Mechanism of Substitution Reactions in Octahedral Complexes

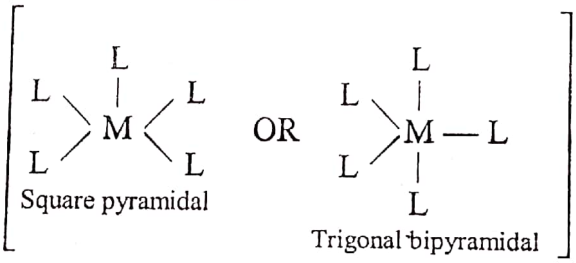
The mechanism of a reaction is the sequence of elementary reactions involved in a reaction. Substitution reactions in octahedral complexes take place through either of the following three mechanisms :

1. Dissociative (D) Mechanism
2. Associative (A) Mechanism
3. Interchange (I) Mechanism

1. Dissociative (D) Mechanism : In the dissociative mechanism, there is a step in which an intermediate of reduced coordination number is formed *i.e.,* the M–X bond is fully broken before the M–Y bond begins to form.

$$[L_5MX] \xrightarrow[-X]{\text{slow}} [L_5M] \xrightarrow[\text{fast}]{+Y} [L_5MY]$$

Intermediate
C.N. =5



Square pyramidal OR Trigonal bipyramidal

where L is an inert ligand, X is labile (leaving ligand) and Y is the entering ligand.

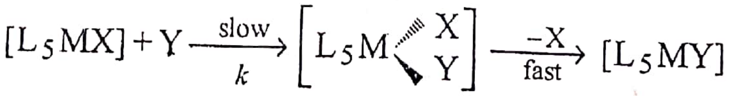
The rate determining step is the slowest elementary reaction. The rate of overall substitution reaction depends only on the concentration of the original complex, $[ML_5X]$ and is independent of the concentration of the incoming ligand Y.

$$\text{Rate} = k[ML_5X]$$

This reaction is of first order in $[ML_5X]$ and $[ML_5X]$ gets dissociated is rate determining step. Thus, this reaction is also called dissociative SN^1 mechanism (substitution, nucleophilic first order).

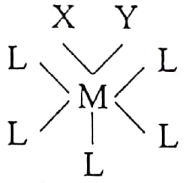
Most substitution reactions in octahedral complexes takes place by dissociative mechanism in which an intermediate of coordination number = 5 (most probable square pyramid) is formed.

2. Associative (A) Mechanism : An associative mechanism involves a step in which an intermediate is formed with a higher coordination number than the original complex *i.e.,* the incoming ligand Y directly attacks the original complex to form an intermediate with a coordination number = 7 in the rate determining step. The rate determining step is slow.



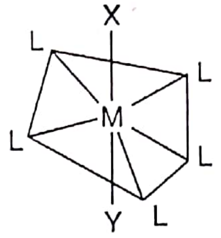
$$[L_5MX] + Y \xrightarrow[k]{\text{slow}} \left[L_5M\begin{matrix}X\\Y\end{matrix}\right] \xrightarrow[\text{fast}]{-X} [L_5MY]$$

Intermediate
C.N. = 7



Monocapped octahedron

OR



Pentagonal bipyramid

This intermediate might be expected a monocapped octahedral structure in which the X and Y ligands share one of the octahedral sites or a pentagonal bipramidal structure. The second step is the dissociation of ligand X to give the product. The rate of reaction depends on the concentration of both ML_5X and Y. Therefore,

$$\text{Rate} = k[ML_5X][Y]$$

This reaction is of second order and this associative mechanism is also called SN^2 (Substitution, nucleophilic, second order) mechanism.

3. Interchange (I) Mechanism : This mechanism takes place in one step without forming a fairly stable intermediate, instead the leaving and entering ligands exchange in a single step forming an activated complex. The interchange mechanism is common for many reactions of octahedral complexes. The activated complex (also called as transition state) has very little or no stabilization energy and immediately passes on to products or reverts to the reactants.

$$L_5MX + Y \longrightarrow \underset{\text{Activated complex}}{[Y\ldots\ldots L_5M\ldots\ldots X]} \longrightarrow [L_5MY] + X$$

In this mechanism the M–X bond begins to break and starts to move away from the metal and the M–Y bonds begins to form simultaneously and Y moves into the coordination sphere and no stable intermediate is formed.

Interchange mechanism is subdevided into two categories :

(i) Interchange Dissociative (I_d)

(ii) Interchange Associative (I_a)

(i) Interchange Dissociative Mechanism (I_d) : The M–Y bond begins to form before the M–X bond is fully broken but the M–X bond breaks preferentially and the interchange is closer to a dissociative than to an associative mechanism, and no detectable intermediate appears.

(ii) Interchange Associative Mechanism (I_a) : The M–X bond begins to break before the M–Y bond is fully formed but the M–Y bond forms preferentially and the interchange is closer to associative and no detectable intermediate appears.

REACTION PROFILES FOR DISSOCIATIVE, ASSOCIATIVE AND INTERCHANGE MECHANISMS

A plot of free energy *versus* reaction pathway is called reaction profile or energy profile.

In an interchange mechanism a reactant absorbs energy and combines with the incoming ligand and form an activated complex or transition state before the formation of product. The energy difference between the reactants and transition state is called energy of activation, E_a. The transition state lies on the top of the reaction profile (like on top of the hill) and at this point reactant converts into product without no hesitation [Figure 7.7(a) and (b)].

If the activation energy is high, then the rate determining step is slow and if the energy of activation is low, rate determining step is fast.

In dissosiative (D) or associative (A) mechanism an intermediate of lower coordination number (= 5) or higher coordination number (= 7) is formed before the formation of product. Because an intermediate is more stable than a transition state, therefore, it will lie in a valley (or bit) in energy profile [Figure 7.7(c) and (d)]. The stability or existing time of an intermediate in a valley depends on how high the energy walls around the intermediate are :

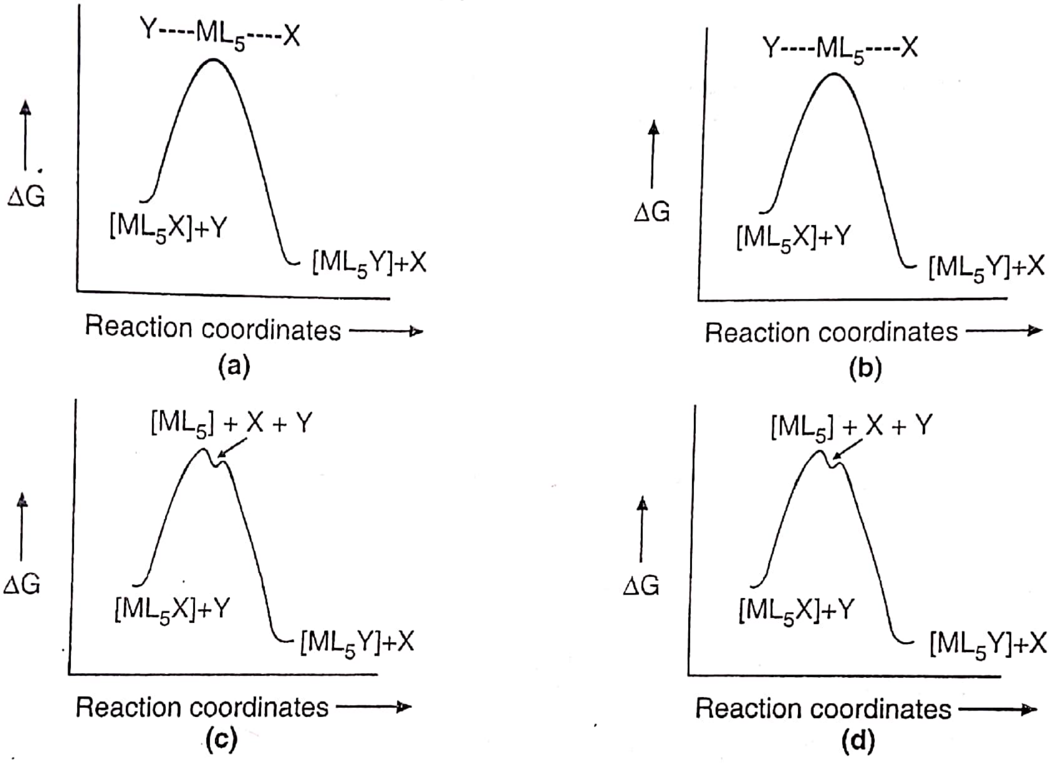


Figure 7.7 Energy Profile for : (a) Interchange dissociative (I_d), (b) Interchange associative (I_a), (c) dissociative (D), (d) Associative (A)

INTERPRETATION OF LABILITY AND INERTNESS OF TRANSITION METAL COMPLEXES

1. On the Basis of Valence Bond Theory : According to VBT, transition metals form, two types of octahedral complexes : (i) outer orbital complexes and (ii) inner orbital complexes. In outer orbital complexes, the outer *nd*-orbitals are involved in sp^3d^2-hybridization and in inner orbital complexes the inner $(n-1)$ d- orbitals are involved in d^2sp^3-hybridization. Thus, the M–L bonds in outer orbital complexes is larger, weaker and higher in energy whereas in inner orbital complexes the M–L bond is shorter, stronger and lower in energy. Thus, the transition metal octahedral complexes undergoing substitution reactions through dissociative mechanism would be labile if the M–L bond is weak and would be inert if M–L bond is comparatively strong . Thus, according to VBT, if the transition metal complexes undergoing substitution reactions through dissociative mechanism then all outer orbital complexes are labile and all inner orbital complexes are inert.