^{3+}}{k_{-1}[H_2O] + k_2[X^-]} \quad \text{------- (ii)}$$

On substituting eqn (ii) in eqn (i), we get,

$$\text{rate} = \frac{k_2 k_1 [Co(NH_3)_5(H_2O)]^{3+}[X^-]}{k_{-1}[H_2O] + k_2[X^-]} \quad \text{------- (iii)}$$

There are two cases arise:

Case-I : At high concentration of $[X^-]$, $k_2 [X^-] \ggg k_{-1} [H_2O]$ and the eqn (iii) simplifies to a form in which the rate is independent of concentration of $[X^-]$,

$$\text{rate} = \frac{\cancel{k_2}\, k_1\, [Co(NH_3)_5(H_2O)]^{3+}\, \cancel{[X^-]}}{\cancel{k_2}\, \cancel{[X^-]}} = \boxed{k_1 [Co(NH_3)_5(H_2O)]^{3+}} \text{ ------- (iv)}$$

(first order)

Case-II : At lower concentration of $[X^-]$, $k_{-1}[H_2O] \ggg k_2 [X^-]$ and the eqn (iii) simplifies to

$$\text{rate} = \frac{k_2\, k_1\, [Co(NH_3)_5(H_2O)]^{3+}\, [X^-]}{k_{-1}\, [H_2O]} = \boxed{k_{obs}\, [Co(NH_3)_5(H_2O)]^{3+}\, [X^-]}$$
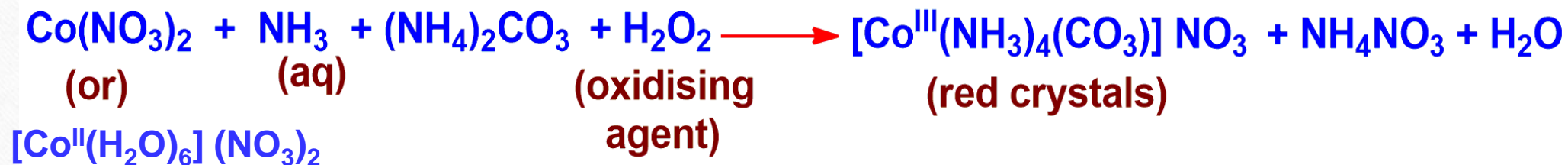
(second order) ------- (v)
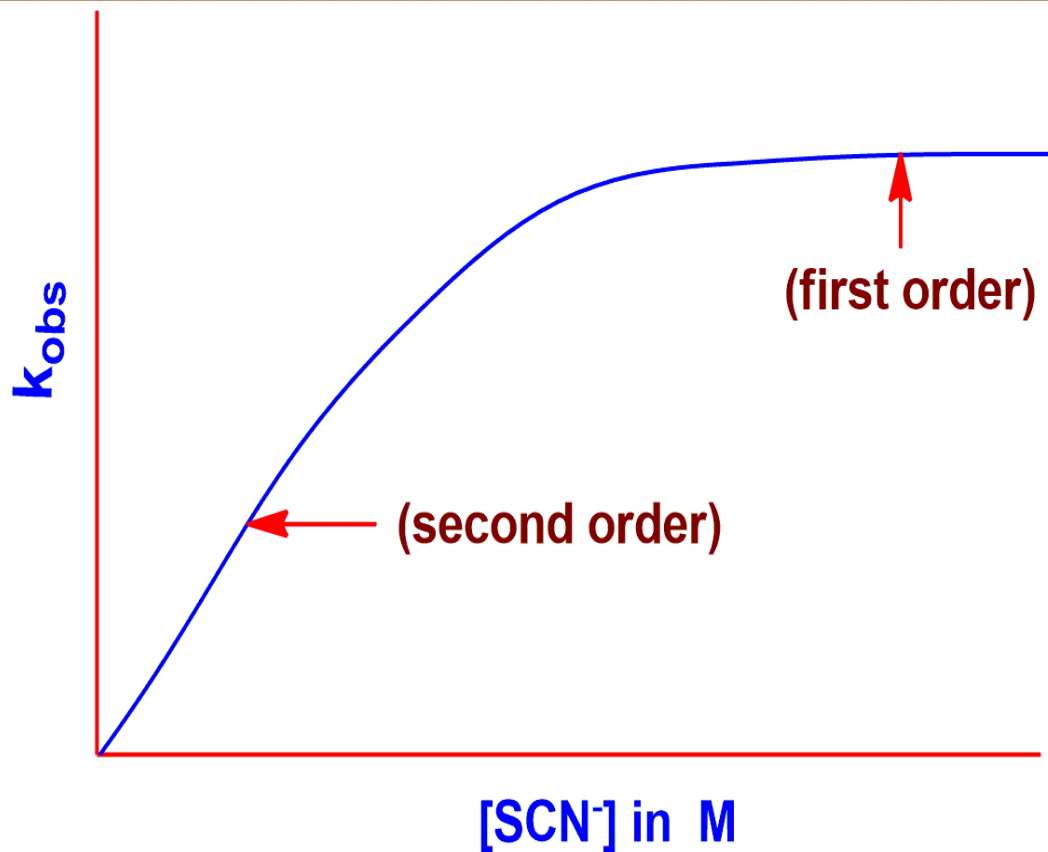
Fig. Dependence of k_{obs} on concn/. of entering ligand [SCN⁻] in H_2O substitution involving a Co(III) hematoporphyrin complex
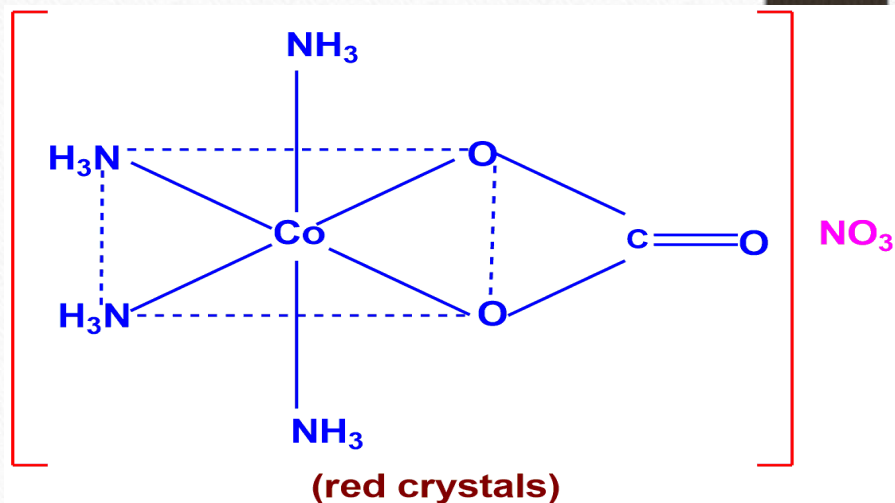
❖ **At lower concentrations of [X⁻], the rate shows a dependence [X⁻]. Thus, from equations (iv) & (v), it follows that the rate of anation reaction, depending upon the conditions applying, may or may not be dependent upon the concentration of the entering anionic ligand. In principle, there occurs a gradual change from 2nd order to 1st order kinetics as the concentration of the substituent increases.**

Synthesis of coordination compounds by substitution reactions

① **Preparation of tetraamminecarbonatocobalt(III) nitrate** $[Co^{III}(NH_3)_4(CO_3)] NO_3$

❖ **The starting material for this synthesis is cobalt(II) nitrate. The formula of the compound is** $Co^{II}(NO_3)_2 .6H_2O$ **and formulated as** $[Co(H_2O)_6] (NO_3)_2$.

❖ **The** d^7 **high spin Co(II) ion (**$t_{2g}^5 e_g^2$**) is predicted to be labile, so in the presence of** NH_3 **and** CO_3^{2-} **, the formation of** $[Co^{II}(NH_3)_4(CO_3)]$ **is possible. If an oxidizing agent (**H_2O_2**) is also present, the intermediate Co(II) carbonato complex can be oxidized to the desired, final product. The overall (unbalanced) reaction is**

$$Co(NO_3)_2 + NH_3 + (NH_4)_2CO_3 + H_2O_2 \longrightarrow [Co^{III}(NH_3)_4(CO_3)] NO_3 + NH_4NO_3 + H_2O$$

(or)   (aq)   (oxidising   (red crystals)
                                    agent)

$[Co^{II}(H_2O)_6] (NO_3)_2$

(red crystals)

② **Preparation of pentaamminechlorocobalt(III) chloride** $[Co^{III}(NH_3)_5Cl]\,Cl_2$
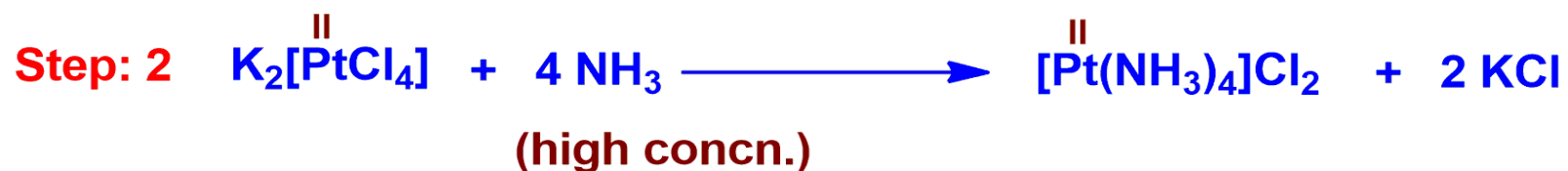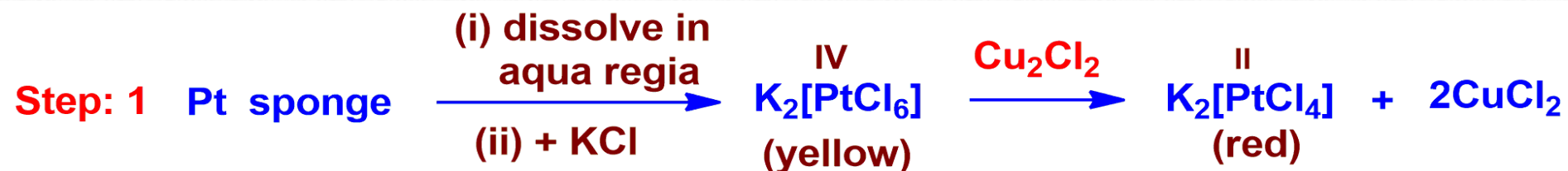
❖ **First carbonato complex of cobalt(III) is prepared from cobalt(II) nitrate as before.**

❖ **Although Co(III) complexes are inert to substitution, a variety of complexes can be prepared from the carbonato complex by the replacement of CO_3^{2-} ligand. For example, pentaamminechlorocobalt(III) ion is formed in the next series of reactions.**
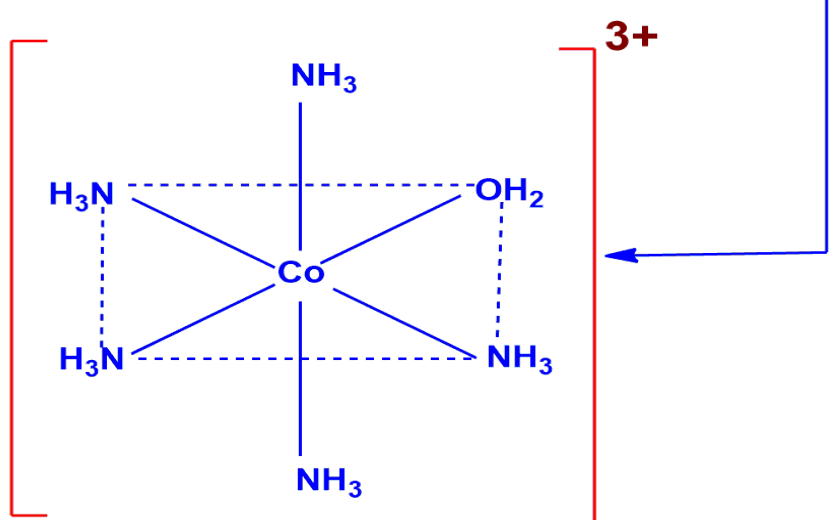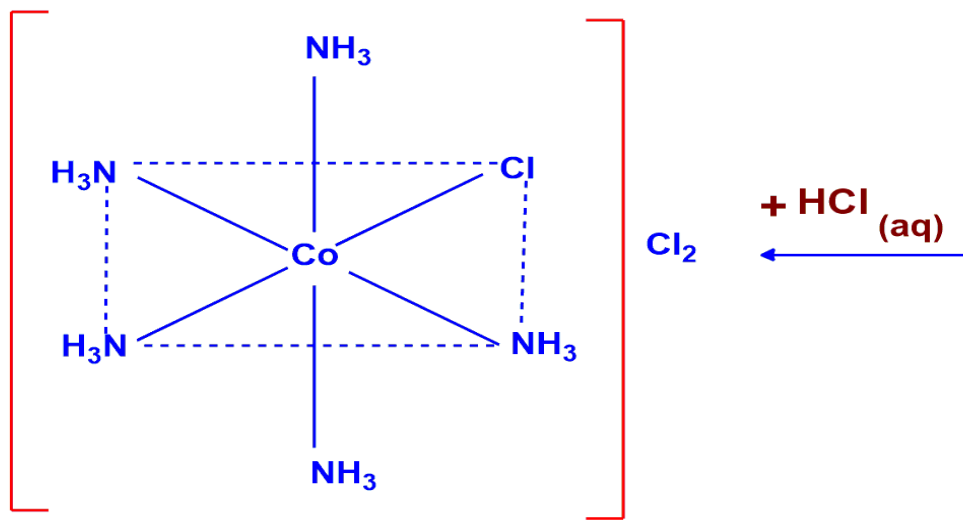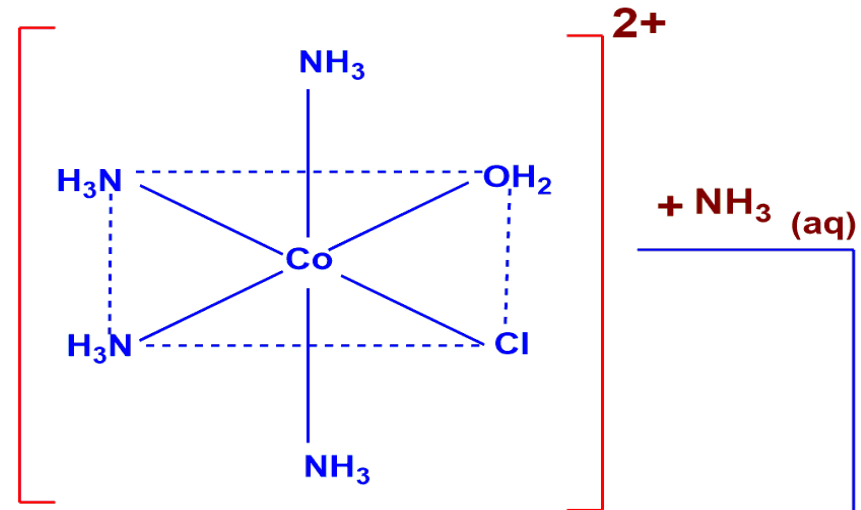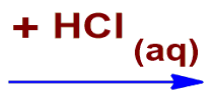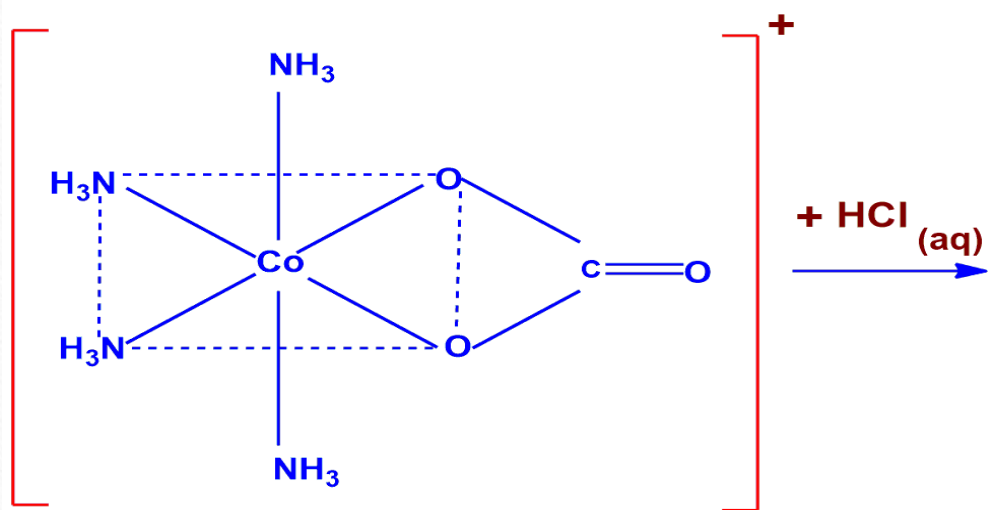
(purple-red crystals)

③ **Preparation of diamminetetrachloroplatinum(IV) from Pt metal** $[Pt^{IV}Cl_4(NH_3)_2]$

Step: 1 Pt sponge $\xrightarrow[\text{(ii) + KCl}]{\substack{\text{(i) dissolve in} \\ \text{aqua regia}}}$ $K_2[\overset{IV}{Pt}Cl_6]$ (yellow) $\xrightarrow{Cu_2Cl_2}$ $K_2[\overset{II}{Pt}Cl_4]$ (red) $+$ $2CuCl_2$

Step: 2 $K_2[\overset{II}{Pt}Cl_4]$ $+$ $4\,NH_3$ $\xrightarrow{\hspace{3cm}}$ $[\overset{II}{Pt}(NH_3)_4]Cl_2$ $+$ $2\,KCl$

(high concn.)

Step: 3 Then $[Pt(NH_3)_4]^{2+}$ is heated with excess of Cl^- (in the form of HCl)

Step: 4

$$\left[\begin{array}{c} H_3N \quad \overset{II}{\underset{Pt}{}} \quad Cl \\ Cl \quad \quad NH_3 \end{array} \right]$$

(trans isomer of square planar cpx.)

$+ Cl_2$ →(oxidative addition)→

$$\left[\begin{array}{c} Cl \\ H_3N \quad \overset{IV}{\underset{Pt}{}} \quad Cl \\ Cl \quad \quad NH_3 \\ Cl \end{array} \right]$$
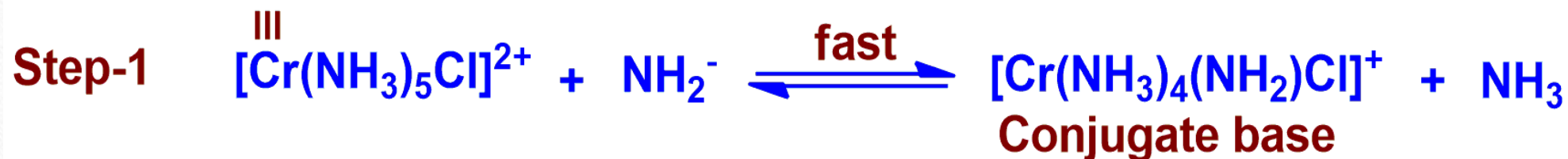
(octahedral Pt(IV) cpx.)
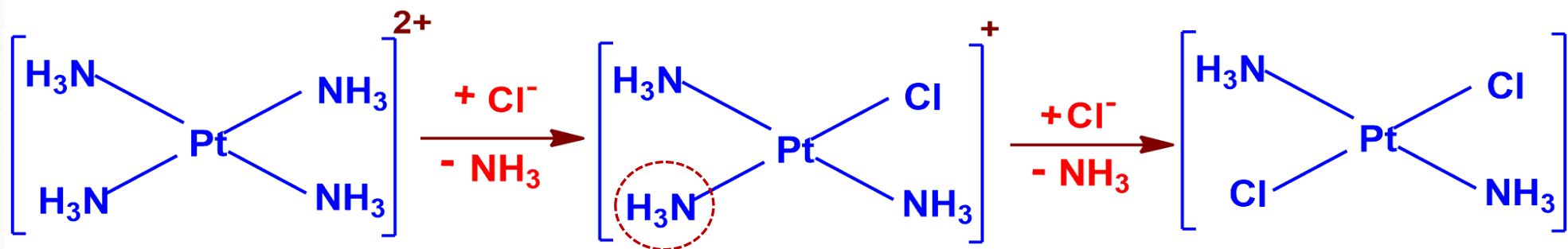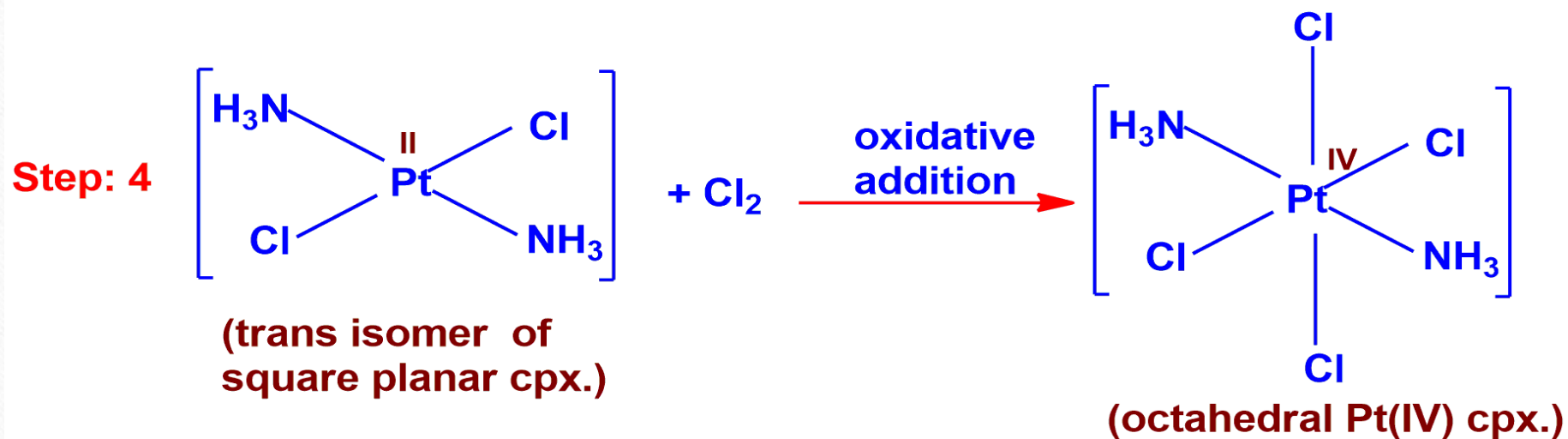
④ **Preparation of hexaamminechromium(III) nitrate** $[Cr^{III}(NH_3)_6] (NO_3)_3$

❖ If anhydrous $CrCl_3$ is allowed to react with liquid ammonia, $[Cr^{III}(NH_3)_5Cl] Cl_2$ will form as the major product. The remaining chloro ligand is displaced slowly. However, the base catalysed solvolysis reactions occur very rapidly. Therefore it is possible to replace the remaining Cl^- ligand by a base catalysed solvolysis in liquid ammonia where amide ion, NH_2^- is the base and the entering ligand is NH_3 . The reaction follows SN_1CB path way.

$$\overset{III}{CrCl_3} + 6\ NH_3 \xrightarrow{\text{liq.}NH_3} [Cr(NH_3)_5Cl]\ Cl_2 \xrightarrow{NH_2^-/\text{liq.}NH_3} \underset{\text{brown}}{[Cr(NH_3)_6]\ Cl_3} \xrightarrow{HNO_{3(aq)}} \underset{\text{yellow}}{\overset{III}{[Cr(NH_3)_6]}\ (NO_3)_3}$$

Mechanism:

Step-1 $\quad \overset{III}{[Cr(NH_3)_5Cl]^{2+}} + NH_2^- \underset{}{\overset{\text{fast}}{\rightleftharpoons}} \underset{\text{Conjugate base}}{[Cr(NH_3)_4(NH_2)Cl]^+} + NH_3$

Step-2 $\quad [Cr(NH_3)_4(NH_2)Cl]^+ \xrightarrow[\text{slow}]{\text{Dissociation}} [Cr(NH_3)_4(NH_2)]^{2+} + Cl^-$

Step-3 $\quad [Cr(NH_3)_4(NH_2)]^{2+} + 2\ NH_3 \xrightarrow{\text{fast}} \overset{III}{[Cr(NH_3)_6]^{3+}} + NH_2^-$
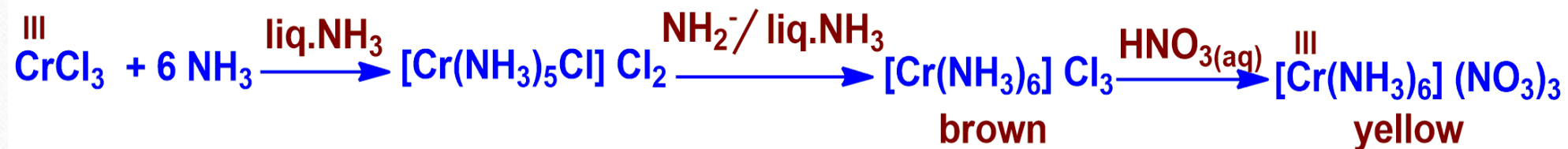
References:

1. Inorganic Chemistry - Principles of Structure and Reactivity
   — James E. Huheey, Keiter, Richard & Medhi.

2. Shriver & Atkins' Inorganic Chemistry — Atkins, Overton, Rourke, Weller & Armstrong.

3. Inorganic Chemistry — Purcell & Kotz

4. Concepts and Models of Inorganic chemistry — Douglas, McDaniel & Alexander

5. Inorganic Chemistry - Gary L. Miessler & Donald A. Tarr.

6. Concise Coordination Chemistry — R. Gopalan & V. Ramalingam

7. Selected topics in Inorganic Chemistry — U. Malik, G. D. Tuli & R. D. Madan.

8. Advanced Inorganic Chemistry - Vol-II — Gurdeep Raj.