

REACTION MECHANISM OF OCTAHEDRAL COMPLEX COMPOUND

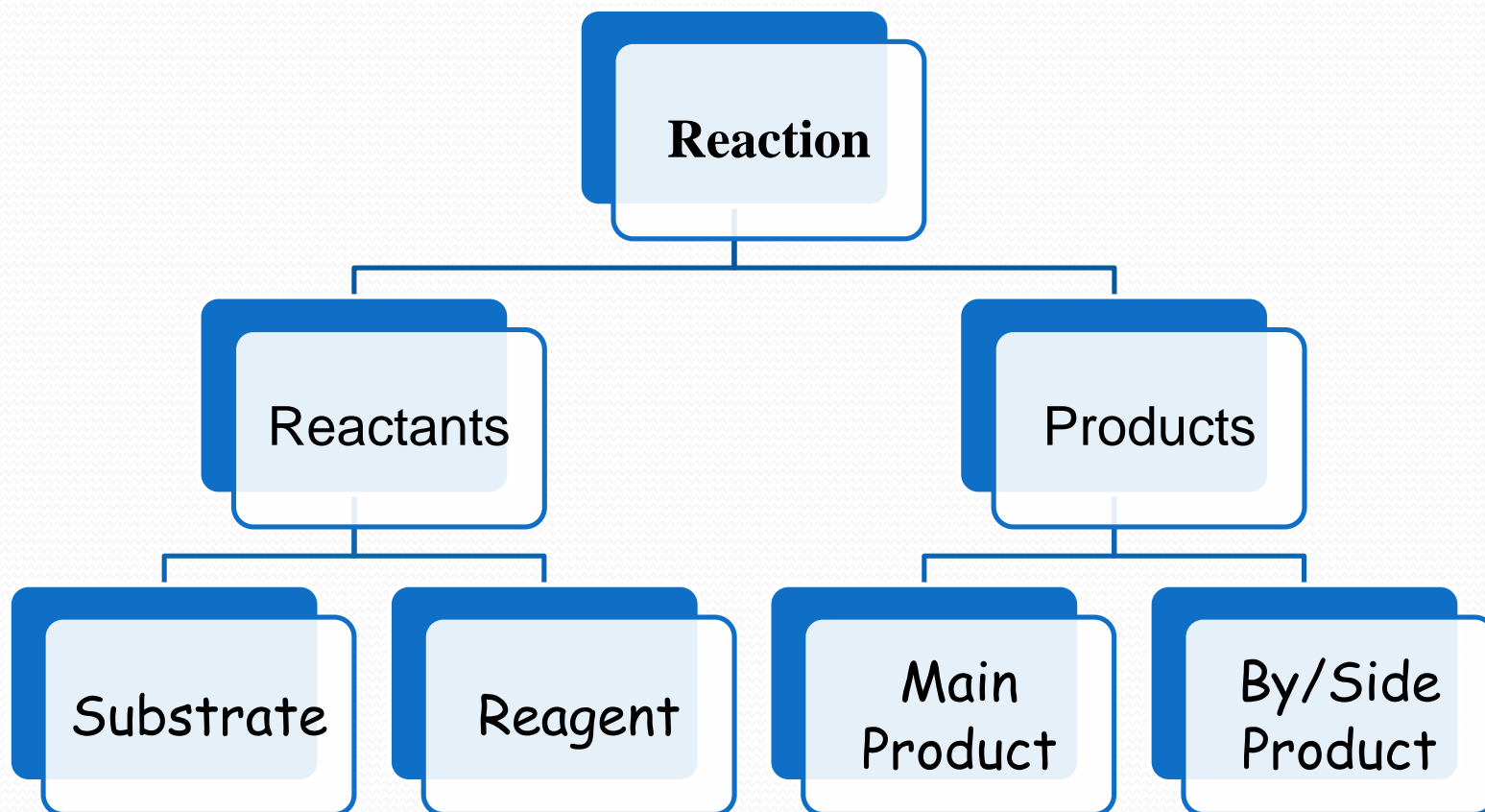
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Reaction Mechanism

Reaction: Breaking of old bond & formation of new bond is called reaction.



Mechanism: Explanation of over all steps occurring from reactant to product. It consists slow or fast step with activated complex & slow step is rate determining step i.e. mechanism determines rate of reaction & order of reaction.

Breaking of Bond

Homolytic fission



It occurs in presence of non polar solvent, H_2O_2 , UV light, diffused sunlight.

Heterolytic fission



Ionic reaction generally in presence of polar solvent, heat

Reaction Profile

Consider the reaction:



$M + L \rightleftharpoons$
Collisions
of > Energy

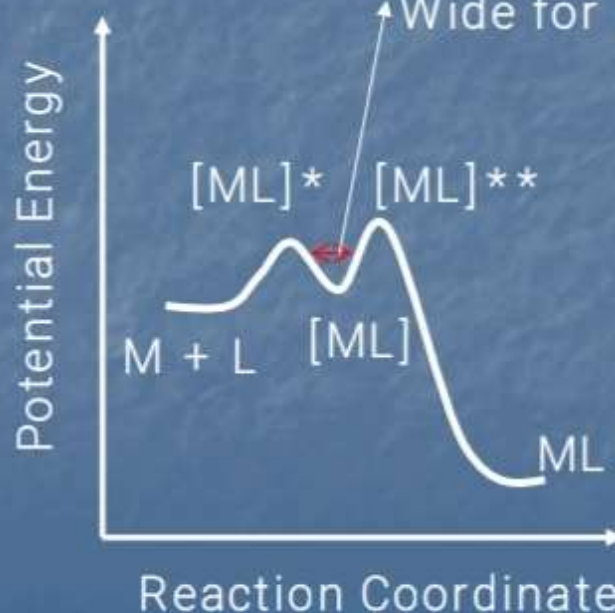
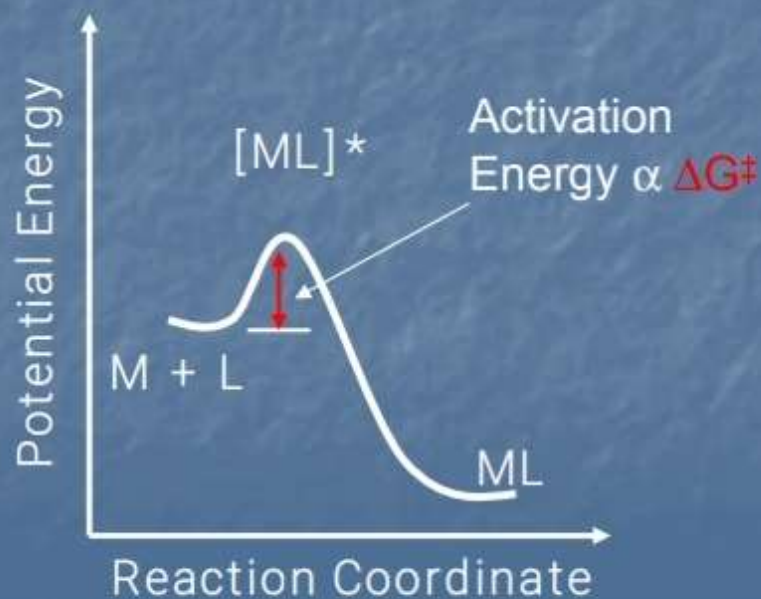
$[ML]^*$
Activated Complex
Transition State

$[ML] \rightleftharpoons$
Intermediate

$[ML]**$
Activated Complex

ML

Width related to entropy
Narrow for $-\Delta S$
Wide for $+\Delta S$



Types of Reactant

Electrophile : +ve charged (M^+) or lewis base (NH_3 , BF_3) / double bonded ($C=C$)

Nucleophile : -ve charged (OH^- , Cl^- , Br^-) or lewis acid / unfilled octet ($AlCl_3$, BF_3) double bonded (except $C=C$)

Types of reaction in complexes

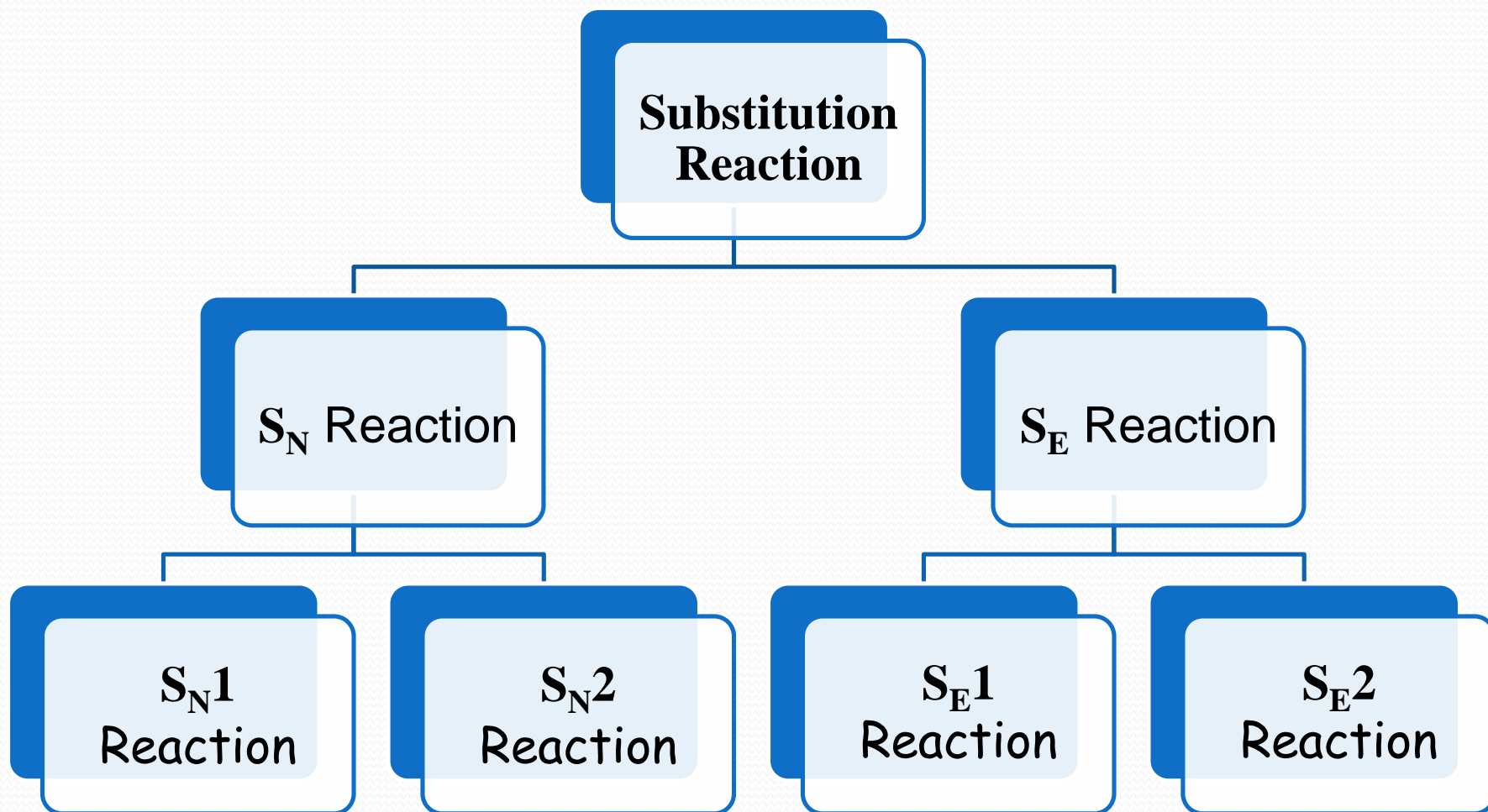
Substitution Reaction

Electron transfer
reaction

Isomerisation or
recemeration reaction

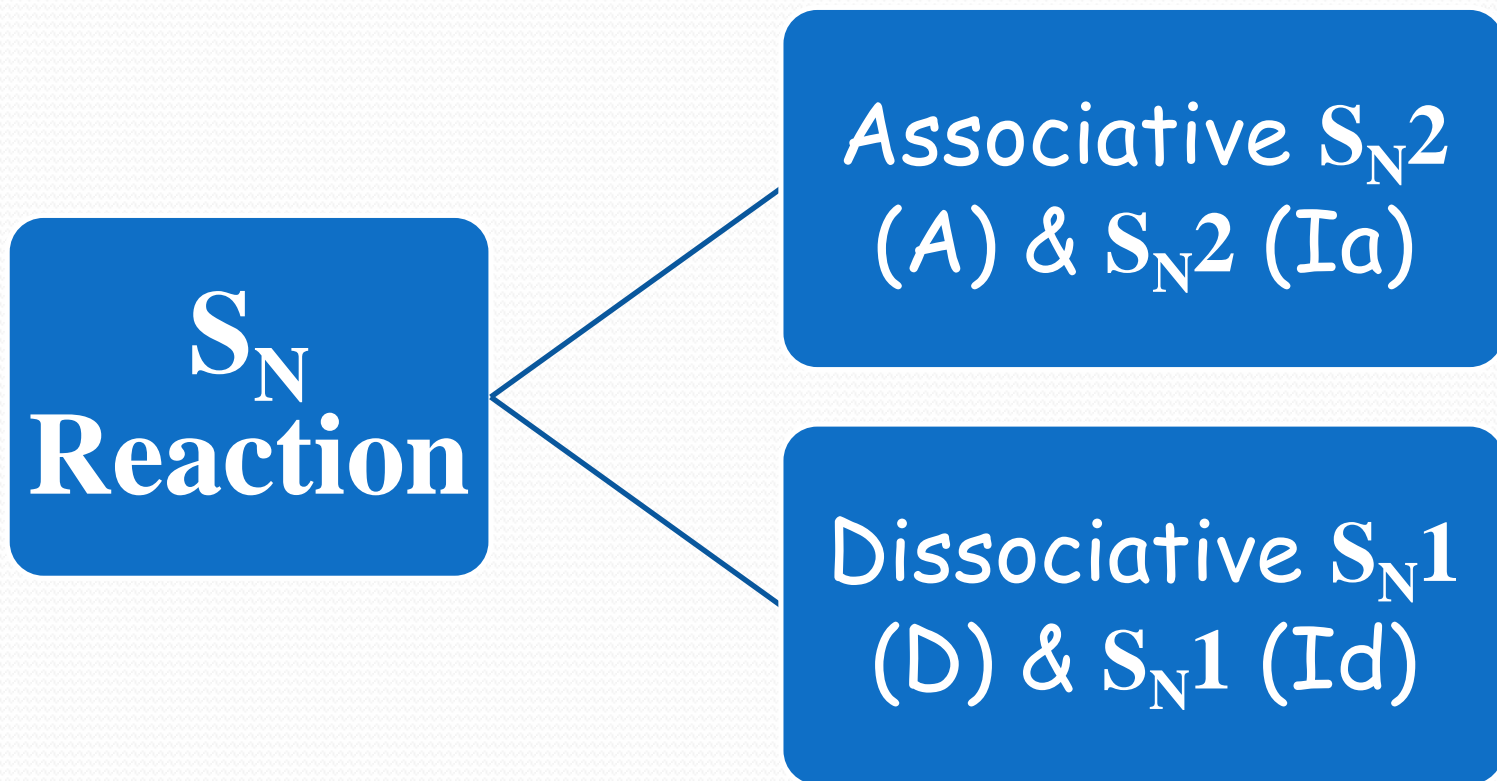
Substitution Reaction

Reaction in which one type of species are substituted by same types of other species. $ML_5X + Y = ML_5Y + X$



In inorganic Chemistry nucleophilic substitution reaction have been classified as modern classification.

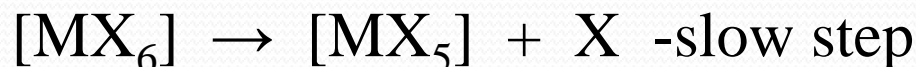
Substitution reactions involved either replacement of nucleophile ligand (S_N) by other ligands or replacement of metal by other electrophile metal ions (S_E) but we concern here with S_N reaction



S_N1 Reaction or Dissociative Mechanism

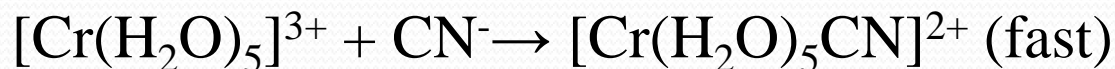
When Rate of reaction depends upon only one concentration term of reactant complex. So it is known as S_N1 reaction.

In this mechanism the complex first undergoes dissociation losing the ligand to be replaced, X and changes into a five coordinated intermediate which then readily adds the new ligand, Y.



Slow step is rate determining step

Example



The characteristics of S_N1 ,

1. Only one species, $[MX_6]$ is involved in the formation of the activated species in the slow step.
2. In the second step, the activated species undergoes fast reaction with incoming ligand, Y.
3. The activation energy for the first step is high and that for the second step is low.
4. The rate of the overall reaction depends on $[MX_6]$ and not on $[Y]$.
5. The reaction is first order with respect to MX_6 and is zero order with respect to Y.
6. In the formation of the activated complex, the coordination number of the metal ion is decreased by one.
7. The rate law for the substitution is $v = k_1[MX_6]$

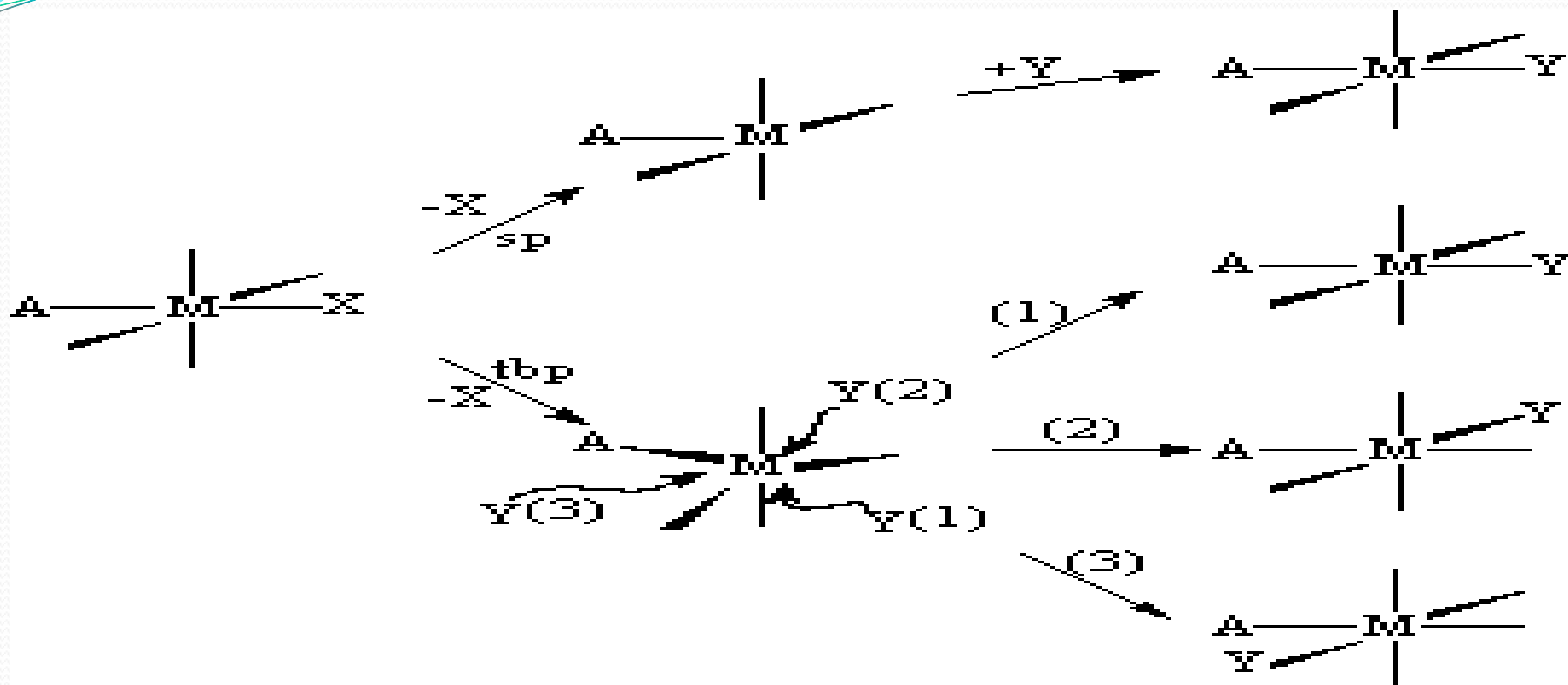
Types of intermediates formed during S_N1 reaction

Consider an octahedral complex MA_5X being attacked by a nucleophile, Y . If the reaction proceeds through a dissociative S_N1 mechanism, two types of intermediates can be formed.

1. The bond $M-X$ dissociates causing least disturbance to the remaining MA_5 intermediate which has a square pyramidal geometry. The intermediate MA_5 is then attacked by Y to produce MA_5Y .

2. The bond $M-X$ dissociates and the remaining MA_5 species immediately adjust the bond angles to produce a trigonal bipyramidal intermediate which is then attacked by Y to produce MA_5Y .

It is evident that the formation of a trigonal bipyramidal



intermediate involves the movement of at least two metal ligand bonds whereas no such movement is required during the formation of a square pyramidal intermediate. S_N1 reactions thus proceed generally through the more stable square pyramidal intermediate unless the trigonal bipyramidal intermediate is stabilized by π bonding.

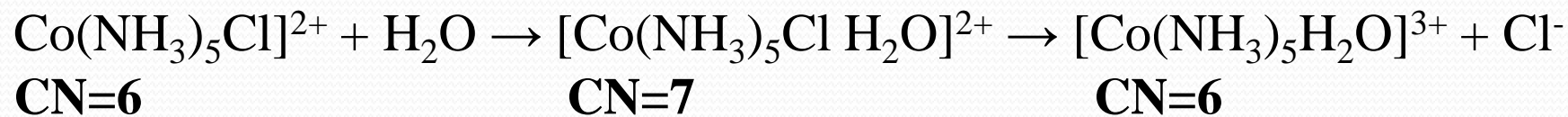
S_N2 or Associative mechanism

According to this mechanism, the new ligand first adds on to the complex to form a seven coordinated activated or intermediate complex which then readily undergoes dissociation to yield the final product.



In this case, the reaction rate depends upon the first step. i.e upon the concentration of the complex as well as the concentration of the incoming ligand Y. So it is associative & S_N2 reaction.

Example



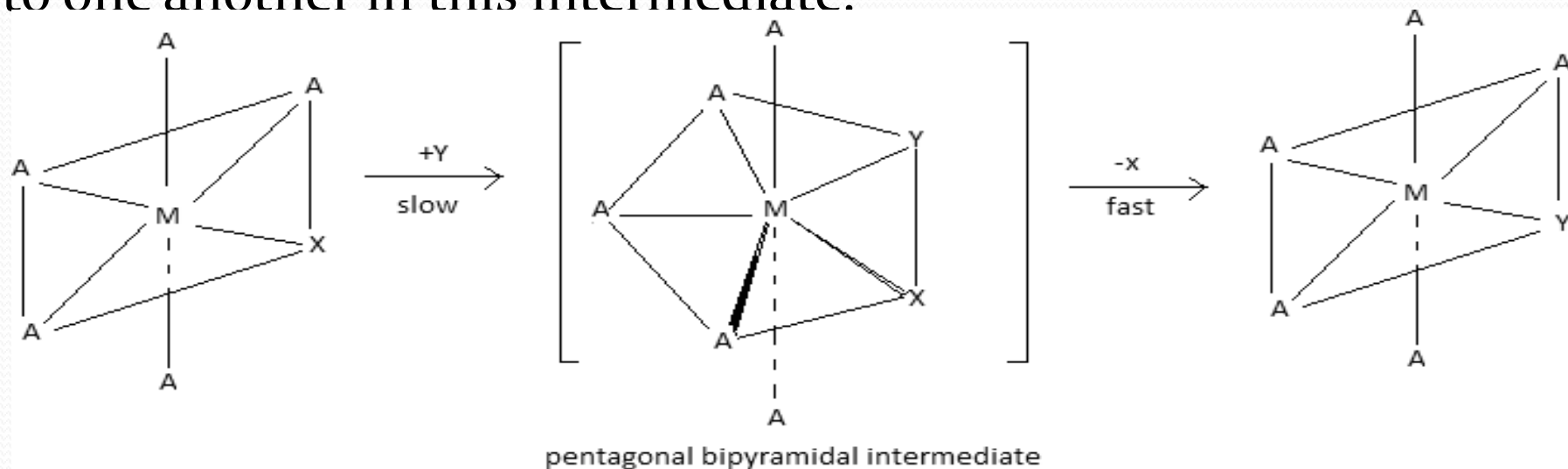
The characteristics of S_N2 ,

1. In this reaction, two species (MX_6 and Y) are involved in the formation of the activated species; Y is added to the reactant complex to form the activated species.
2. In the second fast step, the activated complex loses a ligand and the new ligand Y becomes a permanent part of the molecule.
3. The rate of the overall reaction depends on both $[MX_6]$ and $[Y]$.
4. The reaction is first order with respect to MX_6 and first order with respect to Y ; the overall order is 2.
5. In the formation of the activated species, the coordination number of the metal is increased.
6. The general rate law for the substitution is $v = k_1[MX_6][Y]$.

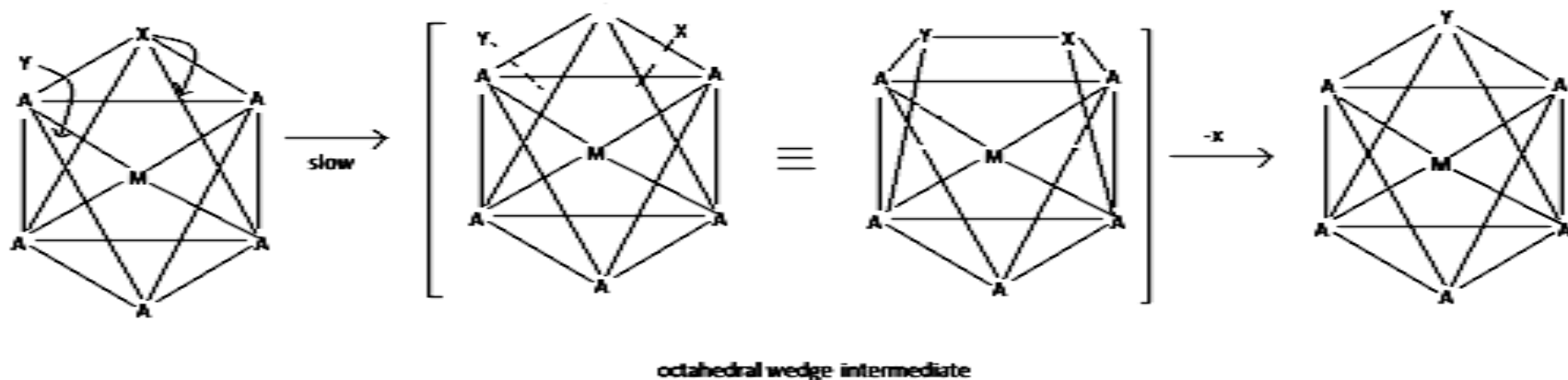
Types of intermediates formed during S_N2 reaction

In associative S_N2 mechanism, there are two types of intermediates.

If the nucleophile Y attacks through one of the edges of the octahedron, a pentagonal bipyramidal intermediate is formed. The formation of pentagonal bipyramidal intermediate requires the movement of at least four ligands to adjust the nucleophile Y . The ligand- ligand repulsions also increase the energy of pentagonal bipyramidal intermediate because the decrease in $A-M-A$ bond angles brings the electron pairs of metal bonds nearer to one another in this intermediate.



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 another triangular face so that the octahedral wedge intermediate formed has both X and Y ligands in equivalent positions. The formation of an octahedral wedge intermediate requires minimum movement of ligands and the ligand- ligand repulsions are less than the repulsions in pentagonal bipyramidal intermediate. i.e it requires less energy than pentagonal bipyramidal intermediate. Therefore S_N2 reactions generally proceed through an octahedral wedge intermediate.



S_N1 Vs S_N2 mechanisms

S_N1 and S_N2 mechanisms can be differentiated from each other by the following points.

1. In S_N1 process, the rate determining slow step is a metal ligand bond breaking step, and the coordination number of the complex is reduced from 6 to 5. In S_N2 process, the rate determining step involves a metal ligand bond making step and the coordination number is increased to 7.
2. The rate of S_N1 mechanism is first order with respect to MX_6 . i.e rate determining is unimolecular. On the other hand, the rate determining step for S_N2 mechanism is bimolecular. i.e its reaction rate is second order: first order with respect to MX_6 and first order with respect to Y.

References & further reading

S & Atkins, Oxford Inorganic Chemistry, Fourth Edition

Alagappa university, M. Sc. Chemistry

Pearson, Inorganic chemistry

Fmiza Hammer Synthesis & reaction of organometallic compound



Thank You

