❖ Mechanisms for Ligand Replacement Reactions

The ligand displacement in metal complexes is said to have been taken place if one of the previously attached ligands got replaced by another ligand from its coordination sphere. The scheme can be shown as:

$$\mathrm{MA}_n\mathrm{L} \quad + \quad \mathrm{E} \quad \rightarrow \quad \mathrm{MA}_n\mathrm{E} + \mathrm{L} \tag{2}$$

Where ligand L is the leaving group present in the complex, E is the entering ligand which is nucleophilic in nature. The coordination number of the complex remains the same.

➢ *Ligand Displacement Mechanism in Octahedral Complexes*

In octahedral complexes, the replacement of the ligand can occur through dissociative, associative or by interchange mechanism. It has also been observed that most of the ligand displacement takes place through the interchange rout rather than purely associative or dissociative.

1. Dissociative or SN₁ Mechanism (D): In this mechanism, first of all, a metal-ligand bond breaks and the coordination number of the complex reduces from six to five forming a penta-coordinated intermediate complex. After that, the entering group attacks this intermediate and the coordination number again gets restored to six giving octahedral geometry. The whole process can be shown as

$$\mathrm{MA_5L} \xrightarrow[-\mathrm{L}]{\text{slow}} \mathrm{MA_5} \xrightarrow[\text{fast}]{+\mathrm{E}} \mathrm{MA_5E} \tag{3}$$

The first step is the slow step and hence it is also the rate-determining step for the process. The overall rate is:

$$\text{Rate} = k[\mathrm{MA_5L}] \tag{4}$$

The reaction is of the first order and is independent of the concentration of the entering ligand. These types of reactions are also called as the unimolecular nucleophilic substitution or $\mathrm{SN_1}$ reactions.

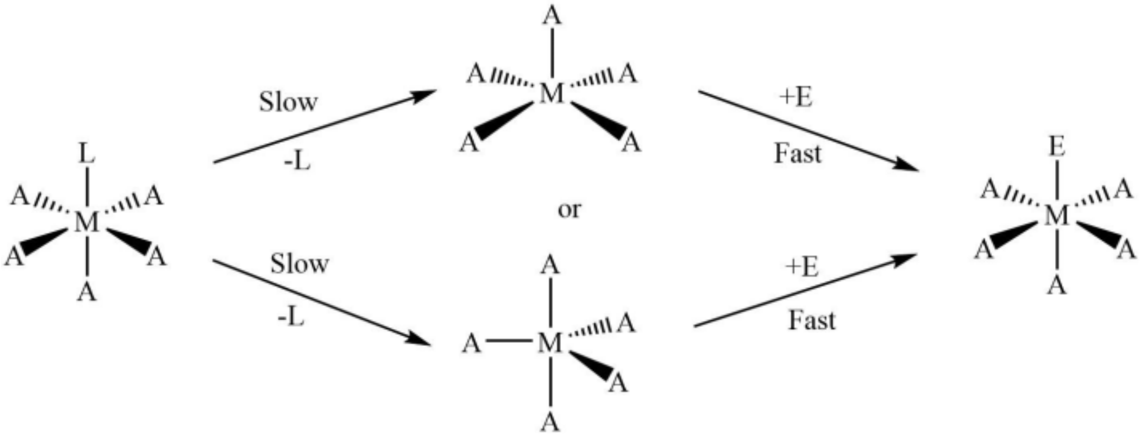


Figure 5. Pathway for ligand displacement reactions in octahedral metal complexes through $\mathrm{SN_1}$.

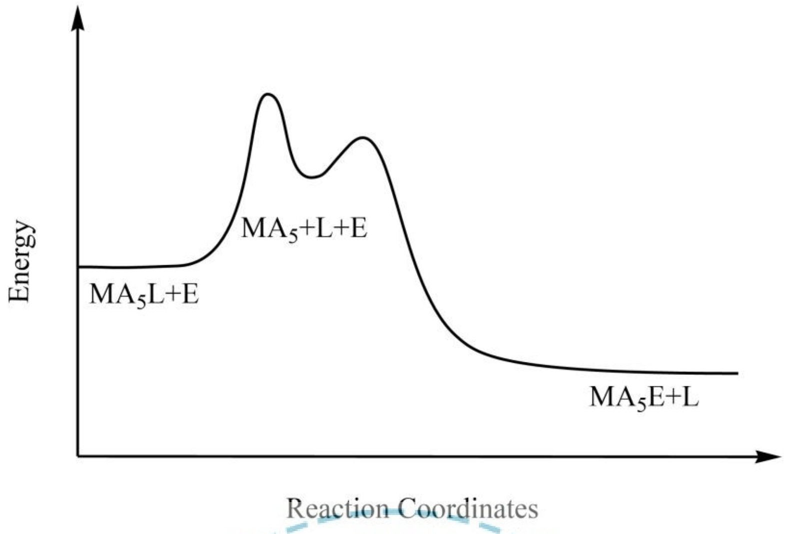


Figure 6. The typical reaction coordinate diagram for ligand displacement reactions in octahedral metal complexes through SN_1 mechanism.

Most of the ligand substitution reactions in octahedral complexes occur through dissociative or by interchange dissociative mechanism which in turn can be evidenced by the following rules.

i) The rate of the ligand substitution is almost independent of the concentration of the entering ligand.

ii) The rate of the ligand substitution increases as the steric bulk around the metal center increase.

iii) The entropy of activation, $\Delta S^\dagger$, is positive as there are more species in activated complex than in reactant.

iv) The volume of activation, $\Delta V^\dagger$, for the reaction is also found to be positive.

2. Associative or SN_2 Mechanism (A): In this mechanism, firstly the bond making with the entering group takes place, and therefore, the coordination number of the metal complex increases from six to seven forming a hepta-coordinated intermediate complex. After that, the leaving group dissociates itself from the intermediate complex completely and the coordination number of the complex again gets restored to six giving octahedral geometry. The whole process can be shown as

$$MA_5L + E \underset{k}{\overset{\text{slow}}{\longrightarrow}} MA_5LE \underset{-L}{\overset{\text{fast}}{\longrightarrow}} MA_5E \qquad (5)$$

The first step is the slow step and hence it is also the rate-determining step for the process. The overall rate is

$$\text{Rate} = k[MA_5L][E] \qquad (6)$$

The reaction is of second order and it depends of the concentration of the reactant complex as well as the concentration of the entering ligand. These types of reactions are also called as bimolecular nucleophilic substitution or SN_2 reactions.

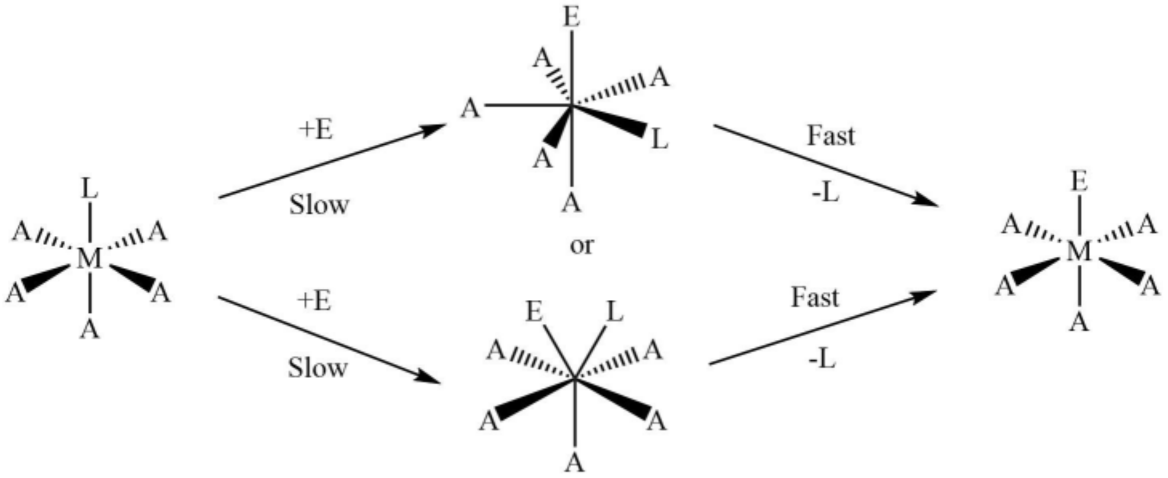


Figure 7. The general reaction mechanism for ligand displacement reactions in octahedral metal complexes through SN_2 pathway.

Figure 8. The typical reaction coordinate diagram for ligand displacement reactions in octahedral metal complexes through SN_2 mechanism.

i) The rate of the ligand substitution is increased with the concentration of the entering ligand.

ii) The rate of the ligand substitution decreases as the steric bulk around the metal center increase.

iii) The entropy of activation, $\Delta S^{\dagger}$, is negative as there are lesser number species in activated complex than in reactant.

iv) The volume of activation, $\Delta V^{\dagger}$, for the reaction is also found to be negative.

3. Interchange mechanism (I): It has been observed that most of the ligand displacement reactions are neither purely associative or dissociative but follow an intermediate mechanism in which bond breaking and bond making takes place simultaneously and no penta-coordinated or hepta-coordinated intermediates have actually been isolated. These types of reactions proceed via a transition state just like in organic SN_2 reactions.

$$\mathrm{MA_5L + E \longrightarrow MA_5LE \longrightarrow MA_5E} \tag{7}$$

However, if the rate of the reaction is strongly dependent on the concentration of the entering ligand which indicates that bond making is more important in determining the rate of the reaction than the displacement is said to have been taken place via interchange associative or I_a mechanism. On the other hand, if the rate of the reaction is almost independent of the concentration of the entering ligand which clearly indicates that bond breaking is more important in determining the rate of the reaction than the displacement is said to have been taken place via interchange dissociative or I_d mechanism.

Figure 9. The typical reaction coordinate diagram for ligand displacement reactions in octahedral metal complexes through the interchange mechanism.

➢ ***Ligand Displacement Mechanism in Square-planar Complexes***

In square-planar complexes, the ligand displacement is much more favorable through the associative route than that of dissociative which can be understood in terms of low steric crowding due to lesser coordination number. The general ligand displacement can be written as:

$$\mathrm{MA_3L + E} \underset{k}{\overset{\text{slow}}{\longrightarrow}} \mathrm{MA_3LE} \underset{-\mathrm{L}}{\overset{\text{fast}}{\longrightarrow}} \mathrm{MA_3E} \tag{8}$$

The intermediate state is trigonal-bipyramidal and undergoes rapid Berry-pseudo-rotation followed by the elimination of the leaving group.

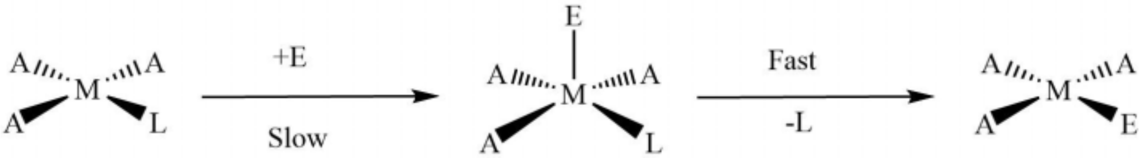


Figure 10. The general reaction mechanism for ligand displacement reactions in square-planar complexes.

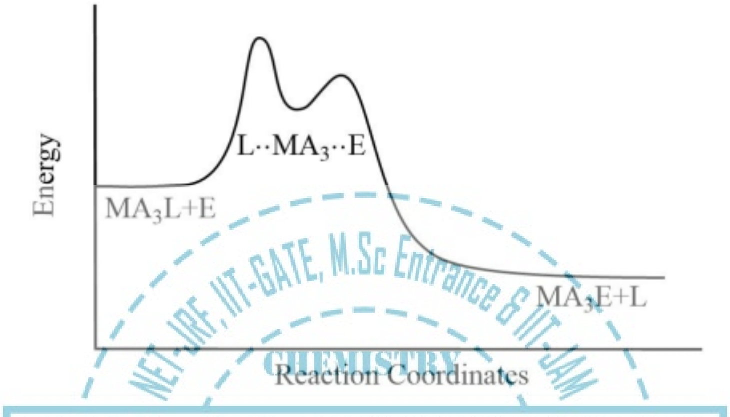


Figure 11. The typical reaction coordinate diagram for ligand displacement reactions in square-planar complexes through the associative mechanism.

A more in-depth visualization of ligand displacement reactions in square-planar complexes is given below in which the involvement of Berry-pseudorotation is depicted more precisely.

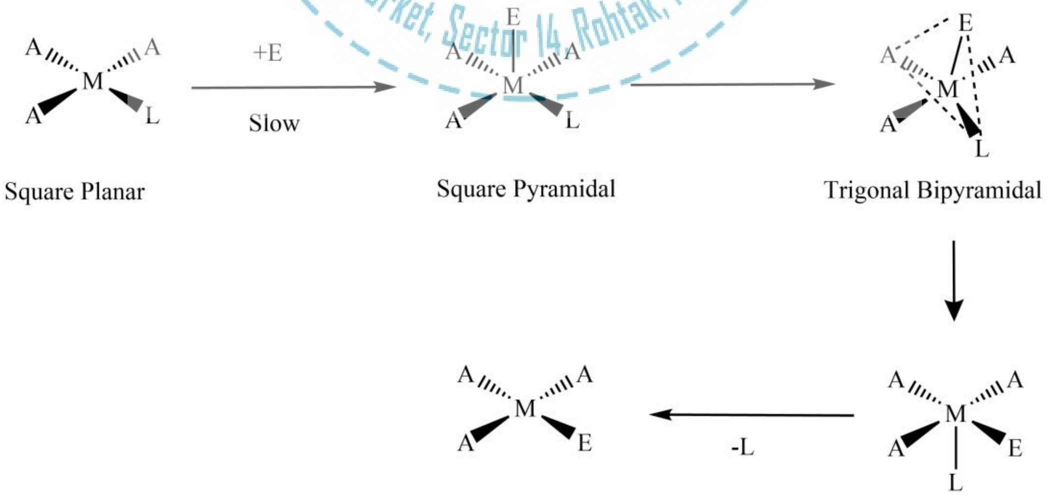
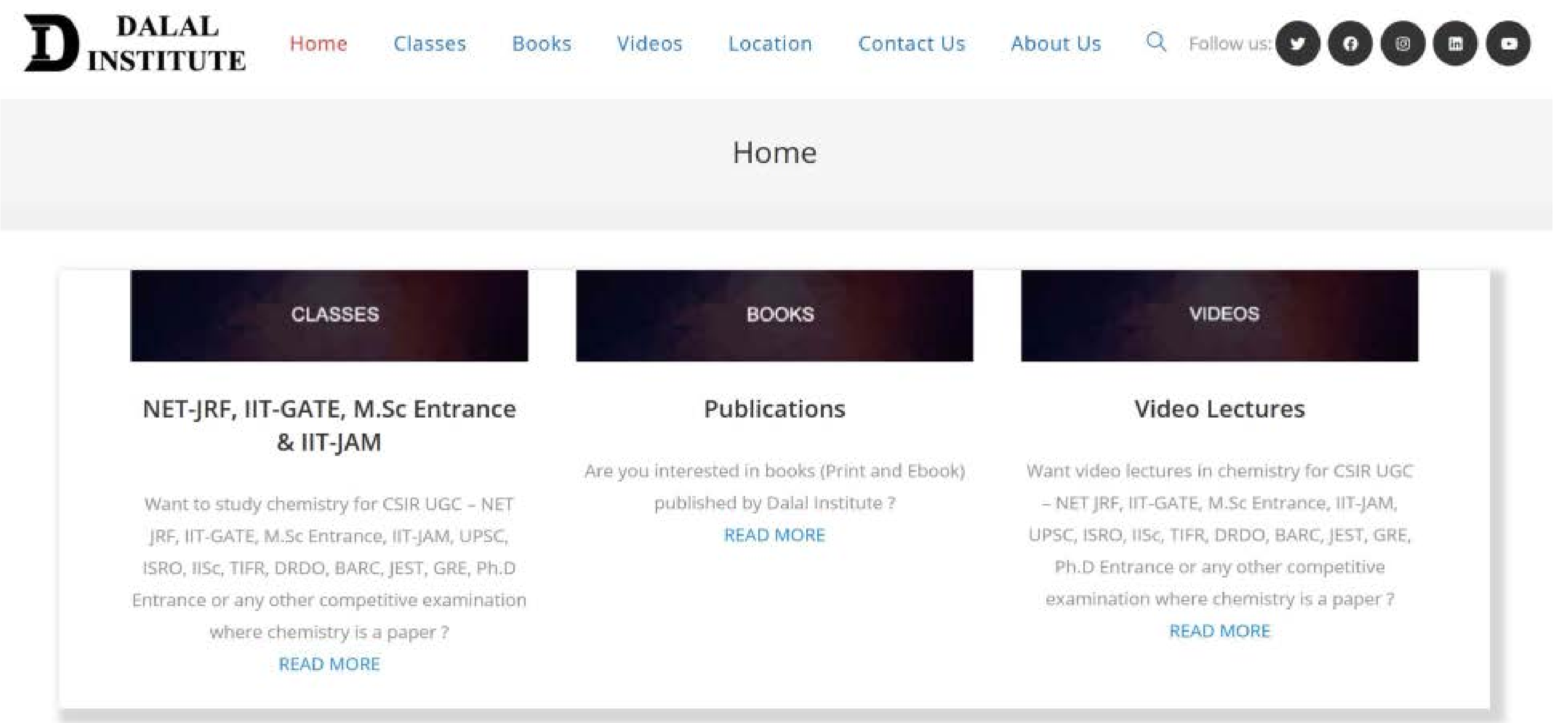


Figure 12. Involvement of Berry-pseudorotation in the ligand displacement in square-planar complexes.



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