Reaction Kinetics and Mechanism

(Part II: Introduction of Reaction mechanism)

B.Sc. (H) Chemistry

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SYLLABUS

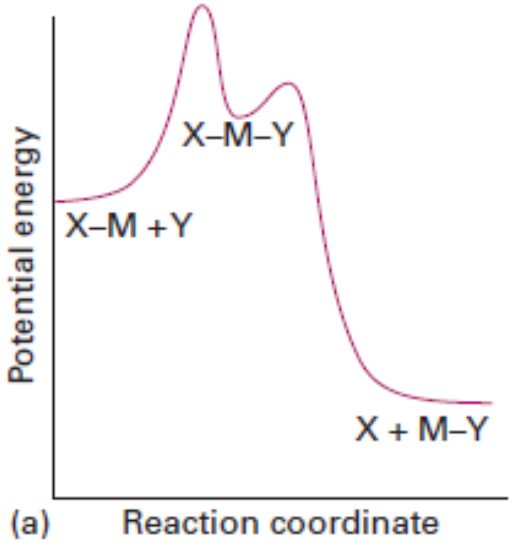
Reaction Kinetics and Mechanism

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.

The rate-determining step

The rate-determining step is classified as associative or dissociative according to the dependence of its rate on the identity of the entering group.

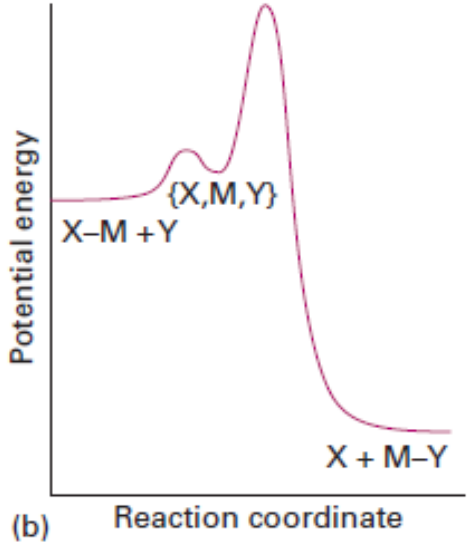
The rate-determining step on entering group Y indicates that the transition state must involve significant bonding to Y. A reaction with an **associative mechanism** (A) will be associatively activated (a) if the attachment of Y to the initial reactant ML_nX is the rate-determining step; such a reaction is designated A_a, and in this case the intermediate ML_nXY would not be detected.



Associative mechanism, A_a

A reaction with a **dissociative mechanism** (D) is associatively activated (a) if the attachment of Y to the intermediate ML_n is the rate-determining step; such a reaction is designated D_a.

Figure a & b shows the reaction profiles for associatively activated A and D mechanisms.



Dissociative mechanism, D_a

A reaction that has an **interchange mechanism** (I) can be either associatively or dissociatively activated, and is designated either I_a or I_d, respectively.

In an I_a mechanism, the rate of reaction depends on the rate at which the M…Y bond forms.

In an I_d reaction the rate of reaction depends on the rate at which the M…X bond breaks

Figure 2 shows reaction profile of reactions with an interchange mechanism: (a) associatively activated, I_a; (b) dissociatively activated, I_d.

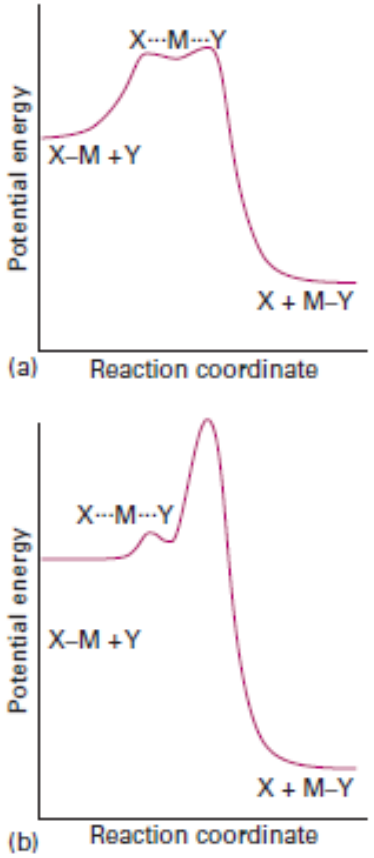


Figure 2

Table 1. Overall summarized as follows, where ML_nX denotes the initial complex:

Mechanism:	*A*		*I*		*D*	
Activation:	*a*	*d*	*a*	*d*	*a*	*d*
Rate-determining step	Y attaching to ML_nX	Loss of X from YML_nX	Y attaching to ML_nX	Loss of X from YML_nX	Y attaching to ML_n	Loss of X from ML_nX

Ligand Substitution reactions in square-planar complexes

Square planar is the common geometry for the d^8 configurations metal ions such as Pt(II), Ni(II), Pd(II) and etc.

The mechanism of ligand exchange in square-planar Pt complexes has been studied extensively .

For square planar

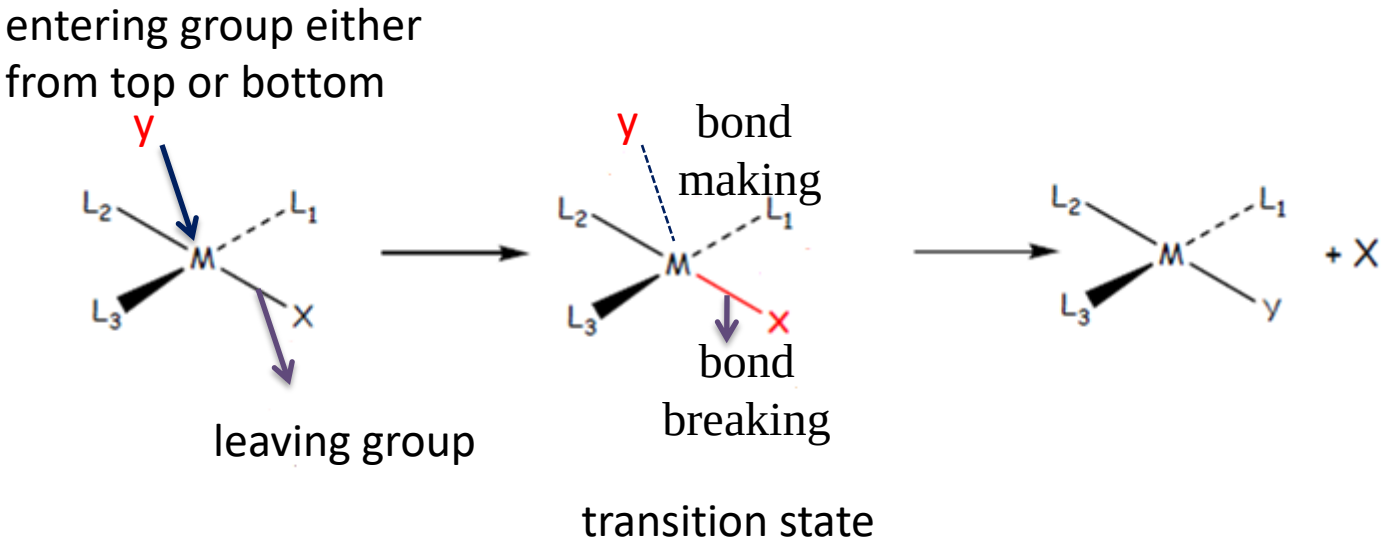
$$ML_3X + Y \longrightarrow ML_3Y + X$$

Rate= $k[ML_3X][Y]$

It depends on the nature of both the leaving group X and the leaving group Y.

Mechanism for square-planar ligand substitution

Both bond breaking and bond making are important in reaction mechanism



Mechanism for square-planar ligand substitution

The elucidation of the mechanism of the substitution of square-planar complexes is often complicated by the occurrence of alternative pathways.
e.g.

$$[PtCl(dien)]^+(aq) + I^-(aq) \rightarrow [PtI(dien)]^+(aq) + Cl^-(aq)$$

is first order in the complex and independent of the concentration of I, then
rate of reaction= $k_{r,1}$[PtCl(dien)].

However, if there is a pathway in which the rate law is first order in the complex and first order in the incoming group (that is, overall second order) then
rate of reaction =$k_{r,2}$[PtCl(dien)][I].

If both reaction pathways occur at comparable rates, the rate law has the form

$$\text{rate} = (k_{r,1} + k_{r,2}\,[I^-])[PtCl(dien)^+]$$

A reaction like this is usually studied under the conditions $[I^-] >> [complex]$ so that $[I^-]$ does not change significantly during the reaction.

This simplifies the treatment of the data as $k_{r,1} + k_{r,2}[I^-]$ is effectively constant and the rate law is now pseudo-first order:

$$\text{rate} = k_{r,obs}[PtCl(dien)^+] \qquad k_{r,obs} = k_{r,1} + k_{r,2}[I^-]$$

Reference: Shriver & Atkins Inorganic Chemistry

Thank You