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REACTION MECHANISM OF TRANSITION METAL COMPLEXES

- Transition metal complexes usually undergo either substitution reactions & redox reactions. In substitution reactions a change will occur in ~~oxidation state associated~~ the co-ordination number of metal during the course of a reaction and no change will occur oxidation state of metal. In redox reactions, transfer of electrons will occur between two metal atoms without any change in co-ordination number.

- In addition to substitution and redox reactions, transition metal complexes may also undergo reactions involving structural changes such as interconversion of geometrical isomers (cis ⇌ trans), configurational isomers (square planar ⇌ tetrahedral), optical isomers (d ⇌ l), linkage isomers (nitrito complex ⇌ nitro complex)

Certain ligand substitution reactions may involve rupture of metal-ligand bond. There are some substitution reactions in which no rupture of metal-ligand bond occurs.

Generally the reactions undergone by metal ligand complexes can be classified into

(a) ligand substitution reactions
(b) Electron transfer reactions.
(c) Reactions of coordinated ligands
(d) Isomerisation reactions.

Ligand Substitution reactions:-

A ligand substitution reaction is a reaction in which one Lewis base displaces another from a Lewis acid.

$$Y + M\text{-}X \longrightarrow MY + X$$

where M is a metal ion or atom, X is leaving group and Y is entering group

- An example for a substitution can be given as

$$[Co(H_2O)_6]^{+2} + Cl^- \longrightarrow [CoCl(H_2O)_5]^{+} + H_2O.$$

The classification of mechanisms

The mechanisms involved in substitution reactions of complexes can be classified

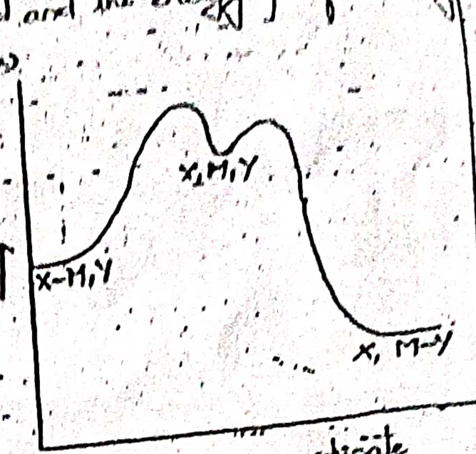
(a) Dissociative mechanism
(b) Associative mechanism
(c) Interchange mechanism.

(a) **Dissociative mechanism** A dissociative mechanism is denoted by 'D' and in this mechanism an intermediate of reduced coordination number is formed by the departure of ~~th~~ the leaving group.

The dissociative mechanism can be given as follows

$$MLnX \longrightarrow MLn + X$$
$$MLn + Y \longrightarrow MLnY$$

- MLn is a true intermediate that can be isolated and the energy profile diag for the dissociative mechanism is shown in the fig(a).



→ Reaction Coordinate
—Fig(a)

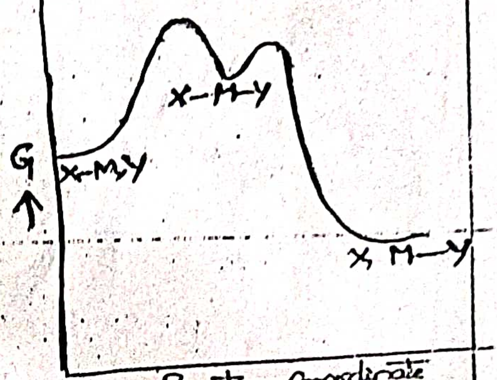
(b) **Associative mechanism:** An associative mechanism is denoted by 'A', in which an intermediate is formed with a higher co-ordination number than the original complex.

The associative mechanism for a reaction in general can be given as

$$ML_nX + Y \longrightarrow ML_nXY$$

$$ML_nXY \longrightarrow ML_nY + X$$

The ML_nXY can be isolated and this mechanism plays a role in many reactions of square planar complexes. The energy profile diagram is as shown in fig (b).

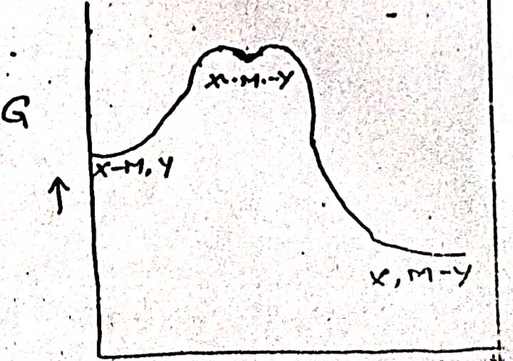


→ Reaction Coordinate
—Fig(b).

(c) **Interchange Mechanisms:** Interchange mechanism is denoted by 'I' and takes place in one step.

$$ML_nX + Y \rightarrow X\cdots ML_n \cdots Y \rightarrow ML_nY + X$$

The leaving and entering groups exchange in a single step by forming an activated complex but not a true intermediate. The energy profile diagram for the interchange mechanism is shown in figure(c).



→ Reaction co-ordinate
—Fig(c)

Rate Determining step:

In dissociative mechanism, as a first step rupture of metal-ligand bond will occur, which is a slow step and rate determining step.

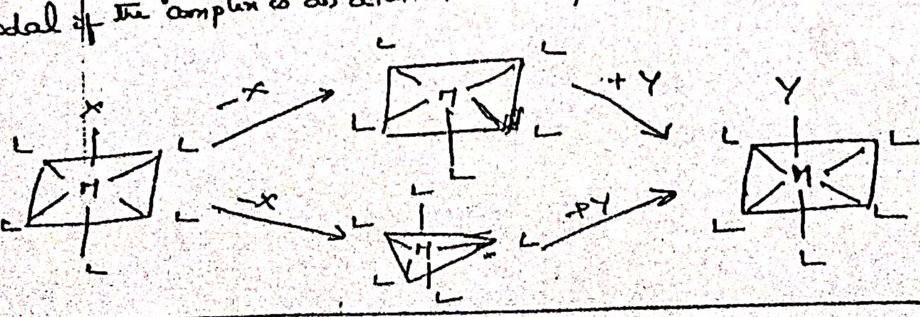
i.e. $ML_nX \xrightarrow{slow} ML_n + X$

ML_n is a true intermediate which has less coordination number than the ~~[illegible]~~ original complex.

In the second step, the ligand Y forms a complex fastly.

$$ML_n + Y \xrightarrow{fast} ML_nY$$

The intermediate in dissociative mechanism can acquire either square pyramidal or trigonal bipyramidal if the complex is an octahedral complex.

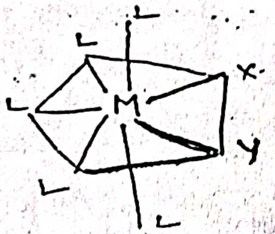


December 22nd

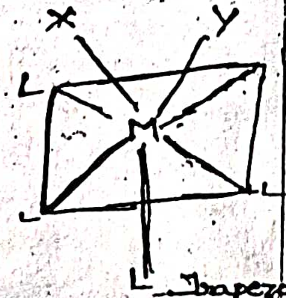
The Intermediate formed in dissociative mechanism is a true intermediate and can be isolated.

The associative mechanism for the substitution reaction can be explained as ligand Y and follows. In the associative mechanism the complex MLnX accept the incoming forms an intermediate of the type YMLnX. This is a slow step and rate determining step. The rate determining step involve the concentration of the complex [MLnX] and the concentration of the attacking nucleophile.

co-ordination number of the intermediate In the associative mechanism, the intermediate usually acquires either pentagonal increase by one than the complex and the intermediate octahedral structure. bipyramidal structure or trapezoidal



Pentagonal bipyramidal structure



Trapezoidal octahedral structure

Inert and Labile complexes:

Thermodynamically the stability of the complex is expressed in terms of formation constant, which is an equilibrium constant of the complex, formed from its constituents.

$$M + nL \rightleftharpoons [ML_n]$$

$$\beta_n = \frac{[ML_n]}{[M][L]^n}$$

Higher the value of β_n greater will be the stability of the complex. This is one of the factors which influence the behaviour of the complex. The other factor which influence the behaviour of the complex is the rate. It is often true that a stable complex reacts slowly and unstable complex reacts rapidly. This may not be true always.

For example, consider the complexes $[Ni(CN)_4]^{-2}$, $[Hg(CN)_4]^{-2}$ and $[Fe(CN)_6]^{-4}$ and their corresponding stability constants

$[Ni(CN)_4]^{-2}$ $\beta_4 \sim 10^{30}$

$[Hg(CN)_4]^{-2}$ $\beta_4 \sim 10^{47}$

$[Fe(CN)_6]^{-4}$ $\beta_6 \sim 10^{37}$

where β_4, β_4 and β_6 are the corresponding stability constants of $[Ni(CN)_4]^{-2}$, $[Hg(CN)_4]^{-2}$ and $[Fe(CN)_6]^{-4}$ respectively. All these three complexes have very large stability constants. Even though $[Ni(CN)_4]^{-2}$ and $[Hg(CN)_4]^{-2}$ complexes have high stability constants, they undergo exchange reactions rapidly i.e. the bound cyanide group can be replaced by cyanide ion [containing isotopic carbon] in the solution. But the exchange is very slow incase of $[Fe(CN)_6]^{-4}$ even though it has less stability constant than $[Hg(CN)_4]^{-2}$.

From this we can say that there is no exact correlation between stability of a complex and rate of exchange of ligands in the complex. Hence it is apt to explain the kinetic behaviour of complexes in terms of lability and inertness as suggested by Taube.

Another example of a complex which is thermodynamically unstable and kinetically inert is $[Co(NH_3)_6]^{+3}$. These labile complexes are those complexes which undergo ligand replacement reactions ~~slowly~~ rapidly

Inorder to explain the kinetic behaviour quantitatively, Taube suggested that, those which undergo ligand replacement reactions within one minute at 25°C and 0.1 Molar reactant concentration are known as labile complexes & otherwise known as inert complexes.

From this discussion, it can be inferred that stability of complex does not imply inertness and it can be concluded more precisely from the following exchange reactions. Let us consider the exchange of CN^- by $^{14}CN^-$ in the complexes $[Ni(CN)_4]^{-2}$, $[Mn(CN)_6]^{-3}$ and $[Cr(CN)_6]^{-3}$.

$$[Ni(CN)_4]^{-2} + 4\,^{14}CN^- \longrightarrow [Ni(^{14}CN)_4]^{-2} + 4CN^- \quad \sim 30 \text{ seconds}$$

$$[Mn(CN)_6]^{-3} + 6\,^{14}CN^- \longrightarrow [Mn(^{14}CN)_6]^{-3} + 6CN^- \quad \sim 1 \text{ hour}$$

$$[Cr(CN)_6]^{-3} + 6\,^{14}CN^- \longrightarrow [Cr(^{14}CN)_6]^{-3} + 6CN^- \quad \sim 24 \text{ days}$$

The exchange of CN^- by $^{14}CN^-$ in $[Ni(CN)_4]^{-2}$, $[Mn(CN)_6]^{-3}$ and $[Cr(CN)_6]^{-3}$ takes place in 20 seconds, one hour and 24 days respectively. Hence $[Ni(CN)_4]^{-2}$ is a labile complex while other two complexes are inert.

The difference between the instability and lability can be explained as follows. The lability of a complex depends upon the activation energy i.e. the difference between the energy of activated complex and the reactants. A small value of activation energy results in fast reaction.

The instability of the complex depends upon the difference between free energy of products and free energy of reactants.

The substitution reactions in inert complexes can be studied by classical methods where as in labile complexes they are studied by modern methods like flash photolysis, relaxation methods.

December 15

Reactivity of octahedral complexes & kinetic behaviour of octahedral complexes ①

Taube suggested that the lability of the octahedral complexes can be explained
by means of electronic configuration as given by the valence bond theory. The kinetic
behaviour of octahedral complexes of elements of first transition series are as follows.

The configuration of the ion of d^3 system and low spin d^4, d^5, d^6 and d^7 systems
are inert. All other configurations exhibit lability i.e. d^0, d^1, d^2 and d^9 and also high
spin d^4, d^5, d^6 and d^7.

The substitution reactions of inner orbital complexes proceed through SN^2
mechanism and the attachment of 7^{th} group (ligand) to the metal will occur. This
attachment is facilitated by the presence of a vacant low energetic d-orbital. If
the inner d-orbitals are filled then the attachement of 7^{th} group to the metal ion
occur through high energetic outer orbital and consequently the reaction is slow. The
decrease in the reactivity is due to high activation energy.

Generally outer orbital complexes are labile in nature and the lability decreases
with increase in charge of metal ion. The lability of outer orbital complexes is due to less
stable outer d-orbitals than the inner d-orbitals. However the kinetic behaviour of outer
orbital complexes cannot be completely explained by valence bond theory.

The kinetic behaviour of octahedral complexes can be explained by using Ligand
field theory. To make use of ligand field theory, it is necessary to have a knowledge of
Ligand field stabilisation energy for various d electron configurations in both weak field
and strong field cases for a regular octahedral structure and the intermediates expected
to be formed in the transition states for two possible mechanisms SN^1 and SN^2

SN^1 mechanism is a dissociative mechanism in which a ligand is lost from the
octahedral complex and results in the formation of a penta co-ordinated intermediate.
Reasonably, the penta co-ordinated intermediate system acquires a square pyramid structure

SN^2 mechanism is an associative in which a ligand is added to the octahedral
complex and results in the formation of hepta co-ordinated intermediate. The hepta co-ordi-
nated intermediate system acquires a pentagonal bipyramid or trapezoidal octahedral
structure.

The difference between the L.F.S.E of the original octahedral structure and
that of the intermediate formed in the transition state may be considered as the
ligand field activation energy [ΔEa]. A large positive value of ΔEa implies a slow rate
~~implies a slow rate~~ of reaction by that particular path. A negative of ΔEa implies
that the original octahedral structure is less stable than the transition state. This not
just probable. The original octahedral structure may be distorted earlier and is further
stabilised in the transition state. Hence ΔEa becomes negative or at least zero. A negative
ΔEa value may also be taken as essentially zero value.

Effect of sizes and charges on rates of dissociative and associative reaction

Changes Made	Dissociative rate	Interchange rate	Associative rate
Increase positive charge of central atom	Decrease	opposing effects	increase
Increase size of central atom	Increase	Increase	Increase
Increase negative charge of entering group.	no effect	Increase	Increase
Increase size of entering group	no effect	decrease	decrease
Increase negative charge of leaving group	decrease	decrease	decrease
Increase size of leaving group	Increase	opposing effects	decrease
Increase negative charge of non-labile ligands	Increase	opposing effects	decrease
Increase size of non-labile ligands.	Increase	opposing effects	decrease

A few Ligand field activation energies for reactions of octahedral complexes:

calculated values of ΔE_a (in Dq)

Systems	Strong field case			Weak field case		
	SN^1	SN^2		SN^1	SN^2	
	Square pyramid	Pentagonal bypiramid	Trapezoidal octahedral	Square pyramid.	Pentagonal bipyramid	Trapezoidal octahedral.
d^0	0	0	0	0	0	0
d^1	−0.57	−1.28	−2.05	−0.57	−1.28	−2.08
d^2	−1.14	−2.56	−0.68	−1.14	−2.56	−0.68
d^3	2.00	4.26	1.80	2.00	4.26	1.80 etc.

The octahedral complexes of d^3, d^8 systems are inert irrespective of the mechanism. ~~The~~ strong field or low-spin complexes of d^4, d^5 and d^6 systems are inert, whereas high spin or weak field complexes of d^4, d^5 and d^6 systems are labile. The octahedral complexes of d^0, d^1, d^2, d^7, d^9, d^{10} systems are labile irrespective of the mechanism.

Substitution reactions in octahedral complexes

(1) ~~Base~~ Base Hydrolysis: ②

The substitution reaction of Co(III) ammine complexes have been studied vastly. The replacement of a ligand in an octahedral complex by H_2O molecule or OH^- ion is known as hydrolysis.

The replacement of ligand by water molecule is known as acid hydrolysis or aquation. The replacement of ligand by OH^- ion is known as base hydrolysis.

The ~~ex~~ base hydrolysis of Co(III) ammine complex can be given as

$$[Co(NH_3)_5Cl]^{+2} + OH^- \longrightarrow [Co(NH_3)_5OH]^{+2} + Cl^-$$

The above reaction can be explained by two mechanisms. One is SN^2 mechanism and the other is SN^1CB mechanism.

SN^2 mechanism:

The associative mechanism for the reaction can be given as

$$[Co(NH_3)_5Cl]^{+2} + OH^- \xrightarrow[\text{rate determining step}]{\text{Slow step}} [Co(NH_3)_5(OH)Cl]^+ \xrightarrow{\text{fast}} [Co(NH_3)_5OH]^{+2} + Cl^-$$

$$\text{Rate} \propto [Co(NH_3)_5Cl^{+2}][OH^-]$$

The rate determining step involve the concentration of the complex and the base. Hence it is bimolecular reaction.

SN¹CB Mechanism:

(a) $[Co(NH_3)_5Cl]^{+2} + OH^- \overset{fast}{\rightleftharpoons} [Co(NH_3)_4(NH_2)Cl]^{+} + H_2O$

conjugate base [CB]

(b) $[Co(NH_3)_4(NH_2)Cl]^{+1} \xrightarrow{slow} [Co(NH_3)_4(NH_2)]^{+2} + Cl^-$

(c) $[Co(NH_3)_4(NH_2)]^{+2} + H_2O \xrightarrow{fast} [Co(NH_3)_5OH]^{+2}$

This mechanism was given by Garrick. The conjugate base mechanism for Cobalt (III) ammine complex is given as above. In the first step the OH⁻ removes a proton from the non-leaving ligand of the complex and transforms the complex into its conjugate base.

From steady state concept

$$K = \frac{[CB][H_2O]}{[Co(NH_3)_5Cl^{+2}][OH^-]} \Rightarrow [CB] = \frac{K[Co(NH_3)_5Cl^{+2}][OH^-]}{[H_2O]}$$

In the second step the conjugate base transforms into a penta-coordinated system by loosing a ligand Cl⁻. This is a slow step and rate determining step of the reaction.

$$\text{Rate} = k'[CB]$$

$$= \frac{k'K[Co(NH_3)_5Cl^{+2}][OH^-]}{[H_2O]}$$

$$\rightarrow \text{Rate} = k''[Co(NH_3)_5Cl^{+2}][OH^-]$$

The rate equation is similar to that of the rate equation of SN² mechanism [Associative mechanism]

Evidences in favour of SN¹CB mechanism:

(a) If conjugate base mechanism operates in the reaction of base hydrolysis of Co(III) ammine complex then the presence of hydrogen atom in the non-leaving ligand of the complex is very necessary. Because OH⁻ removes a proton from the non-leaving ligand of the complex and transforms to its conjugate base i.e. $[Co(NH_3)_5Cl]^{+2}$ transformed into $[Co(NH_3)_4(NH_2)Cl]^{+}$

When a complex which is in lack of protons is considered for base hydrolysis then the reaction should occur slowly and the rate of the reaction is independent of concentration of OH⁻. Similar tendency was observed in the complex $[Co(CN)_5Br]^{-3}$ i.e. the basic hydrolysis of this complex is very slow and is independent of conc of OH⁻. Thus in the absence of proton SN¹CB mechanism is not possible. The basic nature of OH⁻ and acidic nature of the complex are responsible for SN'CB mechanism. The basic nature of OH⁻ dominates the nucleophilic nature of OH⁻.

(b) Consider a reaction which is carried out in DMSO [Dimethyl sulphoxide] solvent.

$$[Co(en)_2NO_2Cl]^+ + Y^- \xrightarrow[Y^- = N_3^- \text{ or } NO_2^- \text{ or } CN^-]{DMSO} [Co(en)_2(NO_2)Y]^+$$

The mechanism of the reaction can be better explained in terms of SN'CB mechanism than in terms of SN^2

The reaction between the complex and ligand in ~~presence~~ presence of DMSO proceeds slowly. But the rate of reaction increases rapidly by the addition of trace amount of OH⁻. The increase in rate is due to the removal of proton from the non-leaving ligand or pyridine of the complex by OH⁻

$$[Co(en)_2NO_2Cl]^+ + OH^- \xrightarrow{fast} [Co(en)(en-H)NO_2Cl]$$

A conjugate base is formed by the removal of proton. In the next step the conjugate base will dissociate into penta co-ordinated system and the ligand will be lost from the co-ordination sphere. In the next step the penta co-ordinated intermediate gets co-ordinated to ligand Y⁻. In the final step hexa co-ordinated complex accepts a proton from H_2O and OH⁻ is regenerated. This factor establishes that the reaction proceeds through SN'CB rather than through SN^2 mechanism.

$$[Co(en)(en-H)NO_2Cl] \xrightarrow{slow} [Co(en)(en-H)NO_2]^+ + Cl^-$$

$$[Co(en)(en-H)NO_2]^+ + Y^- \xrightarrow{fast} [Co(en)(en-H)NO_2Y]$$

$$[Co(en)(en-H)NO_2Y] + H_2O \xrightarrow{fast} [Co(en)_2NO_2Y]^+ + OH^-$$

(c) Another important evidence in favour of SN'CB mechanism is that, the rate of above reaction increases with increase in conc OH⁻. But the rate of the reaction remains unchanged with increase in conc Y⁻ [NO_2^-, N_3^-, CN^- etc]

(d) The base hydrolysis of Co(III) complex in aqueous medium at 25°C is carried out in presence of H_2O_2.

$$H_2O_2 + OH^- \longrightarrow H_2O + HO_2^-$$

Hydrogen peroxide decreases the rate of the reaction as it decreases the concentration of OH⁻ and lead to the formation of HO_2^- which is a weaker base and better nucleophile than OH⁻

If OH^- walks as a nucleophile in the base hydrolysis of Co(III) ammine complex then a better nucleophile than OH^- should enhance the rate of the hydrolysis. This confirms that the reaction proceeds through SN^2 mechanism.

If OH^- acts as a base in the base hydrolysis of Co(III) ammine complex then a weaker base than OH^- should decrease the rate of the reaction. This confirms that the reaction proceeds through SN^1CB mechanism.

The reaction between Co(III) ammine complex and OH^- in aqueous medium at 25°C in the presence of H_2O_2 is observed. The decrease in the concentration of OH^- in presence of H_2O_2 is observed. The decrease in the concentration of OH^- in presence of H_2O_2 decreased the rate of hydrolysis.

$$H_2O_2 + OH^- \longrightarrow H_2O + HO_2^-$$

From this it can be conformed that the reaction proceeds through SN^1CB mechanism rather than SN^2 mechanism.

(2) Acid hydrolysis & Aquation :- ✓ ②

Acid hydrolysis is a substitution reaction in which the ligand is replaced by water molecule. The acid hydrolysis of Co(III) ammine complex can be written as follows:

$$[Co(NH_3)_5Cl]^{+2} + H_2O \xrightarrow{slow} [Co(NH_3)_5(H_2O)]^{+3} + Cl^-$$

This reaction can proceed either through associative mechanism & dissociative mechanism.

Associative mechanism:

$$[Co(NH_3)_5Cl]^{+2} + H_2O \xrightarrow{Slow} [Co(NH_3)_5(H_2O)Cl]^{+2} \xrightarrow{fast} [Co(NH_3)_5(H_2O)]^{+3} + Cl^-$$

Dissociative mechanism for the reaction is:

$$[Co(NH_3)_5Cl]^{+2} \xrightarrow{Slow} [Co(NH_3)_5]^{+3} + Cl^-$$

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

It is not possible to simply say that the reaction proceeds through either associative & dissociative mechanism.

To determine the mechanism of the reaction, the following factors are considered.

(a) Effect of charge of the complex: It was found that the hydrolysis of monovalent dichloro complex proceeds at a rate which is 100 times faster than the hydrolysis of monochloro divalent complex.

The acid hydrolysis of monovalent dichloro cobalt (III) ammine complex is

$$[Co(NH_3)_4Cl_2]^{+} + H_2O \longrightarrow [Co(NH_3)_4Cl(H_2O)]^{+2} + Cl^-$$

The acid hydrolysis of divalent monochloro cobalt (III) ammine complex is

$$[Co(NH_3)_5Cl]^{+2} + H_2O \longrightarrow [Co(NH_3)_5(H_2O)]^{+3} + Cl^-$$

This decrease in rate with increase in charge of the complex indicates that the reaction proceeds through dissociative mechanism rather than associative mechanism. The decrease in rate with increase in charge can be attributed to the reason that the separation of Cl^- ion from a high charged complex is difficult.

(b) **Effect of chelation**: The rate of hydrolysis of Co(III) complexes is found to decrease when ammonia in the complex is replaced by polyamines like ethylenediamine, triethylene tetramine. The effect of chelation should shorten the cobalt nitrogen (Co—N) bond distance and the charge is transferred from polyamines to the 'Co' ion. Hence the effect of chelation should enhance the rate of hydrolysis. The decrease in rate of hydrolysis is explained on the basis of solvation theory. Due to chelation, the size of the complex system is large formed. Thus the rate of hydrolysis decreases due to chelation. This solvation theory cannot explain whether the reaction proceeds either through dissociative or associative mechanism.

But the rate of hydrolysis of Co complexes was observed to be increasing when the polyamines are replaced by substituted polyamines. Because of the substituted polyamines, the complex is more crowded and has large strain. This strain can be reduced by the octahedral complex by transforming into a penta coordinated system. This reveals that the intermediate forms more easily and reaction proceeds through dissociative mechanism rather than associative mechanism, where the strain of the octahedral complex further increased due to association with the incoming ligand.

(c) **Effect of charge on the non-leaving ligand**:

By the replacement of NH_3 ligand in $[Co(en)_2NH_3Cl]^{+2}$ by OH^- it was found that the rate of acid hydrolysis is increased. The increase in the acid hydrolysis rate can be explained as follows.

$$H-\overset{\curvearrowright}{\ddot{O}}-Co\overset{\curvearrowright}{\div}Cl$$

The OH^- ligand possesses a lone pair of electrons on oxygen atom and this pair can be transferred to the metal by an inductive process. This transfer of a pair of electrons results in the formation of a π-bond. The formation of π bond weakens Co—Cl bond and also this π bond formation stabilises the five coordinated intermediate.

$$H\ddot{O}-Co-Cl \longrightarrow H\ddot{O}=Co + Cl^-$$

Hence, with increase in charge of non-labile ligand an increase in the rate of reaction of metal complex indicates that the reaction proceeds through dissociative mechanism rather than associative mechanism.

January

(3) ~~Anation~~: The replacement of water in a complex by a ligand is known as anation. This reversal of acid hydrolysis. The anation reaction of cobalt ammine aquo com... is

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

Kinetics of this reaction is found to be second order dependents reaction. But we cannot conclude that the reaction is bimolecular. The same second ~~or~~ order dependence can be observed for unimolecular process.

$$[Co(NH_3)_5(H_2O)]^{+3} \underset{+H_2O\ (fast)}{\overset{-H_2O\ (slow)}{\rightleftharpoons}} [Co(NH_3)_5]^{+3} \xrightarrow{+X^-} [Co(NH_3)_5X]^{+2} + H_2O$$

In this scheme a pseudo equilibrium exists between penta-coordinated intermediate and cobalt ammine aquo complex. The incoming ligand X^- and water molecule will compete for the intermediate i.e., its rate of formation of the products depends on the concentration of the ligand.

The rate of formation of the product with given conc of X^- is equal to the rate of formation of the intermediate. The exact rate equation for the above reaction can be desired from steady state approximation.

Let us consider the reaction of the type

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B \qquad B + C \xrightarrow{k_3} A$$

The rate of formation of B can be given by

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] - k_3[B][C]$$

Since B is a reactive intermediate in the reaction i.e. the rate of formation of B

$$\frac{d[B]}{dt} = 0.$$

$$\Rightarrow k_1[A] - k_2[B] - k_3[B][C] = 0.$$

$$\Rightarrow [B] = \frac{k_1[A]}{k_2 + k_3[C]}$$

Rate of formation of product.

$$\frac{d[D]}{dt} = k_3[B][C]$$

$$\Rightarrow \frac{d[D]}{dt} = \frac{k_3 k_1[A][C]}{k_2 + k_3[C]}$$

Two limiting cases arise i.e. $k_2 >> k_3[C]$ and $k_3[C] >> k_2$

The rate of formation of D can be written as

case(i) If $k_2 >> k_3[C]$ then the rate of formation of D

$$\frac{d[D]}{dt} = \frac{k_3 k_1}{k_2}[A][C]$$

From this equation, it is clear that the rate of the reaction depends upon the concentration of complex and the concentration of incoming ligand which is a second order dependence

(case(ii)) If $k_3[C] >> k_2$ then the rate of formation of D is

$$\frac{d[D]}{dt} = k_1[A]$$

From this it is clear that the rate of reaction depends upon the concentration of 'A' alone which is an indicative of first order dependence. A few examples of anation reactions are.

$$[Rh(NH_3)_5(H_2O)]^{+3} + Br^- \longrightarrow [Rh(NH_3)_5Br]^{+2} + H_2O.$$

$$[Co(NH_3)_5(H_2O)]^{+3} + SO_4^{-2} \longrightarrow [Co(NH_3)_5SO_4]^{+1} + H_2O.$$

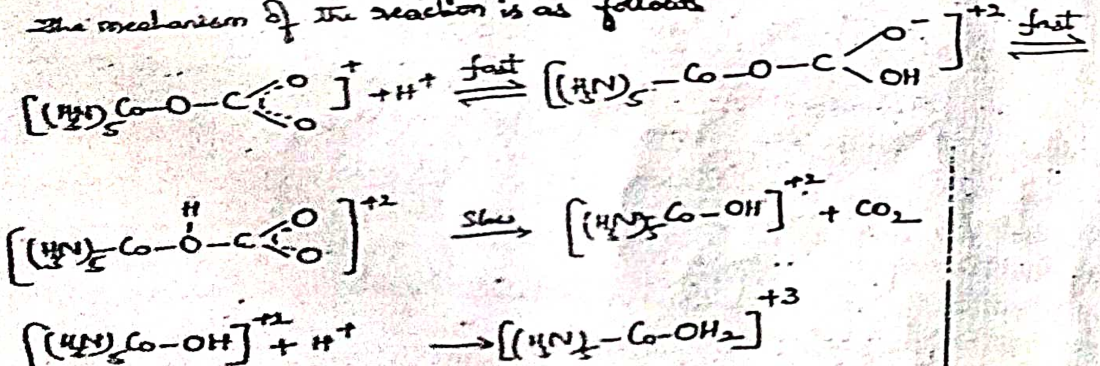
$$[Cr(H_2O)_6]^{+3} + NCS^- \longrightarrow [Cr(H_2O)_5NCS]^{+2} + H_2O.$$

Substitution reaction without Metal-ligand cleavage:

These are certain substitution reactions in which the metal ligand bond will break not break for example. The conversion of Carbonate-Pentammine Co(III) into aquo complex, in presence of excess of acid.

$$[(NH_3)_5Co-O-CO_2]^{+} + 2H^{+} \longrightarrow [(NH_3)_5Co-OH_2]^{+3} + CO_2$$

The mechanism of the reaction is as follows



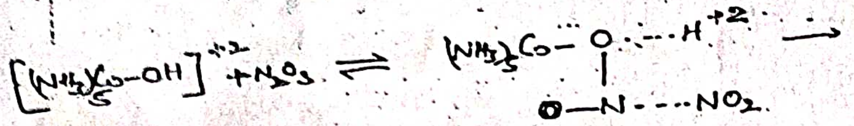
If the above reaction is performed in aqueous medium containing labelled oxygen then it is found that the product (the aqua complex) does not contain labelled oxygen. It proves that the bond between cobalt and oxygen atom of CO_3^{-2} remains intact during the course of substitution reaction. This factor is in favour of above mechanism.

Another important example in which substitution takes place without metal-ligand bond cleavage is, formation of nitrito complex from aqua complex of Co(III) the formation of the nitro complex occurs indirectly through the sequence: chloro complex → aquo complex → nitrito complex → nitro complex. The mechanistic scheme for the overall process is as follows

$$[(H_3N)_5Co-Cl]^{+2} + H_2O \longrightarrow [(H_3N)_5Co-OH_2]^{+3} + Cl^-$$

$$[(H_3N)_5Co-OH_2]^{+3} \rightleftharpoons [(H_3N)_5Co-OH]^{+2} + H^+$$

$$2HNO_2 \rightleftharpoons N_2O_3 + H_2O$$



$$[(NH_3)_5Co-OH]^{+2} + N_2O_3 \rightleftharpoons (NH_3)_5Co-\underset{\substack{|\\ O-N---NO_2}}{O}---H^{+2} \longrightarrow$$

$$[(NH_3)_5Co-ONO]^{+2} + HNO_2$$

$$[(NH_3)_5Co-ONO]^{+2} \rightleftharpoons [(NH_3)_5Co-NO_2]^{+2}$$

Factors affecting the substitution reactions

The various factors that influence substitution reactions in complexes aside from usual factors such as temperature, catalyst etc. are

① Nature of the central metal ion:
(2) Nature of the entering ligand
(3) Nature of the leaving ligand.
(4) Nature of the non-leaving & non-labile ligand.
(5) Nature of the solvent.

(1) Nature of central metal ion:

With regard to nature of central metal ion the following factors affect the substitution reaction.

(a) electronic configuration:

To know the relative reactivity of octahedral complexes of transition metal some ligand field Theory was applied. If the LFSE of the activated complex is greater than that of the coordination compound then there will be gain in the LFSE of the transition state which will result in a low activation energy and reaction rate is increased.

If LFSE of the activated complex is less it will result in a high activation energy and it is less reactive. The kinetic behaviour of octahedral complexes can be explained basing on Ligand field activation energy [ΔEa]. Basing on those calculations of Ligand field activation energy the following conclusions can be made.

The octahedral complexes of d^3, d^8 systems are inert irrespective of the mechanism. The strong field & low spin complexes of d^4, d^5 and d^6 systems are inert, whereas high spin & weak field complexes of d^4, d^5 and d^6 systems are labile. The octahedral complexes of $d^0, d^1, d^2, d^7, d^9, d^{10}$ systems are labile irrespective of the mechanism.

(b) Charge of central ~~metal~~ ion: The higher the charge of the central ion, the lower will be the rate of substitution i.e. with increase in the charge of the central metal ion for the isoelectronic complexes there occurs a decrease in lability.

Eg: The lability of the complexes $[AlF_6]^{-3}$, $[SiF_6]^{-2}$, $[PF_6]^-$ & $[SF_6]$ has been found to be of the following order

Lability order: $[AlF_6]^{-3} > [SiF_6]^{-2} > [PF_6]^- > [SF_6]$

cationic charge: $+3 < +4 < +5 < +6$.

(c) Radius of the central ion: The rate of substitution increases with increase in the radius of central ion.

Eg: Lability order: $[Mg(H_2O)_6]^{+2} < [Ca(H_2O)_6]^{+2}$

cationic size (Å): $0.65 < 0.99$.

(2) Nature of the entering ligand: The rates of substitution reactions in octahedral complexes is also effected by the nature of the entering group.

(a) Increase in negative charge of entering group: If the substitution reaction in octahedral complex proceeds through dissociative mechanism then the dissociative rate is uneffected by the increase in negative charge of entering group. Where as the associative rate increases with increase in negative charge of entering group.

(b) Increase in size of entering group: The dissociative rate of substitution in octahedral complexes is uneffected by the increase in size of entering group. Where as the associative rate ~~increase~~ decreases with increase in ~~large~~ size of entering group.

(3) Nature of leaving ligand:

(a) Increase in Negative charge of leaving ligand: If the substitution in an octahedral complex proceeds through dissociative mechanism then with increase in negative charge of leaving ligand the rate of substitution decreases. The decrease in rate can be attributed to the reason that, it ~~become~~ becomes difficult to remove the ligand from the co-ordination sphere with increase in negative charge of leaving ligand.

(b) Increase in size of leaving group: With increase in size of leaving group the dissociative rate of substitution increases. The increase in rate of substitution can be explained as follo With increase in size of leaving group the steric strain increases and this steric strain can be reduced by dissociative step and hence the rate of substitution increases.

(4) Nature of Non-leaving ligand: The non-leaving in a complex plays an effective role in substitution reactions. For example the presence of a proton on a non-leaving ligand increases the rate of substitution in base hydrolysis which proceeds through SN'CB mechanism.

(a) Increase in negative charge of non leaving ligand: As the negative charge of the non-leavi ligand increases the bond between metal ion and that ligand will be strengthened and as a consequence the bond between metal ion and leaving ligand will be weakened and this weakening of bond facilitates the easy cleavage of the bond and less coordinated intermediate is formed. Hence the rate of dissociative substitution increases with increase in negative change of non-leaving ligand.

(b) Increase in size of non leaving ligand: With increase in size of non leaving ligand the dissociative rate ~~decreases~~ increases as the dissociative step reduces the steric strain of the complex. Where as the associative substitution rate decreases as the steric strain is increased ~~because~~ due to associative step.

(5) Nature of the solvent: The rate of substitution increases with an increase in the co-ordinating ability of the solvent. These solvents can be divided into two types basing on their coordinating abilities.

(a) Good Co-ordinating solvent: These good co-ordinating solvents provide a good pathway for substitution reaction.

(b) Poor Co-ordinating solvents: These poor co-ordinating solvents decrease the rate of substitution in complexes.

Electron transfer reaction:

The simplest of all the redox - reactions are those reactions which involve electron transfer. Electron transfer reactions involve changes in the oxidation state of either. Electron transfer reactions of metal complexes are of two basic types

(a) outer sphere type

(b) Inner sphere type.

Inner sphere mechanism:

In the inner sphere type electron transfer, a transfer of an electron and ligand occurs. The transfer of these two things is possible by an intimate contact between the reductant and oxidant. This requirement is fulfilled by the activated bridge between the two complexes.

The activated bridge contains a ligand which is common to both the coordinated spheres. The redox reaction of Co(III) ammine complex and aqua chromium complex was first studied by Taube and his co-workers in acid medium.

$$[Co(NH_3)_5Cl]^{+2} + [Cr(H_2O)_6]^{+2} + 5H_3O^{+} \longrightarrow [Co(H_2O)_6]^{+2} + [Cr(H_2O)_5Cl]^{+2} + 5NH_4^{+}$$

Mechanism:-

$$[Co(NH_3)_5Cl]^{+2} + [Cr(H_2O)_6]^{+2} \xrightarrow{-H_2O} [(H_3N)_5\underset{e^-}{\overset{+3}{Co}}-\overset{e^-}{Cl}-\overset{+}{Cr}(H_2O)_5]^{+4} \xrightarrow[\text{transfer}]{\text{electron}}$$

$$[(H_3N)_5\overset{+2}{Co}-Cl-\overset{+3}{Cr}(H_2O)_5]^{+4} \longrightarrow [Cr(H_2O)_5Cl]^{+2} + [Co(NH_3)_5]^{+2}$$

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

$$[Co(NH_3)_5(H_2O)]^{+2} + 5H_3O^{+} \longrightarrow [Co(H_2O)_6]^{+2} + 5NH_4^{+}$$

In the first step chromium aqua complex loses a molecule of water and forms an activated bridged intermediate with cobalt (III) ammine complex. The activated bridged intermediate consists of chloride ion as bridge. This chloride ion is provided to the activated complex by inert Co(III) ammine complex. This can be proved by taking labelled chlorine in the reaction and when no labelled chloride ion is present in the chromium complex.

The electron is transferred from Cr^{+2} to Cr^{+3} through chloride bridge to convert Cr^{+2} to Cr^{+3} and Co^{+3} to Co^{+2}. The activated intermediate then decomposes to hexa coordinated chromium complex and ~~pat~~ penta coordinated cobalt (II) complex. The penta ammine Co(II) complex then picks a molecule of water from the medium and transforms into hexa-coordinated Co(II) complex. This complex being labile gets activated and transform into hydrated complex.

The rate of reaction depends upon concentration of Co(III) ammine complex and chromium aquo complex. Similar type of mechanism is observed for the reaction.

$$[Co(NH_3)_5X]^{+2} + [Cr(H_2O)_6]^{+2} + 5H_3O^{+} \longrightarrow [Co(H_2O)_6]^{+2} + [Cr(H_2O)_5X]^{+2} + 5NH_4^{+}$$

The relative rate of electron transfer reactions for various halides is in the order

$$F^{+} < Cl^{-} < Br^{-} < I^{-}$$

Outer Sphere Mechanism: ✓

The outer sphere mechanism will operate in a system where both reducing agent and oxidising agent are inert for substitution and electron transfer occurs at a rapid rate than substitution.

On the other hand the inner sphere mechanism occurs for the system which contains atleast one labile complex. In outer sphere mechanism, the electron transfer occurs directly from one species to other and ligands act as conducting media. The outer sphere mechanism involves the following elementary steps.

(i) The oxidant and reductant interact and form a 'Precursor Complex'.

$$\text{oxidant} + \text{Reductant} \longrightarrow [\text{oxidant} \| \text{reductant}]$$

(ii) In the second step chemical activation of precursor complex occurs, electron transfer and relaxation to successor Complex

$$[\text{oxidant} \| \text{reductant}] \longrightarrow \text{Oxidant}^{-} \| \text{Reductant}^{+}$$

(iii) In the final step, the successor Complex dissociates into products.

$$\text{oxidant}^{-} \| \text{Reductant}^{+} \longrightarrow \text{Oxidant}^{-} + \text{Reductant}^{+}$$

The reaction between Cobalt(III) ammine complex and ferrocyanide ion proceeds through outer sphere mechanism.

$$[Co(NH_3)_5(H_2O)]^{+3} + [Fe(CN)_6]^{-4} \longrightarrow [Co(NH_3)_5(H_2O)]^{+2} + [Fe(CN)_6]^{-3}$$

The mechanism for the above reaction is

(a) $[Co(NH_3)_5(H_2O)]^{+3} + [Fe(CN)_6]^{-4} \longrightarrow [Co(NH_3)_5(H_2O)^{+3} \| Fe(CN)_6^{-4}]$

(b) $[Co(NH_3)_5(H_2O)^{+3} \| Fe(CN)_6^{-4}] \longrightarrow [Co(NH_3)_5(H_2O)^{+2} \| Fe(CN)_6^{-3}]$

(c) $[Co(NH_3)_5(H_2O)^{+2} \| Fe(CN)_6^{-3}] \longrightarrow [Co(NH_3)_5(H_2O)]^{+2} + [Fe(CN)_6]^{-3}$

The co-ordinated ion is sufficiently inert for substitution and electron transfer occurs at rapid rate than substitution.

Another example for electron-transfer in the complex ion of same metal with different oxidation state is -

$$[Fe(CN)_6]^{-4} + [Fe(CN)_6]^{-3} \longrightarrow [Fe(CN)_6]^{-3} + [Fe(CN)_6]^{-4},$$

The reaction occurs very rapidly at 40c and the rate of the reaction is studied
by labelling technique. Both the iron complexes (oxidant and reductant) are inert for
substitution, the normal bond length of Fe-C in ferricyanide is shorter than Fe-C
bond length in ferrocyanide. After electron transfer the bond length of $[Fe(CN)_6]^{-3}$ ion is
longer than Fe-C bond length in $[Fe(CN)_6]^{-4}$. i.e. In the newly formed $[Fe(CN)_6]^{-3}$
the Fe-C bond length is longer than the Fe-C bond length in $[Fe(CN)_6]^{-4}$

The rate of the reaction can be determined basing on π^* & σ^* ~~[illegible]~~ nature of
electron donor molecular orbital of the reductant and receptor molecular orbital of the
oxidant. Much faster reactions can be observed when both the molecular orbitals of
reductant and oxidant are of π^* nature.

But in case of cobalt ammine complexes the electron transfer reactions are
much ~~[illegible]~~ slower

$$[Co(NH_3)_6]^{+2} + [Co(NH_3)_6]^{+3} \longrightarrow [Co(NH_3)_6]^{+3} + [Co(NH_3)_6]^{+2}$$

The difference in the Co-N bond length in the two complexes is much larger
than the difference in Fe(II)|Fe(III) complexes. Hence the reaction occurs at a slow rate.

Another important reason for ~~[illegible]~~ slowness of reaction is wide difference in
the electronic configuration of two complexes [one is $t_{2g}^5 e_g^2$ and the other has t_{2g}^6]. One is
a low spin complex and the other one is high spin complex ∴ Hence a transfer of electron
will result in the transformation of high spin complex to low spin and low spin complex
to high spin complex which requires high activation energy. Thus the reaction
occurs at slow rate.

A net chemical change can be observed in a reaction when the standard free energy
is negative.

The redox reactions between complex ions of different metals is ~~[illegible]~~ called
'Crossed reaction'. The rate of this reaction is faster. The rate constant for such reaction
can be determined by ~~[illegible]~~ 'Marcus treatment' or Marcus Hush equation

The rate constant k_{12} of the crossed reaction can be calculated using

$$k_{12} = (k_1 k_2 K_{12} f)^{1/2}$$

K_{12} is the equilibrium constant of the crossed reaction.

$$[Fe(CN)_6]^{-4} + [Mo(CN)_8]^{-3} \rightleftharpoons [Fe(CN)_6]^{-3} + [Mo(CN)_8]^{-4}$$

k_1 and k_2 are rates of exchange reactions.

$$[Fe(CN)_6]^{-4} + [Fe(CN)_6]^{-3} \xrightarrow{k_1} [Fe(CN)_6]^{-3} + [Fe(CN)_6]^{-4}$$

$$[Mo(CN)_8]^{-3} + [Mo(CN)_8]^{-4} \xrightarrow{k_2} [Mo(CN)_8]^{-4} + [Mo(CN)_8]^{-3}$$

$\cancel{\ln f = \frac{(\ln K_{12})^2}{4 \ln k_1k_2/Z^2}}$ [from [illegible]

f is a parameter

$\ln f = \frac{(\ln K_{12})}{4\ln k_1k_2Z^2)}$ $\cancel{\log f = \frac{\log K_{12}}{4(\log k_1k_2Z^2)}}$

Where Z is a measure of number of collisions occurring between neutral species of solution in unit time at a mean separated distance in the activated complex.

* black Note

Complimentary and non complimentary reactions:

Complimentary reactions are the redox reactions in which the oxidant and reductant are changing the oxidation state by the same number. A consequence such reaction is that only one molecule of each reactant is required to reduce.

Eg: $Sn^{+2} + Tl^{+3} \longrightarrow Sn^{+4} + Tl^{+}$

$Sn^{+2} + Hg^{+2} \longrightarrow Sn^{+4} + Hg^{0}$

Non complimentary reactions are the redox reactions in which oxidant. reductant change their oxidation states by different numbers. So different no. of molecules of oxidant and reductant are to be written in stoichiometric eq.

Eg: $Tl^{+3}_{(aq)} + 2Fe^{+2}_{(aq)} \longrightarrow Tl^{+}_{(aq)} + 2Fe^{+3}_{(aq)}$

$2V^{+4}_{(aq)} + Tl^{+}_{(aq)} \longrightarrow 2V^{+3}_{(aq)} + Tl^{+3}_{(aq)}$

* Note: A large chemical activation is required for cross reaction to occur. But these reactions occur fastly because the large activation energy [Ea] required is partly compensated by a negative free energy change (i.e $\Delta G < 0$) and the products are more stable than reactants. The rate is maximum when electron is transferred from a π^* to a π^* orbital.