

CHAPTER 3

Reaction Mechanism of Transition Metal Complexes – I:

❖ Inert and Labile Complexes

The metal complexes in which the rate of ligand displacement reactions is very fast and hence show high reactivity are called as labile Complexes and this property is termed as lability. On the other hand, the metal complexes in which the rate of ligand displacement reactions is very slow and hence show less reactivity are called as inert complexes and this property is termed as inertness.

Thermodynamic stability is the measure of the extent to which the complex will form or will be transformed into another complex when the system has reached equilibrium while kinetic stability refers to the speeds at which these transformations take place. The thermodynamic stability depends upon the energy difference of the reactant and product if the product has less energy than that of the reactant, it will be more stable than the reactant. The thermodynamic stability of metal complexes is calculated by the overall formation constant. If the value of $\log \beta$ is more than 8, the complex is considered as thermodynamically stable.

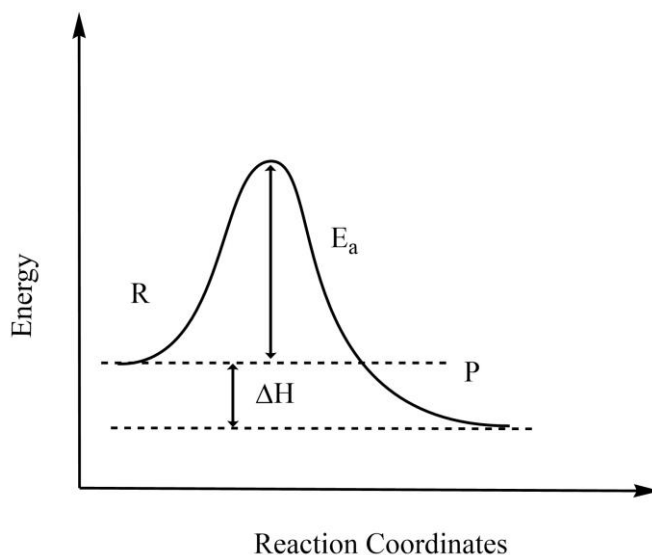


Figure 1. The general reaction coordinates diagram.

The kinetic stability of the complex depends upon the activation energy of the reaction. If the activation energy barrier is low, the reaction will take place at a higher speed. These types of complexes are also called as kinetically unstable. If the activation energy barrier is high, the substance will react slowly and will be called as kinetically stabilized or inert. There is no correlation between thermodynamic and kinetic stability. Thermodynamically stable products may labile or inert and the vice versa is also true.

➤ **Labile and Inert Complexes on the Basis of Valence Bond Theory**

According to the valence bond theory of chemical bonding, octahedral metal-complexes can be divided into two types.

1. Outer orbital complexes: These complexes have sp^3d^2 hybridization and are generally labile in nature. Valence bond theory proposed that the bonds in sp^3d^2 hybridization are generally weaker than that of $(n-1)d^2sp^3$ orbitals and therefore they show labile character. For example, octahedral complexes of Mn^{2+} , Fe^{2+} , Cr^{2+} complexes show fast ligand displacement.

2. Inner orbital complexes: Since d^2sp^3 hybrid orbitals are filled with six electron pairs donated by the ligands, d^n electron of metal will occupy d_{xy} , d_{yz} and d_{xz} orbitals. These d^2sp^3 hybrid orbitals can form both inert or labile complexes. In order to show lability, one orbital out of d_{xy} , d_{yz} , d_{xz} must be empty so that it can accept another electron pair and can form seven coordinated intermediate which is a necessary step for the associative pathway of ligand displacement. On the other hand, if all the d_{xy} , d_{yz} , d_{xz} orbitals contain at least one electron, it will not be able to accept electron pair from the incoming ligand and hence is expected to show inert character.

➤ **Labile and Inert Complexes on the Basis of Crystal Field Theory**

Octahedral complexes react either by SN_1 or SN_2 mechanism in which the intermediates are five and seven-coordinated species, respectively. In both cases, the symmetry of the complex is lowered down and due to this change in crystal field symmetry, the crystal field stabilization (CFSE) value also changes. The cases for lability and inertness are:

1. Labile complexes: If the CFSE value for the five or seven-membered intermediate complex is greater than that of the reactant, the complex will be of labile nature as there is zero activation energy barrier.

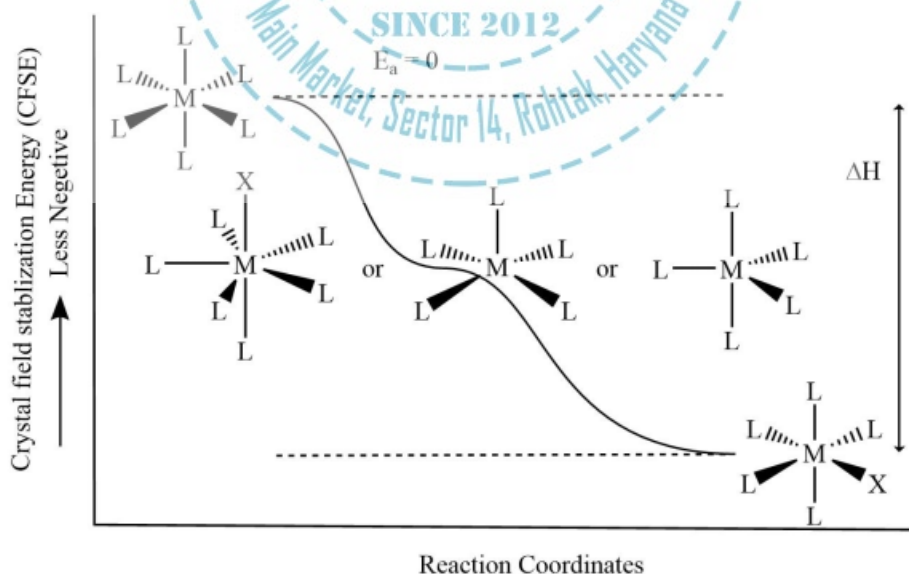


Figure 2. The reaction coordinates diagram for ligand displacement reactions in labile metal complexes.

2. Inert complexes: If the CFSE value for the five or seven-membered intermediate complex is less than that of the reactant, the metal complex will be of inert nature as loss of CFSE will become the activation energy barrier.

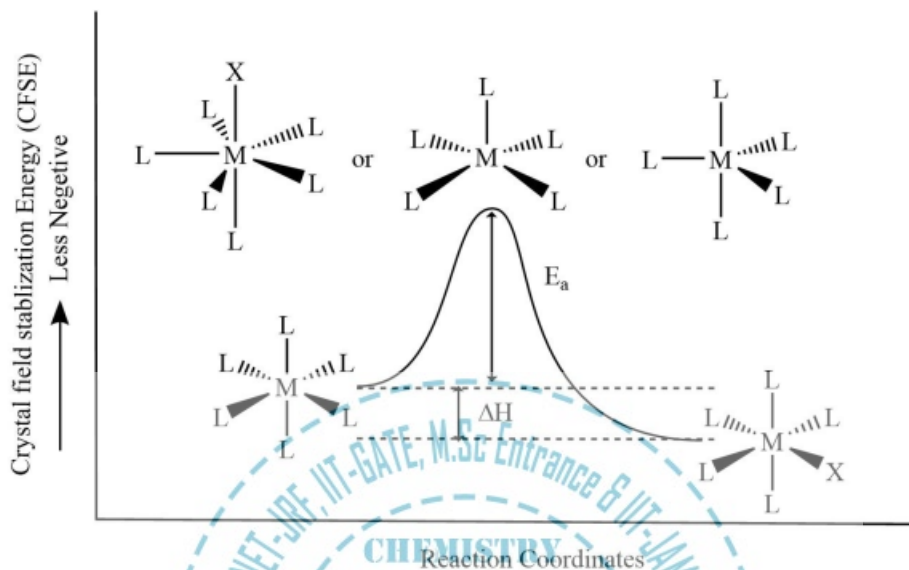


Figure 3. The general reaction coordinates diagram for ligand displacement reactions in inert metal complexes.

Hence, the gain of crystal field stabilization energy will make complex labile while the loss of CFSE will make complex inert. The calculation of CFSE relies upon the following assumptions:

1. All six-coordinated complexes should be treated as perfect octahedral even if the mixed ligands are present.
2. The inter-electronic repulsive forces arising from d -subshell can simply be neglected.
3. The Dq -magnitude for reacting as well as the intermediate complexes are assumed to be the same though they might have considerably different values.
4. The Jahn-Teller distortion should also be neglected in all calculations.

Evidence for the lability and inertness: The ligand displacement can be dissociative or associative depending upon the nature of the reaction.

(i) For SN_1 or dissociative pathway, the 5-coordinate intermediate can be trigonal-bipyramidal or square-pyramidal. However, it has been observed that the dissociative mechanism occurs through a square-pyramidal intermediate. Hence, the gain or loss of the crystal field stabilization energy can be calculated as:

$$\text{CFSE gain or loss} = \text{CFSE of Squarepyramidal Intermediate} - \text{CFSE of Octahedral Reactant}$$

If the CFSE gain-or-loss is negative, it means that activation energy is zero because it cannot be negative.

Table 1. CFSE values of high-spin (HS) and low-spin (LS) octahedral complexes undergoing ligand displacement reactions through SN_1 mechanism

Configuration	CFSE for octahedral reactant (Coordination No = 6)	CFSE for square-pyramidal intermediate (Coordination No = 5)	Gain or loss of CFSE Negative = gain Positive = loss	Kinetic stability
d^0	0	0	0	Labile
d^1	-4	-4.57	-0.57	Labile
d^2	-8	-9.14	-1.14	Labile
d^3	-12	-10	+2.00	Inert
d^4 (HS)	-6	-9.14	-3.14	Labile
d^4 (LS)	-16	-14.57	+1.43	Inert
d^5 (HS)	0	0	0	Labile
d^5 (LS)	-20	-19.4	+0.86	Inert
d^6 (HS)	-4	-4.57	-0.57	Labile
d^6 (LS)	-24	-20	+4.00	Inert
d^7 (HS)	-8	-9.14	-1.14	Labile
d^7 (LS)	-18	-19.14	-1.14	Labile
d^8	-12	-10	+2.00	Inert
d^9	-6	-9.14	-3.14	Labile
d^{10}	0	0	0	Labile

From Table 1, we can say that:

Metal complexes with d^0 , d^1 , d^2 , d^{10} are labile in nature and undergo fast ligand displacement through the dissociative pathway. High spin metal complexes with d^4 , d^5 , d^6 , d^7 are also labile in nature and react quickly through the dissociative pathway. Low spin complexes of d^7 metal ions are also found to be labile due to CFSE gain.

On the other side, d^3 and d^8 metal complexes are inert in nature and undergo slow ligand displacement through the dissociative pathway. Moreover, low spin complexes with d^4 , d^5 and d^6 metal complexes are also

inert due to loss of CFSE during the SN_1 mechanism. Using the order of CFSE loss, the reactivity can be represented as $d^5 > d^4 > d^8 > d^3 > d^6$.

(i) For SN_2 or associative pathway, the 7-coordinate intermediate can be a pentagonal-bipyramidal or octahedral wedge. However, it has been observed that the associative mechanism preferably occurs through an octahedral-wedge intermediate. Hence, the gain or loss of the CFSE can be calculated as:

CFSE gain or loss = CFSE of Octahedral-Wedge Intermediate – CFSE of Octahedral Reactant

Table 2. CFSE values of high-spin (HS) and low-spin (LS) octahedral complexes undergoing ligand displacement reactions through SN_2 mechanism

Configuration	CFSE for octahedral reactant (Coordination No = 6)	CFSE for octahedral-wedge intermediate (Coordination No = 7)	Gain or loss of CFSE Negative = gain Positive = loss	Kinetic stability
d^0	0	0	0	Labile
d^1	-4	-6.08	-2.08	Labile
d^2	-8	-8.68	-0.68	Labile
d^3	-12	-10.20	+1.80	Inert
d^4 (HS)	-6	-8.79	-2.79	Labile
d^4 (LS)	-16	-16.26	-0.26	Labile
d^5 (HS)	0	0	0	Labile
d^5 (LS)	-20	-18.86	+1.14	Inert
d^6 (HS)	-4	-6.08	-2.08	Labile
d^6 (LS)	-24	-20.37	+3.63	Inert
d^7 (HS)	-8	-8.68	-0.68	Labile
d^7 (LS)	-18	-18.98	-0.98	Labile
d^8	-12	-10.20	+1.80	Inert
d^9	-6	-8.79	-2.79	Labile
d^{10}	0	0	0	Labile

The following conclusions can be drawn from the data listed in Table 2.

Metal complexes with d^0 , d^1 , d^2 , d^{10} are labile in nature and undergo fast ligand displacement through the associative pathway. High spin metal complexes with d^4 , d^5 , d^6 , d^7 are also labile in nature and react quickly through the associative pathway. Low spin complexes of d^7 metal ions are also found to be labile due to CFSE gain. It can be seen that d^4 low spin are also labile in nature.

On the other side, d^3 and d^8 metal complexes are inert in nature and undergo slow ligand displacement through the associative pathway. Moreover, low spin complexes with d^5 and d^6 metal complexes are also inert due to the loss of CFSE during the S_N1 mechanism. Using the order of CFSE loss, the reactivity can be represented as $d^5 > d^8 > d^3 > d^6$.

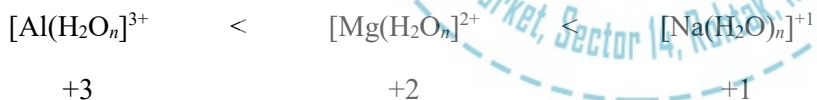
➤ **Factors Affecting the Kinetic Stability or Lability of Non-Transition Metal Complexes**

The kinetic stability of non-transition metal complexes can be rationalized from the valence bond theory (VBT) as well as from the perspectives of crystal field theory (CFT). According to the valence bond model, all of the non-transition metal complexes are outer-orbital in nature; and therefore, are expected to show labile behavior. Similarly, the predictions of kinetic stability of octahedral complexes of non-transition metals are also labile because whatever the path is followed, associative or dissociative, the loss of CSFE will always zero. Nevertheless, the overall trend kinetic stability of transition metal complexes depends upon a number of factors discussed below.

1. Charge on the central metal ion: The Lability of a complex decreases with the increasing charge on the central metal ion. For example, lability order of the following complexes:

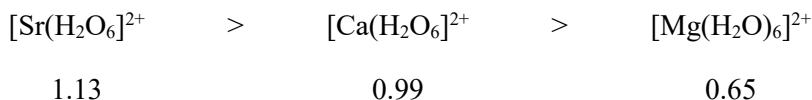


Similarly, the rate of water exchange increases with the decrease of cationic charge as:

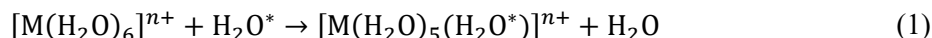


Hence, we can say that the complexes with the highest oxidation state would be most stable kinetically; while complexes with the lowest oxidation state of the metal center would be least stable kinetically.

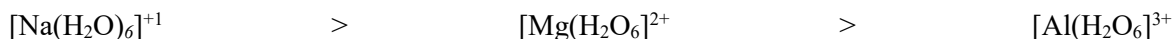
2. Radii of central metal ion: It has been also observed that the kinetic stability greatly depends upon the radius of the metal center in a complex. As the radius of metal ion decreases, the lability of its complex decreases. This can be attributed to smaller metal–ligand bond, which in turn, results in stronger attraction between the metal and ligands involved. In other words, the lability of the complex is proportional to the radius of the cation. For example:



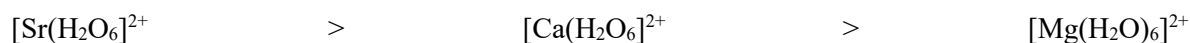
3. Charge to ionic size ratio: It has been observed that for a series of octahedral complexes having the same ligands, the lability of the complexes decreases with the increase of charge to ionic size ratio. For instance, consider the replacement of H_2O^{16} by H_2O^{18} or simply H_2O^* .



The order of lability is:



This trend can be rationalized in terms of the highest charge to ionic-size ratio for hexaaquo complex of trivalent aluminum (6.0), lowest ionic-size ratio for hexaaquo complex of trivalent sodium (1.05). Similarly,



4. Geometry of the complex: Four-coordinated complexes, tetrahedral as well as square planar, reacts more rapidly than that of six-coordinated complexes. This can be explained in terms of lesser steric repulsion and the availability of more sites to the incoming ligand.



Figure 4. The general diagram comparing the steric and site availability for ligand attack in four-coordinated and six coordinated complexes of non-transition metals.

Now although the lability of transition metal complexes mainly depends upon the gain or loss of CFSE during the formation intermediate (what we have already discussed in this section previously), the geometry also plays some role in the same. In other words, in addition to the lability of non-transition metal complexes, 'Figure 4' may also be used to explain some lability profiles in transition metal complexes. For instance, the rate of exchange of CN^- by $^{14}\text{CN}^-$ in $[\text{Ni}(\text{CN})_6]^{2-}$ is greater than what is observed for $[\text{Mn}(\text{CN})_6]^{3-}$ and $[\text{Co}(\text{CN})_6]^{3-}$ complexes. This can be attributed to the easy formation of an activated complex with the incoming ligand, which in turn, facilitates the removal of the previously attached ligand.

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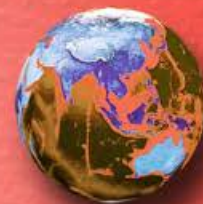
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Volume I

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