
M.Sc Semister 1
Paper I
Inorganic Chemistry

Department of Chemistry

L.S COLLEGE MUZAFFARPUR
B. R. A. BIHAR UNIVERSITY
Dr. Priyanka

TOPIC:-Kinetics of Octahedral Substitution

KINETICS OF OCTAHEDRAL SUBSTITUTION

Substitution reactions involve the activated complex which is most unstable changes to give the product x-y and z. Thus the various steps responsible for the reaction are

$X + Y - Z \rightarrow X .... Y \quad Z \rightarrow X - Y + Z$

Reactants Activated complex Products
(Transition State)
Unstable

The difference in energy between the reactants and the activated complex is called activation energy.

These reaction involves two process (1) SN^1 and SN^2

1. In SN^1 process the rate-determining slow step is a metal-ligand bond breaking step, since the co-ordination No. of the complex MX_5Y (=6) is decreased to 5 which is the co-ordination number of the intermediate MX_5.

For a ligand replacement reaction of the general type

$$[L_nMX] + Y = [L_nMY] + X$$

(For simplicity all charges are omitted), the mechanism analogous to unimolecular nucleophilic substitution (sN^1) at a carbon atom would be:

$$[L_nMX] \xrightarrow{s\ low} [L_nM] + X$$

$$[L_nM] + y \xrightarrow{fast} [L_nMY] + X$$

The rate of SN^1 mechanism is first order with respect to MX_5Y, i.e. the rate-determining step in this mechanism is unimolecular.

On the other hand the rate determining step for SN^2

mechanism is bimolecular, i.e. its rate of reaction is second order

first order with respect to MX_5Y and first order with respect to Z. Thus

for SN^1 mechanism rate = K $[MX_5Y]$,

and

for SN^2 mechanism rate = K $[MX_5Y][Z]$

Here, it may be mentioned that the kinetic data would be equally compatible with ion-pair formation (if both reactants are ions) followed by a unimolecular reaction of the ion-pair:

$$[L_n MX] + Y \xrightarrow{k1} [L_n MX]\, Y$$

$$[L_n MX]\, y \xrightarrow{slow} [L_n MY] + X$$

This leads to

$$\frac{d}{dt}[L_n MY] = \frac{k_1 k_2 [L_n MX][Y]}{k_{-1} + k_2}$$

$$= k[L_n MX][Y]$$

where

$$k = \frac{k_1 k_2}{k_{-1} + k_2}$$

Detailed investigation of such a reaction can lead to a value for k_1/k_{-1}, the equilibrium constant for ion-pair formation.

6.3.1 Nucleophilic Substitution

As has been motioned, nucleophile substitution reactions in octahedral complexes follow either of the two mechanisms, the dissociation mechanism or the $SN^{-}1$ mechanism and the association mechanism or the $SN^{-}2$ mechanisms. The rate determining step in association or dissociation, may be worked out by analysing the rate-laws of the reactions taking place and the specific conditions under which the reactions take place. The difference in these two mechanisms depends on, whether the rate determining steps is the formation of a new Y............. M bond or the dissociation of an old M. .... X bond.

(a) SN^{-1} or Dissociation Mechanism

The nucleophilic substitution unimolecular reaction actually proceeds in two steps. In the first, slow and rate determining step, one ligand Y is lost and a five coordinated intermediate is formed.

In the second step the short-lived penta-coordinated intermediate of very limited stability is attacked rapidly by the nucleophilic reagent, Z to give the complex, MX_5Z.

There two steps are diagrammatically shown in Fig. 6.3

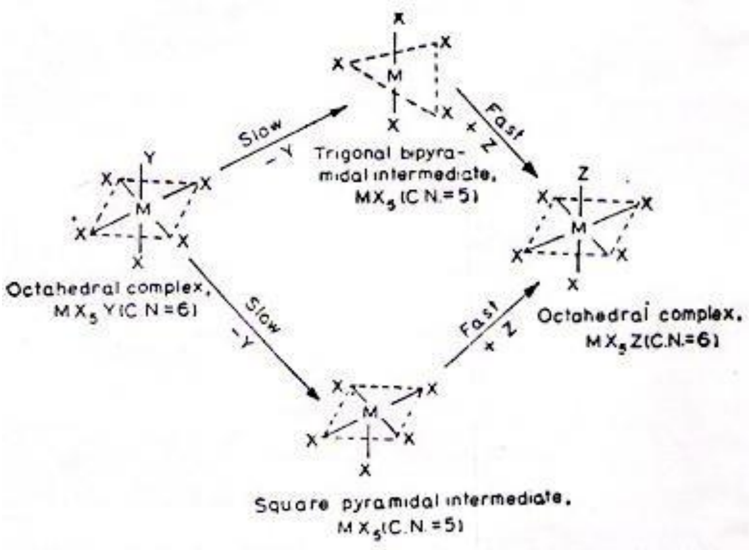

Fig. 6.3: S_N1 or dissociation mechanism for the substitution reaction $MX_5Y + Z \rightarrow MX_5Z + Y$

For the S_N1 mechanism, the following points are important:

(1) The trans effect of the ligands would not be operative due to the dissociation of the ligand completely from the octahedral complex.

(2) The rates of S_N1 substitution (k_1) should be inversely proportional to the strength of the Co-L bond, and depend on the charge, steric factors, and chelating effects of the leaving group L.

(3) Increase in the electron density on Co atom by the electron donors in S_{Nn} should assist the M-L bond breaking.

(4) k_1 is independent of the nature of E as well as its concentration except for the OH^- group for which the reaction is of the second order.

(5) Cis effect. Ligands having another pair of electrons like CNS^- or OH^- increase the rate of hydrolysis of the complexes about ten fold when present cis to L, as compared to the rate when they are present trans to L. This is due to the stabilization of the square pyramidal complex by the electron pair donation by OH^- or CNS^- along the Cis position through p-d-π bonding (Fig. 6.4). No rearrangement takes place and the product is 100 percent Cis isomer. The ligands that do not show the eis effects are those that do not have an extra pair of electrons (NH_3) or are themselves π acceptors (NO_2^-, CO, NO, etc.).

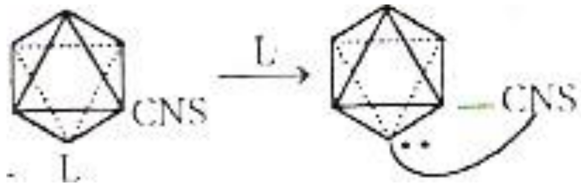

Fig. 6.4: Cis-effect

From Table 6.4, it can be seen that for the formation of the 5-coordinate intermediate, high energy changes are required for the low spin d^3, d^6 and d^8 and high spin d^3 and d^8 ions. Hence, these complexes do not favour the S_N1 mechanism for the substitution.

Table 6.4 Changes in LFSE (in Dq) for Changing a 6-coordinate Complex to a 5-Coordinate (SP) or a 7-Coordinate (Pentagonal Bipyramid) species.

System	High spin		Low spin	
	CN = 5	CN = 7	CN = 5	CN = 7
d^o, d^{10}	0.00	0.00	0.00	0.00
d^1	0.57	1.28	0.57	1.28
d^2	1.14	2.56	1.14	2.56
d^3	-2.00	-4.26	-2.00	-4.26
d^4	3.14	-1.07	-1.43	-2.98
d^5	0	0	-0.86	-1.70
d^6	0.57	1.28	-4.00	-3.52
d^7	1.14	2.56	1.14	-5.34
d^8	-2.00	-4.26	-2.00	-4.26
d^9	3.14	-1.07	3.14	-1.07

+ value indicate gain in CFSE while - values indicate loss in CFSE.

(b) SN-2 or Association Mechanism

SN-2 or the nucleophilic bimolecular substitution reaction also proceeds through two steps:

The first step is slow step and involves the attachment of the incoming nuclepohile, Z to MX_5Y to form a seven-coordinate unstable intermediate (perhaps transition state) which is probably pentogonal bipyramidal in shape. Obviously it is a metal-ligand bond-making step.

$$MX_5Y \xrightarrow{Slow(+Z)} MX_5YZ$$

(C.N.=6) Unstable seven-coordinatee
Intermediate (C.N.=7)

This reaction is rate-determining and bimolecular because two reactants viz MX_5Y and Z are involved in this step. Thus the rate of this rate-determining reaction is of second order: first order with respect to the complex, MX_5Y and first order with respect to the entering ligand, Z, i.e.,

Rate of reaction = $K[MX_5Y][Z]$

In the second step either at the same as Z adds to MX_5Y or shortly thereafter, Y leaves MX_5YZ rapidly to give MX_5Z. This is a fast step.

$$MX_5YZ \xrightarrow[-Y]{Fast} MX_5Z$$

Unstable seven-coordinatee Intermediate (C.N.=7)   (C.N.=6)

Both these steps are shown diagrammatically in Fig. 6.1

This mechanism is similar to Eigen-Wilkins Mechanism, which presents formation of the association complex $[L\text{-}MX_5\text{-}Z]$ in the pre-equilibrium step: Thus the following equilibrium will be established:

$$LMX_5 + Z \leftrightarrows MX_5.\ Z;\ K = \frac{[LMX_5.Z]}{[LMX_5][Z]}$$

The value of the equilibrium constant, K, for the association complex, may be obtained using Fuoss-Eagan equation,

$$K = \frac{4}{3}\pi a^3 N_A e^{-v/RT}$$

where, a = Nearest reach-distance

v = Coulomb potential energy at a-distance

N_A = Avogadro number = $(Z_1Z_2e^2/4\pi ea)$

As in the octahedral complexes, the six ligands are already present along the three C_4 axes along which the e_g orbitals are concentrated, the t_{2g} orbitals that lie along the C_2 axes most probably have to be approached by the seventh ligand to form the associated complexes in the S_N2 process.

Hence, if the t_{2g} orbitals are filled (Co^{2+} in low spin octahedral complexes), the higher activation energy required to empty one of the t_{2g} orbitals will make the complex inert.

Table 6.4 also shows that due to the loss of the CFSE energies, the d^3 and low spine d^6 ions require highest activation energies, followed by d^7, d^8 (Ni^{2+}complexes are labile due to the expulsion of ligand by the e_g orbitals) and high spin d^3 and d^8 ions.

Thus, S_N-1 and S_N-2 reactions differ in the following points:

(i) In S_N1 process the rate-determing slow step is a metal-ligand bond breaking step, since the coordination number of the complex, MX_5Y (=6) is decreased to 5 which is the coordination number of the intermediate, MX_5. On the other hand in S_N2 process the rate-determining step involves a metal-ligand bond making step, since C.N.=6 is increased to 7.

(ii) The rate of S_N1 mechanism is first order with respect to MX_5Y, i.e., the rate-determining step in this mechanism is unimolecular. On the other hand the rate-determining step for S_N2 mechanism is bimolecular, i.e. its rate of reaction is second order: first order with respect to MX_5Y and first order with respect to Z. Thus:

for S_N1 mechanism rate = $K[MX_5Y]$

and for S_N2 mechanism rate = $K[MX_5Y][Z]$