Reaction Kinetics and Mechanism

(Part I: Introduction of Reaction mechanism)

B.Sc. (H) Chemistry

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SYLLABUS

Reaction Kinetics and Mechanism

Introduction to inorganic reaction mechanisms. Substitution reactions in square planar complexes, Trans- effect, theories of trans effect, Mechanism of nucleophilic substitution in square planar complexes, Thermodynamic and Kinetic stability, Kinetics of octahedral substitution, Ligand field effects and reaction rates, Mechanism of substitution in octahedral complexes.

Ligand substitution reactions

The most fundamental reaction a complex can undergo is **ligand substitution**, a reaction in which one Lewis base displaces another from a Lewis acid:

$$Y + M\text{-}X \rightarrow M\text{-}Y + X$$

This class of reaction includes complex formation reactions, in which the leaving group, the displaced base X, is a solvent molecule and the entering group, the displacing base Y, is some other ligand. An example is the replacement of a water ligand by Cl^-:

$$[Co(OH_2)_6]^{2+}(aq) + Cl^-(aq) \rightarrow [CoCl(OH_2)_5]^+(aq) + H_2O(l)$$

Rates of ligand substitution

The rates of substitution reactions span a very wide range and correlate with the structures of the complexes; complexes that react quickly are called labile, those that react slowly are called inert or nonlabile.

Complexes that undergo more rapid equilibration (less than one minute) are called **labile,** while the complexes survive for more than a minute is called **inert.**

An example of each type is the labile complex $[Ni(OH_2)_6]^{2+}$, which has a half-life of the order of milliseconds before the H_2O is replaced by another H_2O or a stronger base, and the nonlabile complex $[Co(NH_3)_5(OH_2)]^{3+}$, in which H_2O survives for several minutes as a ligand before it is replaced by a stronger base.

There are two broad generalizations which governs the stability of complexes.

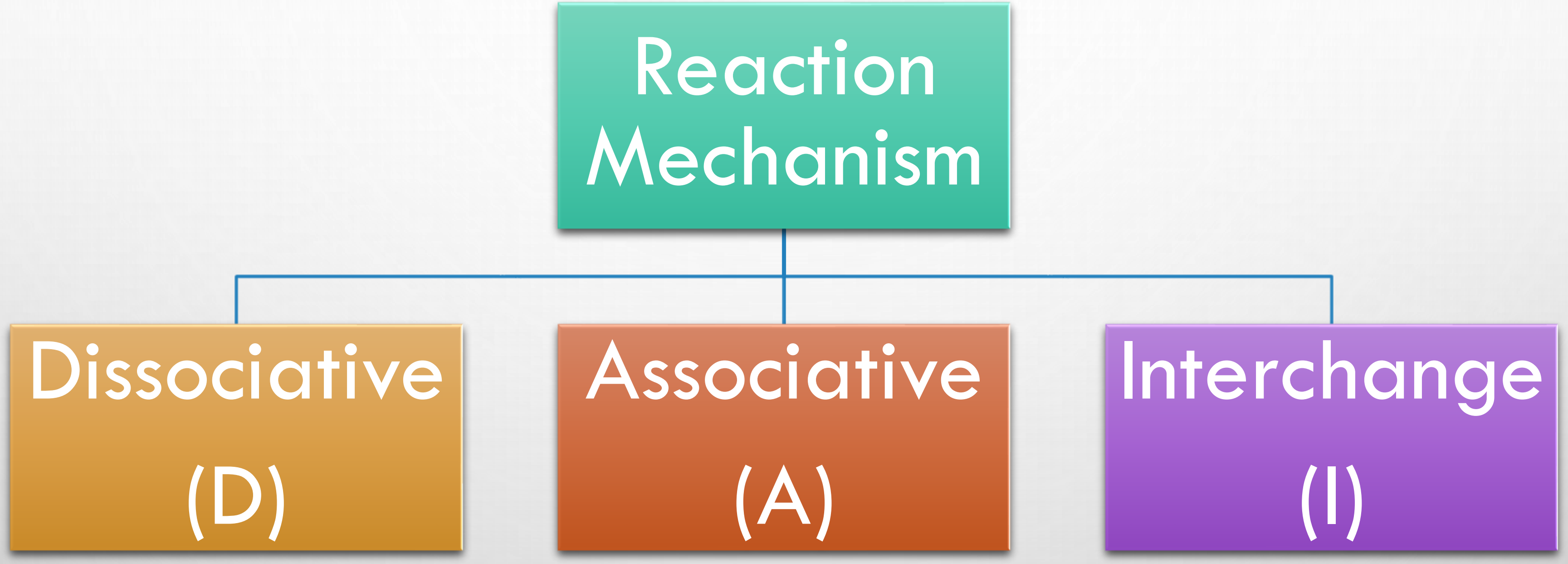
1. Complexes of metals that have no additional factor to provide extra stability (for instance, the LFSE and chelate effects) are among the most labile. Any additional stability of a complex results in an increase in activation energy for a ligand replacement reaction and hence decreases the lability of the complex.
2. Very small ions are often less labile because they have greater M-L bond strengths and it is sterically very difficult for incoming ligands to approach the metal atom closely.

Some further generalizations are as follows:

1. All complexes of s-block ions except the smallest (Be^{2+} and Mg^{2+}) are very labile.
2. Complexes of the M(III) ions of the f block are all very labile.
3. Complexes of the d^{10} ions (Zn^{2+}, Cd^{2+}, and Hg^{2+}) are normally very labile.
4. Across the 3d series, complexes of d-block M(II) ions are generally moderately labile, with distorted Cu(II) complexes among the most labile.
5. Complexes of d-block M(III) ions are distinctly less labile than d-block M(II) ions.
6. d-Metal complexes with d^3 and low-spin d^6 configurations (for example Cr(III), Fe(II), and Co(III)) are generally nonlabile as they have large LFSEs. Chelate complexes with the same configuration, such as $[Fe(phen)_3]^{2+}$, are particularly inert.
7. Non-lability is common among the complexes of the 4d and 5d series, which reflects the high LFSE and strength of the metal-ligand bonding.

The classification of mechanisms

Three main classes of reaction mechanism have been identified.



Reaction Mechanism

Dissociative (D)

Associative (A)

Interchange (I)

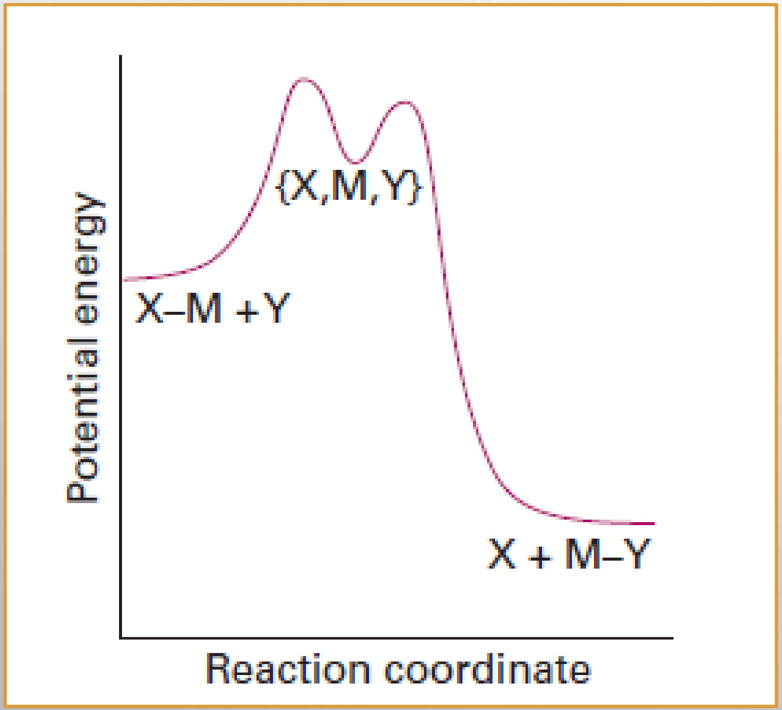
Dissociative mechanism

denoted as *D*,

A reaction sequence in which an intermediate of reduced coordination number is formed by the departure of the leaving group.

$$ML_nX \rightarrow ML_n + \mathrm{X}$$
$$ML_n + \mathrm{Y} \rightarrow ML_n\mathrm{Y}$$

Here ML*n* (the metal atom and any spectator ligands) is a true intermediate that can, in principle, be detected (or even isolated).



For example:

The substitution of hexacarbonyltungsten by phosphine takes place by dissociation of CO from the complex

$$\mathrm{W(CO)_6} \rightarrow \mathrm{W(CO)_5} + \mathrm{CO}$$

Followed by coordination of phosphine:

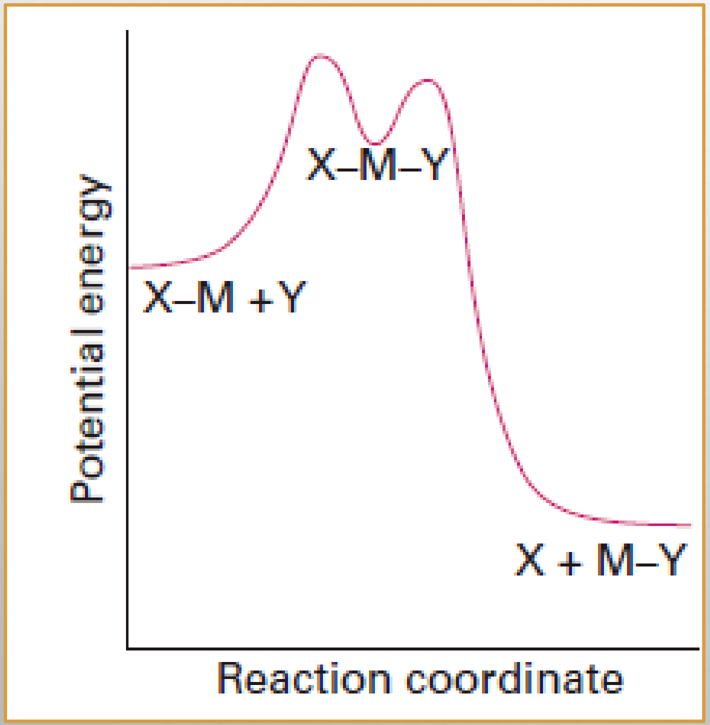
$$\mathrm{W(CO)_5} + \mathrm{PPh_3} \rightarrow \mathrm{W(CO)_5\,PPh_3}$$

Associative mechanism

denoted as *A*,

involves a step in which an intermediate is formed with a higher coordination number than the original complex.

$$ML_nX + Y \rightarrow ML_nXY$$
$$ML_nXY \rightarrow ML_nY + X$$



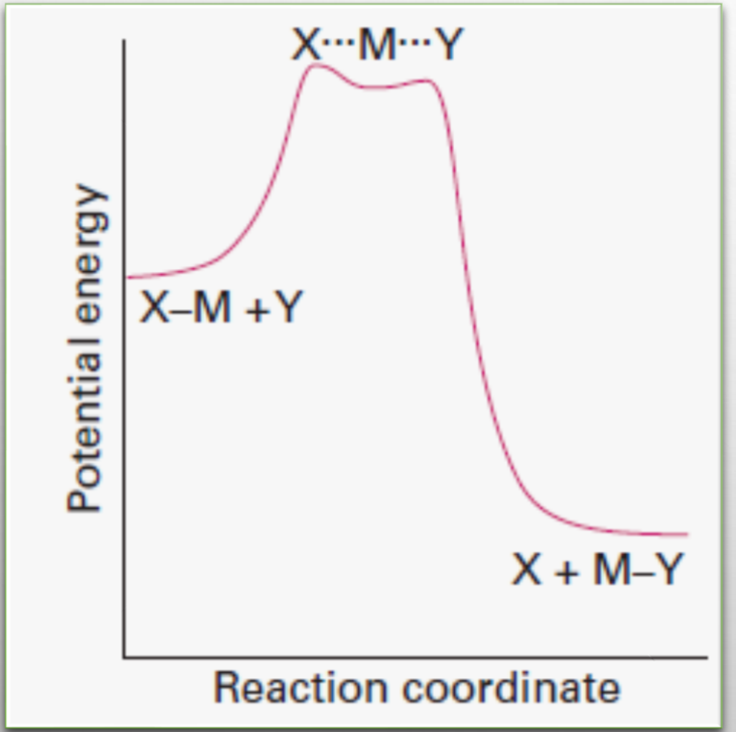
The intermediate ML_nXY can, in principle at least, be detected. This mechanism plays a role in many reactions of square-planar Au(III), Pt(II), Pd(II), Ni(II), and Ir(I) d^8 complexes.

Interchange mechanism

denoted as *I*,

takes place in one step:

$$ML_nX + Y \rightarrow X\cdots ML_n\cdots Y \rightarrow ML_nY + X$$



The leaving and entering groups exchange in a single step by forming a *transition state* but *not a true intermediate*. The interchange mechanism is common for many reactions of six-coordinate complexes.

Reference: Shriver & Atkins Inorganic Chemistry

Thank You