Reaction Mechanism:

5.1 DIFFERENT TYPES OF REACTIONS OF METAL COMPLEXES

Different types of reactions of metal complexes are as follows:

- ligand substitution reactions
- metal substitution reactions
- isomerisation and recemisation reactions
- redox (*i.e.* electron transfer) reactions
- reactions of coordinated ligands (*i.e.* activation of ligands).

5.2 CLASSIFICATION OF SUBSTITUTION REACTION

These are classified as follows:

- nucleophilic substitution (S_N)
- electrophilic substitution (S_E)

In **nucleophilic substitution reactions, a nucleophile** (*i.e.* Lewis base) donates its electron cloud to a positively charged centre, *i.e.* nucleus (*i.e.* Lewis acid) through the replacement of another nucleophile.

$$M - X + Y \rightarrow M - Y + X \ (S_N)$$

(Charges not shown)

Here both X and Y are the nucleophiles (*i.e.* ligands). Y is the *entering* or *incoming nucleophile* while X is the *leaving group* or *leaving nucleophile*. The metal centre (*i.e.* M) is the Lewis acid. Thus in a nucleophilic substitution reaction, one Lewis base (*i.e.* ligand) displaces another Lewis base from a Lewis acid (*i.e.* metal centre).

Thus the ligand substitution reaction is a case of nucleophilic substitution reaction. In ligand substitution reactions, other ligands (*i.e. nonleaving groups*) are called the **spectator ligands**.

$$L_5M - X + Y \rightarrow L_5M - Y + X$$

Here the ligands denoted by L_5 are called the *spectator ligands that may influence the rate and process of the substitution reaction through the steric and electronic effects.*

In an electrophilic substitution reaction, the metal centres (*i.e.* electron seeking, Lewis acids) are replaced, *i.e.* one metal centre replaces another one. In metal complexes, the *ligand substitution* (*i.e.*

nucleophilic substitution) reactions are abundant while the *metal substitution* (*i.e.* electrophilic substi-
2 tution) reactions are relatively rare.

5.3 DIFFERENT TYPES OF LIGAND SUBSTITUTION REACTIONS

These are illustrated with some specific examples.

Acid hydrolysis: The leaving group is replaced by H_2O (*i.e.* solvent in aqueous media) in acidic condition.

$$[Co(NH_3)_5X]^{2+} + H_2O \rightarrow [Co(NH_3)_5(OH_2)]^{3+} + X^-$$

This is also called the *aquation* or simply the *dissociation* reaction.

Base hydrolysis: The leaving group is replaced by OH^- group in aqueous media. This is also a case of dissociation reaction.

$$[Co(NH_3)_5X]^{2+} + OH^- \rightarrow [Co(NH_3)_5(OH)]^{2+} + X^-$$

Anation: The coordinated solvent molecule (*i.e.* H_2O in aqueous media) is replaced by an anion (X^-).

$$[Co(NH_3)_5(OH_2)]^{3+} + X^- \rightarrow [Co(NH_3)_5X]^{2+} + H_2O$$

This is also described as the *formation reaction.*

Solvent exchange: This is illustrated below.

$$[M(OH_2)_n] + H_2O^* \rightarrow [M(OH_2)_{n-1}(^*OH_2)] + H_2O, \text{ (in aqueous solvent)}$$

Ligand exchange: This is illustrated below.

$$[PtCl_2(py)_2] + 2^*Cl^- \rightarrow [Pt(^*Cl)_2(py)_2] + 2Cl^-$$

Formation reaction: Replacement of a coordinated solvent molecule by a ligand other that the solvent itself.

$$[M(OH_2)_n] + L \rightarrow [M(OH_2)_{n-1}(L)] + H_2O$$

Solvolysis reaction (*cf.* Hydrolysis reaction): Replacement of a ligand by the solvent itself.

$$M — L + S \text{ (solvent)} \rightarrow M — S + L$$

5.4 THERMODYNAMIC AND KINETIC STABILITY: LABILITY AND INERTNESS (*cf.* Sec. 4.1)

Thermodynamic stability of a complex is determined by β_n.

$$M + nL \rightleftharpoons ML_n, \quad \beta_n = \frac{[ML_n]}{[M][L]^n}$$

The higher value of β_n indicates its higher thermodynamic stability. Thus it gives the measure of the extent to which the equilibrium can proceed but it cannot say anything regarding the speed with which the equilibrium is attained. Thus the thermodynamic and kinetic stability are not necessarily correlated. A thermodynamically stable complex may react slowly or fast depending on the condition. This can be illustrated by considering the different cyanido complexes which are extremely stable (*i.e.* very high value of β_n) but they behave quite differently in terms of the rate of exchange of the radiocarbon labelled cyanide.

$$[Hg(CN)_4]^{2-} + 4\,^{14}CN^- \rightleftharpoons [Hg(^{14}CN)_4]^{2-} + 4CN^-, \textbf{ very fast}$$

$$[Ni(CN)_4]^{2-} + 4\,^{14}CN^- \rightleftharpoons [Ni(^{14}CN)_4]^{2-} + 4CN^-, t_{1/2} \approx 30\,s, \textbf{ very fast}$$

$$[Pt(CN)_4]^{2-} + 4\,^{14}CN^- \rightleftharpoons [Pt(^{14}CN)_4]^{2-} + 4CN^-, t_{1/2} \approx 1\text{ min}$$

$$[Mn(CN)_6]^{3-} + 6\,^{14}CN^- \rightleftharpoons [Mn(^{14}CN)_6]^{3-} + 6CN^-, t_{1/2} \approx 1\text{ h}$$

$$\left[\mathrm{Cr(CN)_6}\right]^{3-} + 6\,{}^{14}\mathrm{CN}^- \rightleftharpoons \left[\mathrm{Cr(^{14}CN)_6}\right]^{3-} + 6\mathrm{CN}^-,\ t_{1/2} \approx 24\ \mathrm{d},$$

$$\left[\mathrm{Fe(CN)_6}\right]^{3-/4-} + 6\,{}^{14}\mathrm{CN}^- \rightleftharpoons \left[\mathrm{Fe(^{14}CN)_6}\right]^{3-/4-} + 6\mathrm{CN}^-,\ \textbf{(very slow)}$$

All the above complexes are thermodynamically very stable (*cf.* $[Ni(CN)_4]^{2-}$, log $\beta_4 \approx 29$; $[Pt(CN)_4]^{2-}$, log $\beta_4 \approx 40$; $[Hg(CN)_4]^{2-}$, log $\beta_4 \approx 42$; $[Fe(CN)_6]^{3-}$, log $\beta_6 \approx 44$; $[Fe(CN)_6]^{4-}$, log $\beta_6 \approx 37$; etc.) but their kinetic stabilities differ widely. *The thermodynamically stable complexes like* $[Ni(CN)_4]^{2-}$, $[Hg(CN)_4]^{2-}$, etc. *react fast in the ligand exchange reactions but* $[Cr(CN)_6]^{3-}$ *which is also thermodynamically stable reacts slowly* and $[Fe(CN)_6]^{4-}$ also reacts very slowly.

- For some **square planar Pt(II) – complexes**, the lability and thermodynamic stability follow the same sequence, *i.e.* **the most stable complex is the most labile one**.

Complex:	$[PtCl_4]^{2-}$	$[PtBr_4]^{2-}$	$[PtI_4]^{2-}$	$[Pt(CN)_4]^{2-}$
~ logβ_4:	17	20	30	40
~ $t_{1/2}$ (min):	850	6	4	1

$$\xrightarrow{\hspace{10em}}$$

Increasing lability (*cf*. Secs. 5.30.5,6) **and stability**

- **Dissociation of $[Co(NH_3)_6]^{3+}$** in aqueous acidic media is thermodynamically highly favoured but the process is kinetically highly disfavoured.

$$\left[\mathrm{Co(NH_3)_6}\right]^{3+} + 6\mathrm{H_3O^+} \rightleftharpoons \left[\mathrm{Co(OH_2)_6}\right]^{3+} + 6\mathrm{NH_4^+},\ \log K_{eq} \approx 25.0$$

The tremendous thermodynamic driving force for the forward reaction arises from the protonation of the basic NH_3 ligands, but the complex remains unchanged in a fairly strong acid medium for weeks at room temperature. In fact, the salt $[Co(NH_3)_6]Cl_3$ can be crystallised from a hot aqueous solution of HCl without any noticeable decomposition. Thus, *stability of the complex arises not from the thermodynamic stability but from the kinetic stability.*

- **$[M(en)_3]^{3+}$ and $[M(bigH)_3]^{3+}$** (M = Cr, Co): The biguanide complex is more stable than the ethylenediamine complex but with respect to the acid catalysed dissociation reaction, $[M(bigH)_3]^{3+}$ reacts much faster than the $[M(en)_3]^{3+}$ complex.

$$\left[\mathrm{M(en)_3}\right]^{3+} \xrightarrow{\mathrm{H_3O^+}} \left[\mathrm{M(OH_2)_6}\right]^{3+} + 3\mathrm{enH^+}$$

$$\left[\mathrm{M(bigH)_3}\right]^{3+} \xrightarrow{\mathrm{H_3O^+}} \left[\mathrm{M(OH_2)_6}\right]^{3+} + 3\mathrm{bigH_2^+}$$

In fact, $[Co(bigH)_3]^{3+}$ undergoes dissociation in acid medium at a measureable rate at 30°C (*cf.* D.Banerjea et al, *J. Inorg. Nucl. Chem.*, **26,** 1233, 1964) and $[Co(en)_3]^{3+}$ remains completely unchanged in 1 M $HClO_4$ at room temperature even for months.

Note: The kinetic favour for dechelation of the biguanide ring arises from the *its possibility of protonation before ring opening* but such a protonation cannot occur prior to opening of the chelate ring for the ethylenediamine complex.

- To differentiate between the thermodynamic stability and kinetic stability, H. Taube has coined the kinetic terms: **lability** and **inertness.** The kinetically stable complexes are called the **inert complexes** while the kinetically unstable complexes are called the **labile complexes.** The simple terms — stable and unstable refer to the thermodynamic parameters.
- In ligand substitution reactions, the rate can span a very wide range of time scale — **nanosecond (ns) to years.**

$$[Cu(aq)]^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+}, \textbf{ (instantaneous)}$$
(blue purple)
$$[Co(NH_3)_6]^{3+} \text{ or } [Co(en)_3]^{3+} \rightarrow \text{Hydrolysis, } \textbf{(years)}$$

- *There is no sharp border line to distinct between the labile and inert complexes.* However, H. Taube has described the complexes as the **labile complexes** having $t_{1/2}$ (substitution half life) ≤ 30 s in a particular reaction while the complexes with $t_{1/2} > 30$ s as the **inert complexes.** Rate process for the inert complexes can be followed by the conventional techniques while for the labile complexes, it requires some special techniques (*e.g. stopped flow, P–jump, T–jump,* etc.). This is why, more information is available for the inert complexes.
- The lability or inertness depends on the **activation energy,** *i.e.* high activation energy imparts the inertness while low activation energy imparts the lability (*cf.* Fig. 4.1.1). The inertness or lability is determined by $\Delta G^{\neq}$ **(free energy of activation).**

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq},\ \Delta H^{\neq} = \textbf{enthalpy of activation},\ \Delta S^{\neq} = \textbf{entropy of activation.}$$

The stability of a complex is determined by the free energy change (ΔG^0) (*cf.* Fig 4.1.1) in a reaction.

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

$\Delta G^{\neq}$ depends on the reaction pathway (*i.e.* reaction mechanism) while ΔG^0 depends on the difference in free energy between the reactant and product.

Labile and inert complexes of 3d–series

It depends on d^n–configuration.

Labile centres: d^0, d^1, d^2, d^4 (h. s.), d^5 (h. s.), d^6 (h.s.), d^7, d^8, d^9

Inert centres: d^3, d^4 (l. s.), d^5 (l. s.), d^6 (l. s.)

These can be explained by CFT. These aspects will be discussed later.

5.5 NUCLEOPHILICITY vs. BASICITY; ELECTROPHILICITY

- It has been already mentioned that the nucleophiles are basically the Lewis bases but the term **basicity** refers to the thermodynamic concept (*i.e.* equilibrium concept). The analogous kinetic term is called **nucleophilicity** (nucleophile = nucleus loving). In an associative pathway, the entering nucleophile (*i.e.* entering ligand) makes a bond with the metal centre in producing the **activated complex or transition state**. The *kinetic ease* with which a nucleophile can attack the metal centre to produce the activated complex gives the measure of its nucleophilicity. Relative nucleophilicity of a particular ligand L is measured with reference to that of a standard ligand L^0 by comparing their rates of substitution reaction (occurring through the **associative process**) at a chosen metal centre, *i.e.*

$$\text{Nucleophilicity of } L = \frac{\text{rate of substitution by } L}{\text{rate of substitution by } L^0}$$

The details of nucleophilicity scale will be discussed later (*cf.* Sec. 5.30.5)

The Lewis acids act as *electrophiles.*

- **Acidity** is a thermodynamic term while the analogous kinetic term is **electrophilicity** (electrophile = electron loving). The rate of reaction of a Lewis acid (*i.e.* metal centre in the complexes) with the Lewis bases (*i.e.* entering ligands or entering nucleophiles) gives the measure of the electrophilicity of the Lewis acid. Just like the relative nucleophilicity scale, a relative electrophilicity scale can be generated.

5.6 METHODS OF FOLLOWING KINETICS (*i.e.* RATE MEASUREMENT)

(1) **For the inert systems,** conventional techniques like: UV–Visible spectroscopic method, potentiometry, conductometry, polarography, polarimetry, titrimetry, etc. can be used to follow the rate process. In fact, reactions of the complexes of Cr(III), Co(III), Rh(III), Ir(III), Pt(II) and some complexes of Ni(II) can be studied by the conventional techniques. Some examples are given below.

- **Direct chemical analysis:** Direct chemical estimation of either the reactants or products at regular intervals during the progress of reaction is possible in many cases.

(a) $[PtCl(NH_3)_3]^+ + H_2O \rightarrow [Pt(NH_3)_3(OH_2)]^{2+} + Cl^-$
(b) $[CoCl_2(en)_2]^+ + H_2O \rightarrow [CoCl(en)_2(OH_2)]^{2+} + Cl^-$
(c) $[Co(NCS)(NH_3)_5]^{2+} + OH^- \rightarrow [Co(NH)_5(OH)]^{2+} + SCN^-$
(d) $[Co(NH_3)_5(S_2O_3)]^+ + L \rightarrow [Co(L)(NH_3)_5]^{n+} + S_2O_3^{2-}$
(L = different nucleophiles)

In the reactions (a) and (b), the released Cl^- can be estimated by *argentometry* (*i.e.* titration by $AgNO_3$) or by *potentiometry* (using an electrod reversible with respect to Cl^-, *e.g.* Ag/AgCl electrode). However, there is a possibility by the *direct attack* of Ag^+ *on the bound* Cl^- (*i.e.* overestimation of Cl^-). This can be minimised, if it is carried out at low temperature and in a mixed solvent like acetone-water mixture. In the reaction (c), released SCN^- can be also estimated similarly by titration with $AgNO_3$. In the reaction (d), the released $S_2O_3^{2-}$ can be estimated iodimetrically as usual.

- **Spectrophotometric method:** Generally, the coordination compounds are coloured and concentration of a coloured coordination compound can be determined from the optical density measurement at a suitable wavelength (A = optical density = εCl, ε = molar extinction coefficient, C = molar concentration, l = optical path length). Generally, in a particular reaction, the absorption spectra of the product and reactant are different and the most suitable wavelength for the optical density measurement is the wavelength at which absorption of the reactant and product differs most.

If the measured optical density (*OD*) is due to a particular compound whose formation or decay experiences a first order kinetics then the plot of $\log\frac{A_0 - A_\infty}{A_t - A_\infty}$ *vs.* t (time) will give the first order rate constant.

A_t = *OD* at time t; A_0 = *OD* at zero time; A_∞ = *OD* at infinity (*i.e.* at the end of reaction).

Note: For a first-order reaction, we can write:

$$C_t = C_0 \exp(-kt), \; i.e. \; k = \frac{2.303}{t}\log\frac{a}{a-x}$$

$C_0 = a$ = initial concentration (*i.e.* $t = 0$), $C_t = (a - x)$ = concentration at t.

If a physical property P (like *OD*), directly proportional to its concentration is available, then we can write:

$$k = \frac{2.303}{t}\log\frac{P_0 - P_\infty}{P_t - P_\infty}; \text{ slope of the plot, } \log\frac{P_0 - P_\infty}{P_t - P_\infty} \; vs. \; t \text{ is } \frac{k}{2.303}$$

- **Electrometric method** (*i.e.* measurement of conductance, emf, pH, etc.): In the following aquation reactions, conductance increases remarkably during the progress of reaction.

$[CoCl_2(en)_2]^+ + H_2O \rightarrow [CoCl(en)_2(OH_2)]^{2+} + Cl^-$
$[PtCl(NH_3)_3]^+ + H_2O \rightarrow [Pt(NH_3)_3(OH_2)]^{2+} + Cl^-$

Thus conductance measurement with time can be practised to study the above reactions. The rate of Cl^- release can also be measured potentiometrically by using an electrode sensitive to Cl^-

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In the following reaction, during the progress of reaction, pH decreases due to the release of H^+ ion.

$$M^{2+} + LH \rightarrow ML^+ + H^+$$

Thus the pH measurement with time can evaluate the rate constant of the process.

- **Polarimetric method:** The measurement of optical rotation with time can be used to determine the rate constant of a racemisation processes.

$$\Delta-\left[Co(bigH)_3\right]^{3+} \rightleftharpoons \Lambda-\left[Co(bigH)_3\right]^{3+}$$

It should be taken into consideration that the light used in the optical rotation measurements may accelerate the isomerisation process in some cases. In such cases, the method becomes erratic.

- **Isotope tracer technique:** The electron exchange reactions in the couples like $[Ru(NH_3)_6]^{3+}$/$[Ru(NH_3)_6]^{2+}$, $[Fe(CN)_6]^{3-}$/$[Fe(CN)_6]^{4-}$, $[Fe(OH_2)_6]^{3+}$/$[Fe(OH_2)_6]^{2+}$, etc. may be followed by using the labelled isotope. Isotopic tracer techniques may be used to follow the metal exchange and ligand exchange reactions.

(2) For following the fast reactions of labile centres, it needs some special techniques like stopped-flow, spectrophotometry, T–jump, P–jump, NMR, etc. depending on the $t_{1/2}$ of the reactions.

- **Stopped-flow spectrophotometry:** In the stopped-flow technique, the mixing time between the reactants is about 1 ms (*i.e.* 10^{-3} s) and the reactions faster than the mixing time cannot be studied by the stopped-flow spectrophotometry. In the stopped-flow spectrophotometry, after mixing of the reactants within the reaction cell, progress of the reaction can be followed spectrophotometrically with the help of a fast recorder device.

- **Perturbation technique (*i.e.* T–jump, P–jump):** This technique is applicable for the reactions of $t_{1/2}$ in the time scale of μs (= 10^{-6} s). In this technique, the equilibrium is perturbed suddenly (fraction of μs or less) by a temperature change, *ca.* 5 – 10°C (in T–jump) or a pressure change, *ca.* a few hundred atmosphere (in P–jump). This change of temperature or pressure directs the equilibrium in a direction as demanded by *Le Chatelier's principle.* This relaxation of the system towards the new equilibrium position can be followed spectrophotometrically by using a fast recorder device. This is why, this perturbation technique is referred to as the **relaxation technique.** It may be mentioned that

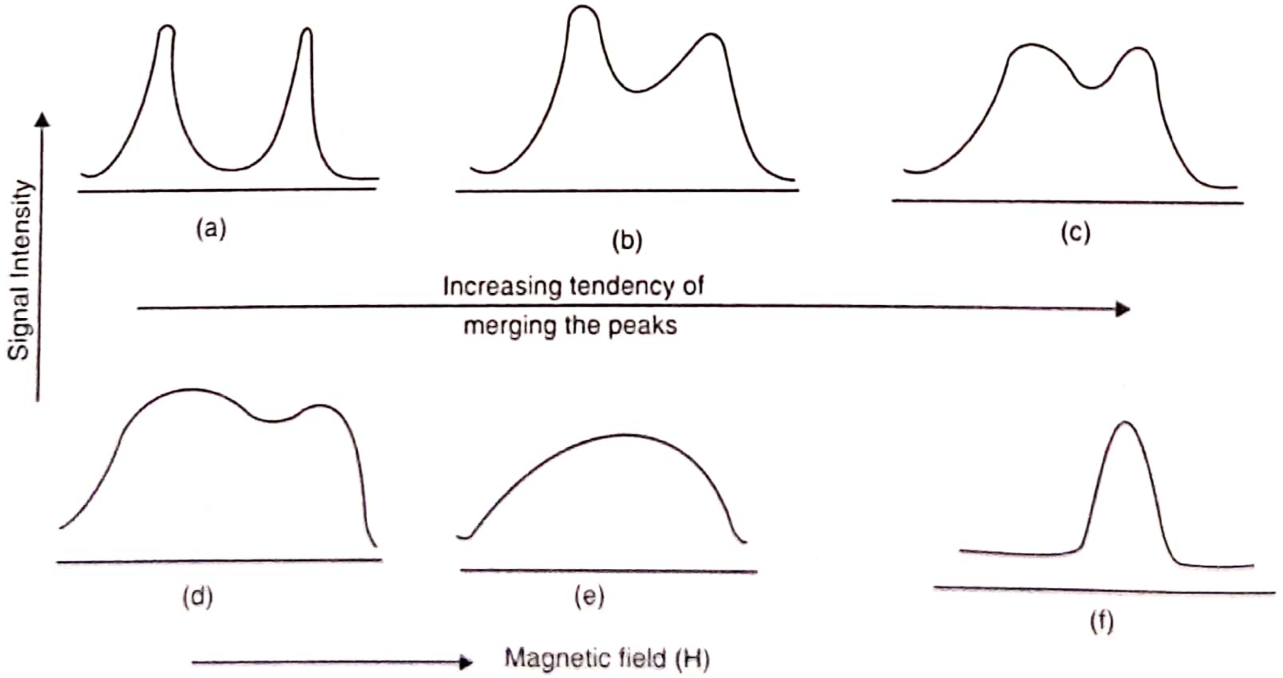

Fig. 5.6.1 Change of the NMR signals with the gradual increase of exchange rates (*e.g.* proton exchange process between two sites X — H and Y — H) from (a) → (f). (a) Exceedingly slow exchange rate (*i.e.* practically no exchange); (b) to (e) Gradually increasing rate; (f) Very rapid exchange rate (*see* Sec. 12.2.15, Fig. 12.2.15.1).

the T–jump technique can be applied to all systems but the P–jump technique can only be applied to the systems where there is a change in the number of species in the reaction (more correctly, where there is a molar volume change).

● **NMR technique** (*cf.* Sec. 12.2.15): For the studies of *fast exchange reactions* (both ligand exchange and metal exchange), the NMR method is very much important. For the studies of water exchange reactions, $^{17}\text{OH}_2$ is used. The NMR spectra of a particular NMR-active centre depends on its chemical environment. Thus the NMR spectra of ^{17}O are different for metal bound $^{17}\text{OH}_2$ and $^{17}\text{OH}_2$ present in bulk solvent. If the water exchange rate is slow, then the NMR signals of ^{17}O for two different chemical environments are quite distinct. *But with the increase of exchange rate, the signals will move to merge or overlap* (*i.e.* the peak will be broadening). If the exchange rate is extremely fast, then a single peak is noticed. Thus from the nature of merging the peaks, it is possible to determine the exchange rate constant. Merging of peaks due to an exchange reaction is qualitatively shown in Fig. 5.6.1.

5.7 MECHANISM OF LIGAND SUBSTITUTION REACTION: INTIMATE AND STOICHIOMETRIC MECHANISM

● **Stoichiometric mechanism:** It deals with the *sequence of elementary steps* leading to a chemical reaction. It looks at the *reactants, products* and *intermediates* but not at the transition states. Thus the stoichiometric mechanism looks at the species residing at the **potential minima** along the reaction coordinates. Consideration of the involved elementary steps can lead to the rate law. There are three types of stoichiometric mechanism of ligand substitution reaction. These are:

Dissociative (D), Interchange (I) and Associative (A)

Dissociative and associative reactions are the **two-step reactions** passing through an **intermediate,** while interchange reaction is a **one-step reaction** without the formation of a **true intermediate.**

● **Intimate mechanism:** It deals with the *activation process* leading to the formation of an activated complex at the rate determining step. It looks at the species residing at **the highest point** (*i.e.* activated complex or transition state) on the reaction coordinate. Thus it considers the *energetics of the formation of the activated complex* and *consequently the rate.*

If the rate of formation of the activated complex at the rate determining step (*i.e.* rate of the overall reaction) depends strongly on the nature of the entering ligand (say *L*) then it indicates that the enering ligand makes a new bond to a significant extent to generate the activated complex. Thus the *activation process* is **associative (*a*)**. On the other hand, if the reaction rate is strongly dependent on the nature of the leaving group (say *X*) and almost independent of the nature of enterging group (*L*), then it indicates that bond breaking by the leaving group is important to generate the activated complex. Thus the *activation process* is ***dissociative* (*d*)**.

Here it is worth mentioning that the **associative activation** and **dissociative activation** are denoted by **a** and **d** respectively (not by **A** and **D** which denote the stoichiometric associative and dissociative reaction mechanisms respectively).

● **Relationship between the stoichiometric and intimate mechanism: D mechanism** must involve the **dissociative (d) activation** while **A mechanism** must involve the **associative (a) activation. I mechanism** involves **both the dissociative and associative activation,** *i.e.* both bond breaking by the leaving group and bond formation by the entering group contribute at the rate determining step. If in this process of activation, bond breaking (*i.e.* dissociative) is the predominant factor then it is referred to as I_d. On the other hand, if in the interchange process, bond formation (*i.e.* associative) by the entering group is the predominant factor then it is referred to as I_a.

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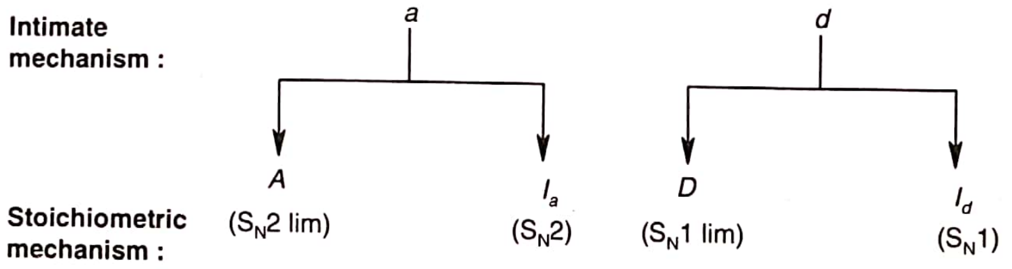
Thus the **combined notations** describing both the stoichiometric and intimate mechanisms are:

A, I_a, I_d, D (Langford-Gray notation)

- **Relationship between Langford-Gray notation and Hughes-Ingold notation used in organic chemistry:** According to Basolo and Pearson, *A mechanism* is equivalent to **S_N2 lim**. (*i.e.* limiting situation of S_N2) while *D mechanism* is equivalent to **S_N1 lim**. I_a and I_d correspond to S_N2 (not limiting) and S_N1 (not limiting) respectively.

Note: $S_N1 \Rightarrow$ substitution nucleophilic unimolecular; $S_N2 \Rightarrow$ substitution nucleophilic bimolecular.



- For both the **D** and **I_d** processes, the intimate mechanism is **d** (*i.e.* **d**–activation) but for the D–process, the intermediate (*i.e.* **long life time**) of lower coordination number is detectable while the intermediate is not detectable (*i.e.* **very small life time**) for the I_d process. Thus their stoichiometric mechanisms (*i.e.* sequence of elementary steps) differ.
- Similarly for both the **A** and **I_a** processes, the intimate mechanism is **a** (*i.e.* **a**–activation). The intermediate of higher coordination number is detectable for the **A**–pathway but not for the I_a–pathway. Thus their stoichiometric mechanisms (*i.e.* sequence of elementary steps) differ.

- **Cases involving a fast pre-equilibrium step followed by the rate determing step:** The fast preequilibrium step may lead to the formation of reactive intermediates like **ion pair (IP), conjugate base (CB), conjugate acid (CA),** etc. and then these reactive intermediates participate at the rate determining steps. In such cases, notation of the reaction mechanism depends on both the nature of the reactive intermediate (formed in a rapid preequilibrium step) and the nature of rate determining step involving the reactive intermediate. This aspect is illustrated below.

$$\begin{array}{c}\text{Reactants} \rightleftharpoons \text{Intermediate}\ \text{(fast pre-equilibrium)}\\ \big\downarrow \text{rds}\\ \text{Product.}\end{array}$$

Notation of the mechanism: Nature of the rds (*i.e.* A or D or I) – nature of the intermediate (*i.e.* IP or CA or CB).

If the intermediate is *IP*, and the rds is a *A*–pathway, then the mechanism is designated by ***A–IP*** (*i.e.* ***S_N2–IP*** in old nomenclalure). Similarly we can have:

D–IP **(*i.e.* S_N1 lim–*IP*, in short S_N1–*IP*)** meaning *IP* as the intermediate, and rds as the *D*-pathway;

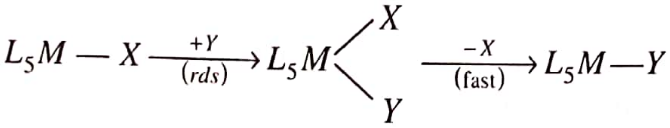
D–CA **(*i.e.* S_N1 lim–*CA*, in short S_N1–*CA*)** meaning *CA* as the intermediate and rds as the *D*-pathway;

D–CB **(*i.e.* S_N1 lim–*CB*, in short S_N1–*CB*)** meaning *CB* as the intermediate, and rds as the *D*-pathway;

Similarly, we can write: ***I_d–CB, I_d–IP, I_a–IP***, etc.

5.8 REACTION PROFILE FOR DIFFERENT STOICHIOMETRIC MECHANISMS

A. Associative (A) process: Two step reaction with two transition states and one intermediate



$$L_5M-X\xrightarrow[(rds)]{+Y}L_5M\begin{matrix}X\\ \\ Y\end{matrix}\xrightarrow[(fast)]{-X}L_5M-Y$$

The entering ligand (*Y*) makes a new bond with the metal centre at the rate determining step to **increase the coordination number by unity.** In attaining this intermediate of higher coordination number, there is no bond breaking by the leaving group. After the rate determining step (rds), the leaving group (*X*) is lost from the intermediate at a faster step.

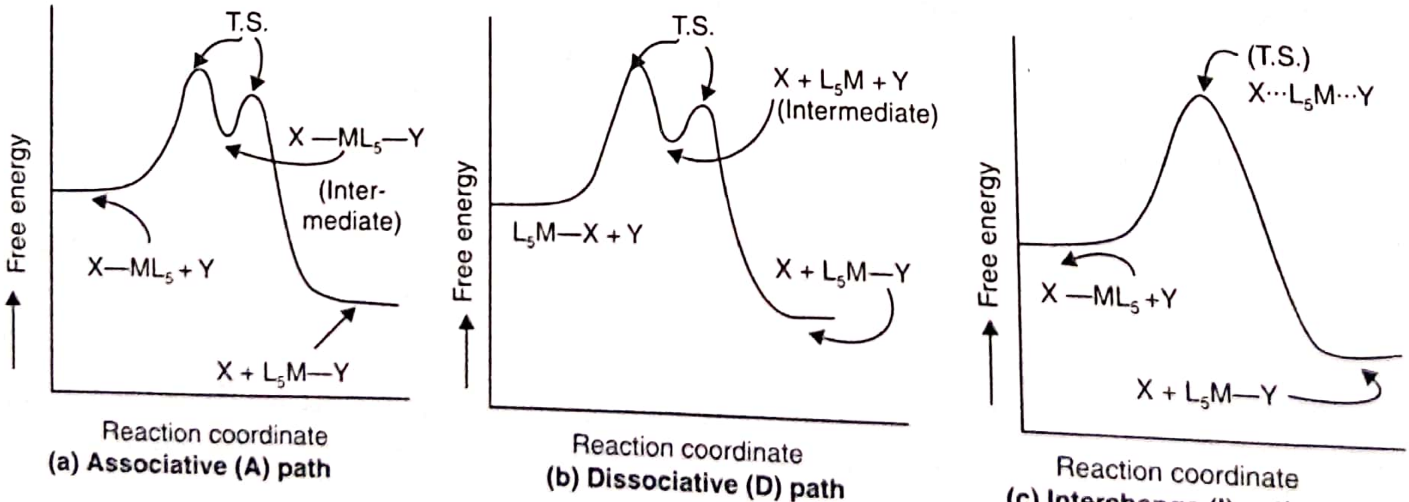
The reaction pathway involves the formation of a **single intermediate** ($Y-ML_5-X$) and **two transition states (T.S.)** — one for the formation of the intermediate and another for the decomposition of the intermediate to the product. The energy barrier for the decomposition of the intermediate is relatively lower.

B. Dissociative (*D*) process: Two step reaction with two transition states and one intermediate

$$L_5M-X\xrightarrow[(rds)]{-X}L_5M\xrightarrow{+Y}L_5M-Y$$

The leaving group (*X*) is lost at the rate determining step through the rupture of the $M-X$ bond to generate an intermediate (L_5M) with **a lower coordination number** (*i.e.* coordination number decreases by unity for the unidentate leaving group). At this stage of generation of the intermediate, there is no interaction with the entering ligand. After the rate determining step, the entering group enters into the coordination sphere at a faster step to give the final product.

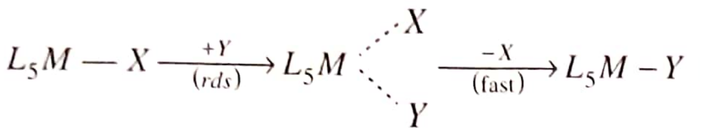
As in the *A* process, in the *D*–process also, there is **a single intermediate** but of lower coordination number, and **two transition states** – one leading to the formation of the intermediate and the other leading to the product from the intermediate. The energy barrier leading to the formation of the intermediate is higher.



(a) Associative (A) path
(b) Dissociative (D) path
(c) Interchange (I) path

Fig. 5.8.1 Energy-profile diagram for the different mechanisms of ligand substitution reactions.

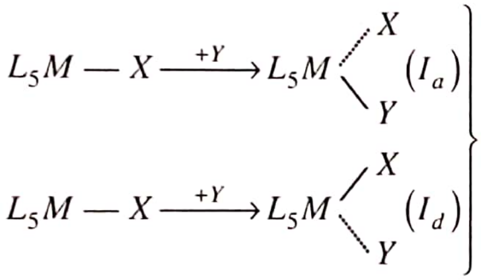
C. Interchange (I) Process: Single step reaction with a single transition state



(⋯ denotes breaking or forming bond)

Both the leaving and entering group are involved in **a single step** to generate the **activated complex (not the true intermediate because it is too short-lived to be detected).** In attaining this activated complex, both the bond breaking by the leaving group (*i.e.* **slight rate dependance on the nature of the leaving group**) and bond formation by the entering group (*i.e.* **slight rate dependance on the nature of the entering group**) are important. In other words, bond formation by the entering group and bond rupture by the leaving group go on simultaneously in a *concerted manner* and ultimately the incoming group gets completely bound with the metal centre and the leaving group is completely dislodged. The reaction profile is characterised by a **single transition state** (T.S.).

Depending on the relative importance of the bond formation by the entering group and bond dissociation by the leaving group in the interchange process, two different situations may arise giving rise to two different types of transition states.



Bond denoted by .... makes a less contribution in the activation process.

Thus in $\mathbf{I_a}$, the new bond formation by the entering group is more important (*i.e.* rate is relatively more sensitive on the nature of the entering group) while in $\mathbf{I_d}$, bond rupture by the leaving group is more important in the activation process.

First Order :

we can finally write for a complex undergoing ligand substn. by 'D' : $-dc/dt = K_1$

$$\text{or, } k_1 = \frac{2.303}{t} \log \frac{a}{a-x}$$

where k_1 is the first order rate constant and a and $(a - x)$ are the concentrations of the reactant complex at times zero and t respectively. When a property P, directly proportional to the reactant concentration, is measured we have :

$$k_1 = \frac{2.303}{t} \log \frac{P_O - P_\infty}{P_t - P_\infty}$$

A plot of log $(P_O - P_\infty) / (P_t - P_\infty)$ against t will give a straight line whose slope (change in log $((P_O - P_\infty) / (P_t - P_\infty))$ over a time $(t_2 - t_1)$ divided by change in time $(t_2 - t_1)$ is equal to $k_1/2.303$.

Second Order : For a single reactant or two reactants of equal initial concentration a, we have :

$$k_2 = \frac{1}{t}\left(\frac{1}{a-x} - \frac{1}{a}\right)$$

where k_2 is the second-order rate constant. For two reactants of unequal initial concentration a and b we have :

$$k_2 = \frac{2.303}{t(b-a)} \log \frac{a(b-x)}{b(a-x)}$$

These equations enable suitable graphical plots to be made of the reactants (or products) concentrations measured at various times ; the reaction order and the rate constant are deduced from the relation which best describes the system.

Plots of rate data may depart significantly from linearity due to simultaneous or consecutive reactions.

Rate constants are expressed in units of LM^{-1} sec^{-1} (or M^{-1} sec^{-1}) at a given temperature.

Order of Reaction and Reaction Mechanism : The fact that a system exhibits first or second order behaviour does not necessarily mean that an unambiguous reaction mechanism can thereby be postulated. It is not correct to assume that a bimolecular reaction will show second order kinetics and a unimolecular reaction first order kinetics. Actual nature of the reaction may be influnced by the relative concentration of the reactants, the experimental conditions and the complexities of the overall mechanism. An interesting example is the role played by solvent water in acid hydrolysis of amminehalometal complexes. Acid hydrolysis (at pH below 4) shows no acid dependence. The observed rate law is simple first order.

$$[MXA_5]^{n+} + H_2O \rightleftharpoons [MA_5(H_2O)]^{(n+1)+} + X^-$$

$$\text{rate} = k[MXA_5^{n+}]$$

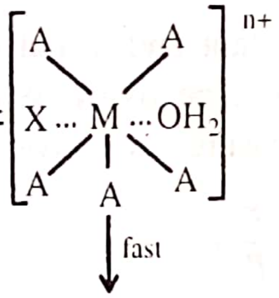
This rate law is compatible with the following two mechanisms (a) and (b) :

$$\text{(a) } [MXA_5]^{n+} \underset{\text{fast}}{\overset{k_a,\ \text{slow}}{\rightleftharpoons}} [MA_5]^{(n+1)+} + X^-$$

$$[MA_5]^{(n+1)+} + H_2O \xrightarrow{\text{fast}} [MA_5(H_2O)]^{(n+1)+}$$

$$\text{rate} = k_a[MXA_5^{n+}]$$

$$\text{(b)}\ [MXA_5]^{n+} + H_2O \xrightleftharpoons{k_b,\ \text{slow}}$$



$$[MA_5(H_2O)]^{n+1} + X^-$$

$$\text{rate} = k_b[MXA_5^{n+}]\ [H_2O] = k'_b[MXA_5^{n+}]$$

Since solvent water is present in the system in large excess ($[H_2O] \simeq 55M$), the $[H_2O]$ may be taken as constant. Hence the observed kinetics of a substitution reaction rarely gives the mechanism unambiguously. So knowledge of the order of a reaction must be combined with additional information before a mechanism can be proposed with any confidence.

Activation Energy :

It is the minimum energy that a molecule (for a dissociative subtitution reaction) or a pair of molecules (for an associative reaction) must possess before they can be ready for a particular chemical reaction. The rate of almost all reactions increases with temperature by about two to three times for a temperature rise of 10°C. Arrhenius equation satisfactorily describes the variation of reaction rate constant with temperature :

$$k = Ae^{-E_a/RT}$$

where the pre-exponential term A is called the frequency factor and E_a the activation energy. The pre-exponential factor A is virtually independent of temperature. In logarithmic form we have :

$$\log k = \log A - \frac{E_a}{2.303RT} = \text{constant} - \frac{E_a}{2.303RT}$$

A plot of log k against $1/T$ would give a straight line with slope $-E_a/2.303\,R$. Experimental activation energies are obtained by measuring k at several temperatures, plotting log k against $1/T$ and calculating E_a. E_a is expressed in calories (when R is in cal deg^{-1} mole^{-1}) or in Joules (when R is in Joules deg^{-1} mole^{-1}).

A large activation energy indicates a slow reaction. Even when a reaction is thermodynamically favourable (i.e. when the equilibrium product has a large formation constant K) a large activation energy will make the reaction slow-going.

For better understanding, Arrhenius relation has been replaced by Eyring equation which is based on transition state theory especially when considering reactions in solution. The equation is :

$$k = \frac{RT}{Nh}e^{-\Delta G^{\neq}/RT}$$

The above equation can also be written in the form :

$$k = \frac{RT}{Nh} e^{\Delta S^{\neq}/R} e^{-\Delta H^{\neq}/RT}$$

Where R is the universal gas constant; T, the absolute temperature ; N, Avogadro's number; h, Planck's constant ; $\Delta H^{\neq}$, the enthalpy of activation ; $\Delta S^{\neq}$, the entropy of activation; and $\Delta G^{\neq}$ represents the standard Gibbs free energy of activation. The quantities $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are the differences in enthalpy and entropy respectively between the transition state and the reactants. The above equation can also be written as :

$$\log k = \log\frac{RT}{Nh} + \frac{\Delta S^{\neq}}{2.303R} - \frac{\Delta H^{\neq}}{2.303RT}$$

Plot of log k vs. $1/T$ will be a linear plot. The slope and intercept of the plot will provide the value of $\Delta H^{\neq}$ and $\Delta S^{\neq}$. The values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are extremely useful in the assignment of mechanism.

The enthalpy of activation ($\Delta H^{\neq}$) will usually include :

(i) Significant electrostatic contribution representing energy required to bring charged reactants close to each other.

(ii) Energy required for internal reorganization of the bonds within the reactant molecule i.e. this will include the enthalpy terms for the rupture of the M-X bond already present and formation of new metal ligand bond M-Y in the activated state, the relative contributions of which depend on the type of mechanism.

(iii) Solvation energies of reactants and activated complex in the transition state.

The entropy of activation represents the total change in entropy of the reactants and solvent in the formation of activated complex. Negative entropies of activation are in general indicative of an associative mechanism and positive entropies of a dissociative mechanism. For a 'D' mechanism, in going from the initial state to the transition state, there is an increase in disorder, that is the entropy increases ($\Delta S^{\neq} > 0$). For an 'A' mechanism the randomness of the transition state is smaller than the initial state and $\Delta S^{\neq} < 0$. For interchange mechanism, intermediate values are expected. The brief analysis, gives the salient feature of the expected trends, but it is certainly idealized. It does not illustrate contributions from other changes. Solvation changes in the formation of transition state from the reactants may play a significant role in entropy of activation (electrostriction effect).

Acid Hydrolysis : Evidence for Substitution mechanism in octahedral complexes : Of the replacement reactions of octahedral coordination compounds the most widely studied are these in which aqua complexes are formed by acid hydrolysis :

$$[MXA_5]^{n+} + H_2O \longrightarrow [MA_5H_2O]^{(n+1)+} + X^- \ (X^- = \text{anion})$$

An alternative term to acid hydrolysis is aquation. It should be noted that acid hydrolysis implies no more than hydrolysis under acid conditions; the rate of the reaction may or may not be proportional to the concentration of acid. The greater bulk of work performed has been concerned with the acid hydrolysis of Co(III) complexes since it is known that most substitution processes of Co(III) in aqueous solution proceed indirectly via reaction with

Kinetics, and Mechanisms

TRANS EFFECT : Application and Theories :

14

Despite extensive study, inorganic chemistry has yet to achieve the understanding of reaction mechanisms enjoyed by organic chemistry. This fact, alluded to previously (Chapter 5), results from the task of trying to handle more than one hundred elements with a single scheme. Unfortunately, even attempts to predict from one element in a group to another in the same group are not always successful. The lack of understanding of mechanisms carries over into synthesis; the methods used in synthesizing coordination compounds often include some combination of redox chemistry and displacement of ligands (often water) by the desired ligands. Thus the well-known synthesis of hexaamminecobalt(III) cation is typical. Starting with stable and common cobalt(II) salts (such as the nitrate or carbonate) the desired ligand, ammonia, is added in high concentrations to replace those present (usually water or chloride ion), and an oxidizing agent (air or hydrogen peroxide, with a charcoal catalyst) effects the change in oxidation state:

$$[CoCl_4]^{-2} \xrightarrow[-\ 4Cl^-]{+\ 6NH_3} [Co(NH_3)_6]^{+2} \xrightarrow[-e^-]{[O]} [Co(NH_3)_6]^{+3} \qquad \textbf{(11.1)}$$

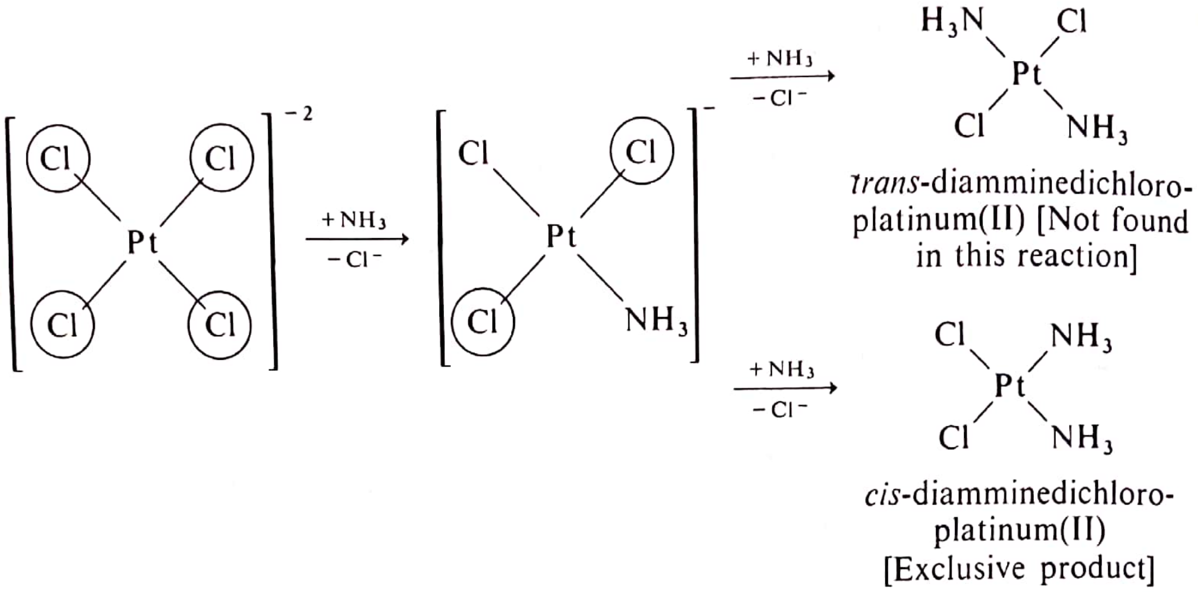
Occasionally, synthetic "tricks" are discovered that allow the synthesis of a desired compound or isomer without interference from an undesired one. Thus, quite early, Werner discovered that certain *cis* isomers could be prepared by using a carbonato compound that would react with acid to evolve carbon dioxide and insert two anions of the acid as ligands:

$$[Co(en)_2CO_3]^+ + 2HCl \longrightarrow cis\text{-}[Co(en)_2Cl_2]^+ + H_2O + CO_2\uparrow \qquad \textbf{(11.2)}$$

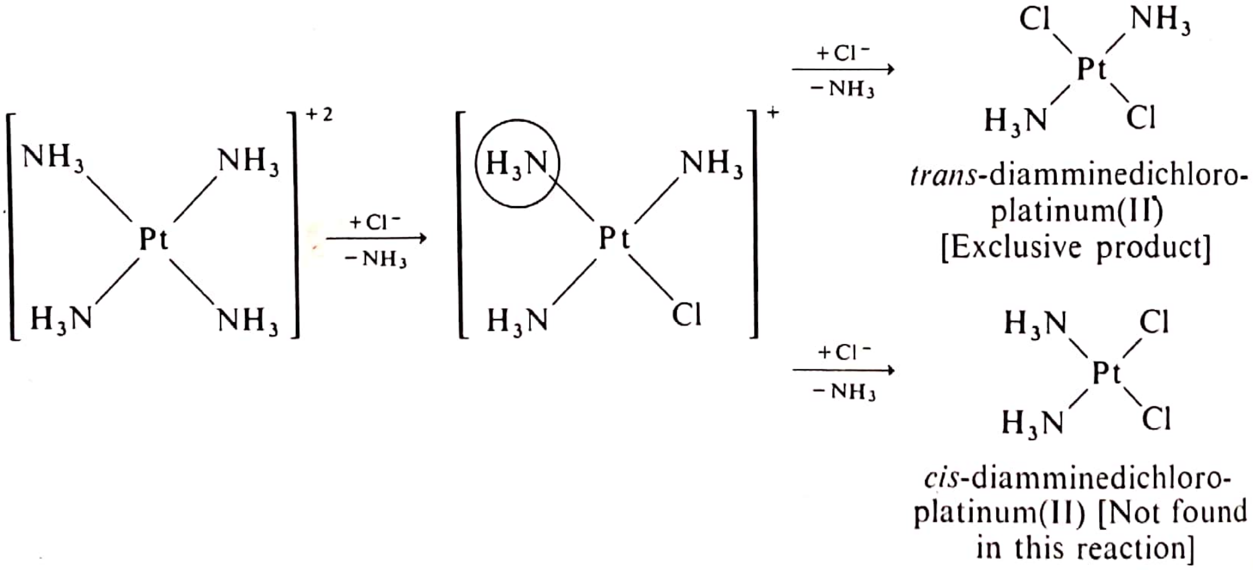
More rarely, reactions are known in which predictions can be made about a wide variety of complexes involving different metals and different ligands and for which the mechanism is fairly well understood. A good example of this type of reaction is that of four-coordinate, square complexes in which the *trans effect* operates and allows systematization to be made.

THE *trans* EFFECT

The presence of large deposits of platinum ores in Russia caused an intensive study of the coordination compounds of platinum early in the development of coordination chemistry. As a result of these studies by the Russian school, the first stereospecific displacement reaction was discovered. Consider two means of forming diammine dichloroplatinum(II): (1) displacement of Cl^- ions from $[PtCl_4]^{-2}$ by NH_3; (2) displacement of NH_3 from $[Pt(NH_3)_4]^{+2}$ by Cl^- ions. It is found that two different isomers are formed:

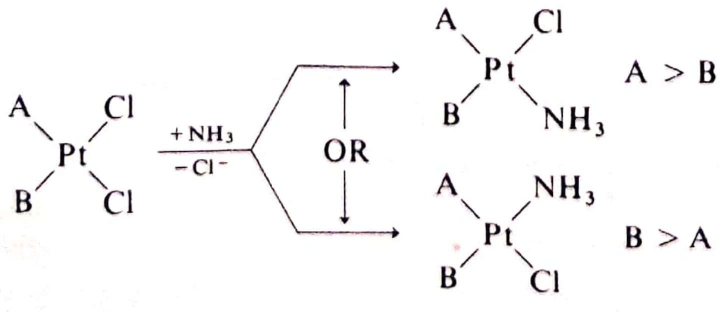


(11.3)



(11.4)

Reactions in Eqs. (11.3) and (11.4) can be rationalized as follows: (1) Step one is a simple displacement and since all four groups present (either NH_3 or Cl) are identical, only one compound is formed; (2) in step two, two products can potentially be formed in either reaction but in practice only one is found and it differs between the two reactions. In both reactions, however, the isomer that is found is that which forms by substitution of a ligand *trans* to a chloride ion. The ligands *trans* to chloride ions have been circled in Eqs. (11.3) and (11.4) to emphasize this fact. The *trans effect* may be defined as *the labilization of ligands trans to other, trans-directing ligands*. By comparison of a large number of reactions, it is possible to set up a *trans-directing series*:

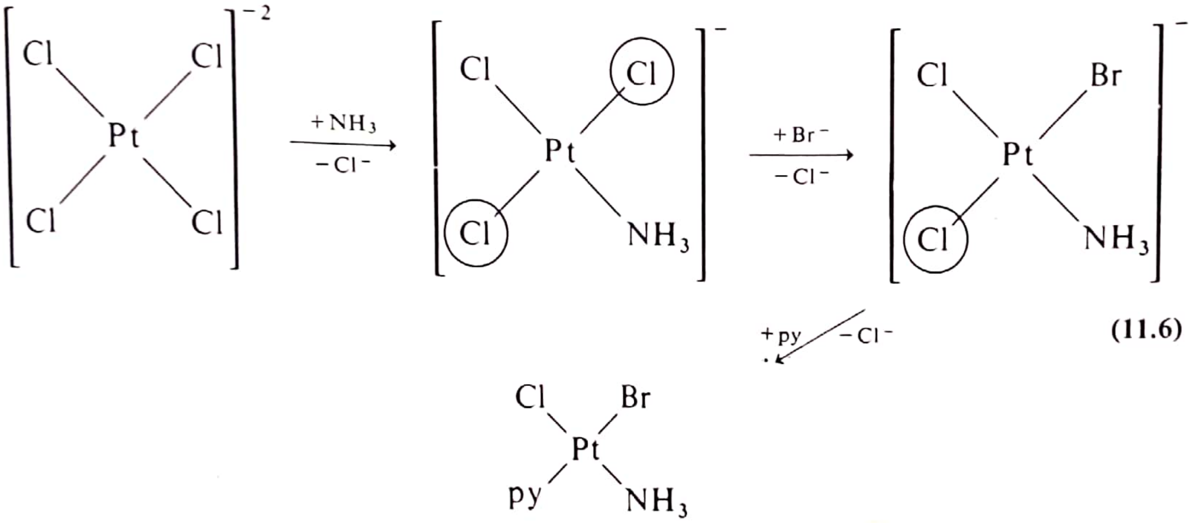


(11.5)

The ordering of ligands in this series is as follows: $CN^- \sim CO \sim NO \sim H^- > CH_3^- \sim SC(NH_2)_2 \sim SR_2 \sim PR_3 > SO_3H^- > NO_2^- \sim I^- \sim SCN^- > Br^- > Cl^- > py > RNH_2 \sim NH_3 > OH^- > H_2O$.

The *trans* effect in synthesis

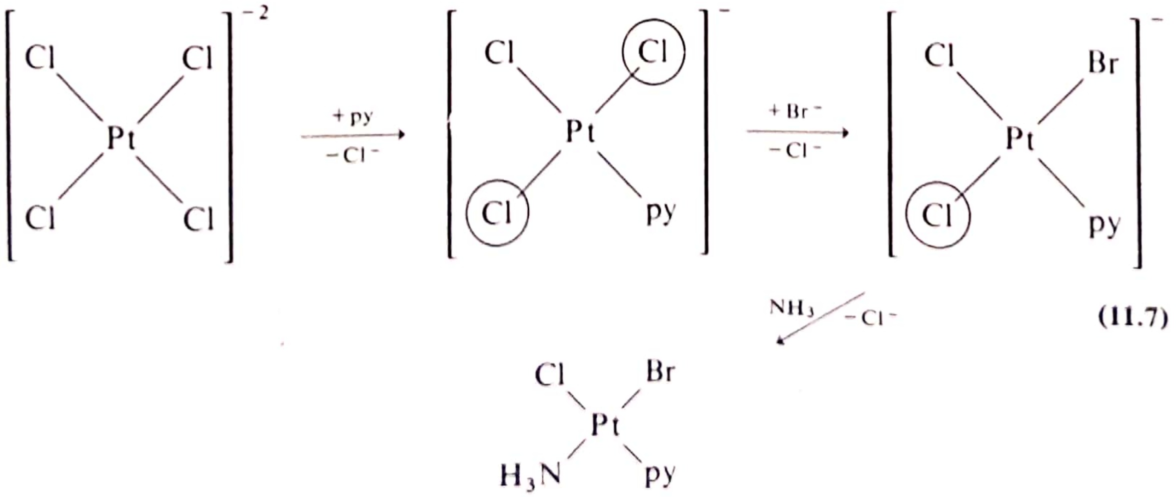
By ordering the sequence of addition of substituents, the *trans* effect may be utilized to provide the desired isomer in an otherwise complicated system. For example, consider the problem of the synthesis of the three geometrical isomers of amminebromochloro(pyridine)platinum(II). By utilizing a knowledge of the *trans* effect, the following reactions were suggested and carried out[1]:



(11.6)

In addition to the *trans* effect, use is made of the general principle that, other things being equal, a metal–halogen bond is more labile than a metal–nitrogen bond. In this case "other things equal" means that in step 2 the chloride ion *trans* to another chloride ion will be replaced more readily than a nitrogen atom *trans* to a chloride ion. The group *trans* to the most influential *trans* director is again circled. Note that the results of the last reaction indicate the bromide ion to be a better *trans* director than chloride.

The synthesis of the second isomer follows a similar pattern:



(11.7)

Here, too, the lability of a metal–chlorine bond results in preferential replacement of chloride ion instead of pyridine in the second step and the *trans* influence of the bromide ion determines the final geometry.

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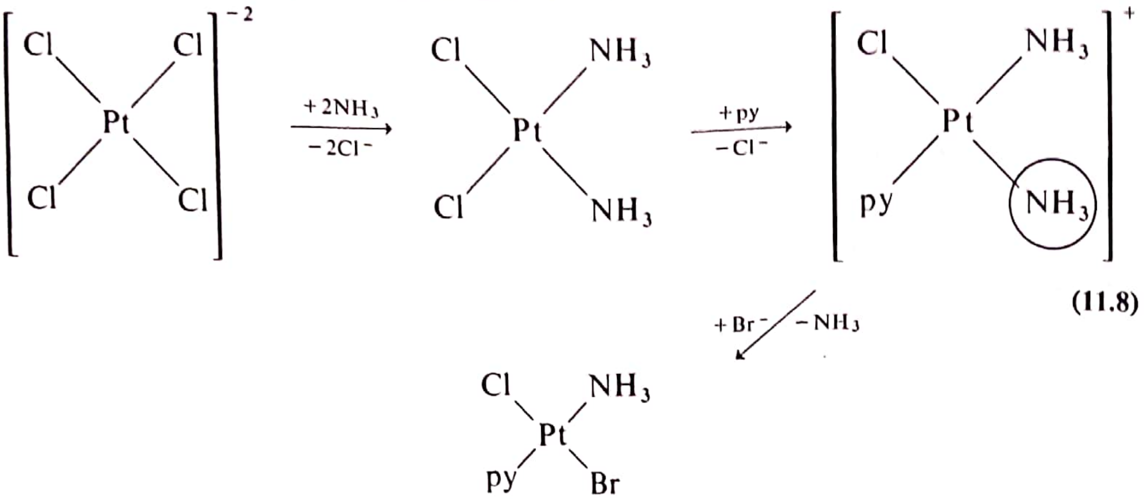
[1] A. D. Hel'man, E. F. Karandashova, and L. N. Essen, *Dokl. Akad. Nauk. S.S.S.R.*, **63**, 37 (1948).

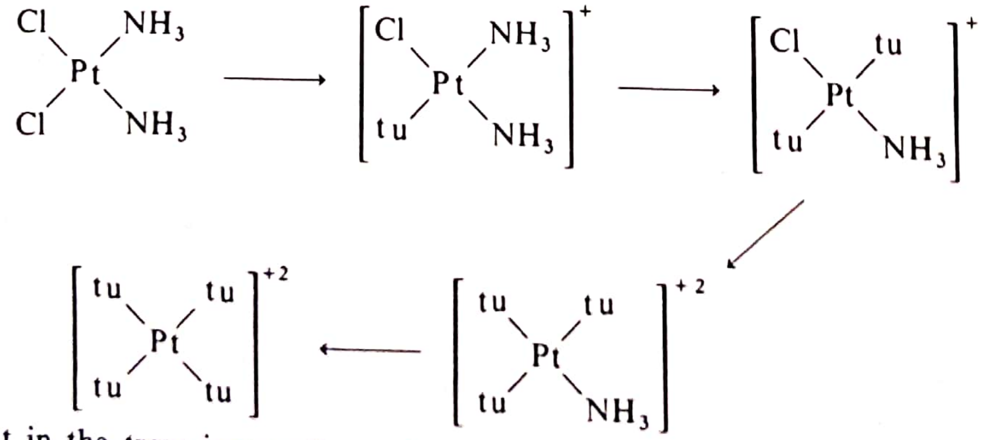
The third isomer may be formed as follows:



(11.8)

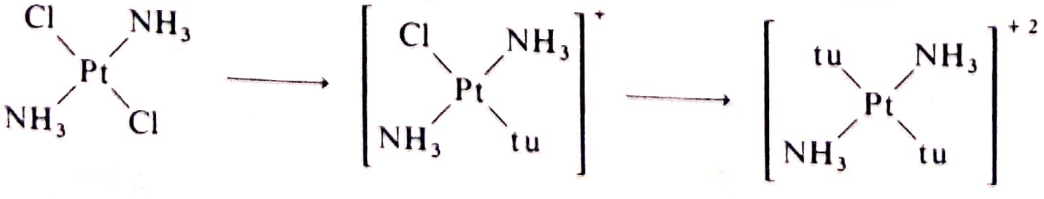
In this synthesis the *trans* effect predicts the formation of the *cis* isomer in the first step and the replacement of the ammonia molecule *trans* to the chloride ion (rather than the one *trans* to pyridine) in the final step. The inherent lability of the platinum–chlorine bond directs the second step. In the third step, this inherent lability runs counter to the labilizing *trans* effect. Hence the fact that the entering bromide ion displaces an ammonia molecule rather than the chloride ion can only be set down as an empirical observation. This is a good example of the fact that the *trans* effect provides us with qualitative information concerning which ligands will be *more* labile (than they would be in the absence of a *trans* director) but no information on the *absolute* lability of the various ligands. Nevertheless, considerable ordering is provided by application of the *trans* effect and empirical observations (such as the inherent lability of M—Cl bonds). If on occasion the two rules run counter to one another and we are unable to choose with certainty, we should not be too discouraged—imagine the chaos resulting from reactions (11.6) to (11.8) if they were completely random!

An interesting application of the *trans* effect is in distinguishing between *cis* and *trans* isomers of complexes of the type $[PtA_2X_2]$ where A = amine and X = halide (Kurnakov test). Addition of thiourea (tu) to the *cis* complex results in complete replacement of the former ligands:



(11.9)

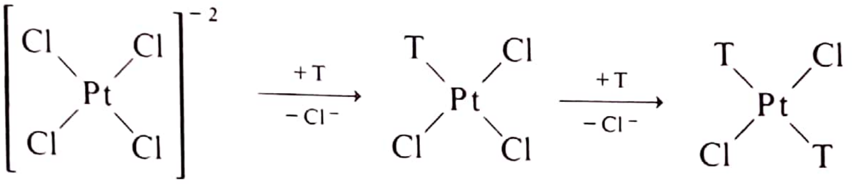
but in the *trans* isomer the replacement stops after the two halide ions have been replaced since the *trans* ammonia molecules do not labilize each other:



(11.10)

Mechanism of the *trans* effect

The *trans* effect must be kinetically controlled since the thermodynamically most stable isomer is not always produced. This is obvious since it is possible to form two different isomers (Eqs. (11.3) and (11.4)) or three different isomers (Eqs. (11.6), (11.7), and (11.8)) depending upon the reaction sequence and only one of the isomers can be the most stable in a thermodynamic sense. Furthermore, we observe that the best *trans* directors (T) are often those that are the best pi bonders. Hence in the formation of bis isomers of the sort $[PtCl_2T_2]$ from $[PtCl_4]^{-2}$, the *trans* isomer is always observed:



(11.11)

even though, in general, the *cis* isomers are favored thermodynamically (see page 554). Such kinetically controlled reactions are common in both organic and inorganic chemistry and represent examples of reactions in which the energy of activation of the activated complex is more important in determining the course of reaction than the energy of products.

Two viewpoints have been advanced with respect to the mechanism of the *trans* effect. The first is essentially a static one emphasizing a weakening of the *trans* bond, the second is the lowering of the activation energy of *trans* replacement. The earlier literature made no attempt to distinguish between the two effects, but in view of the above discussion it is important to separate them.[2] The "*trans effect*" may be defined[3] as "the effect of a coordinated group [T] upon the *rate* of substitution reactions of ligands opposite to it." In contrast, the "*trans influence*" may be defined[4] "as the extent to which that ligand weakens the bond *trans* to itself in the equilibrium state of a substrate."

The earliest theory that still has current application is the polarization theory of Grinberg.[5] The latter suggested that in a completely symmetrical complex such as $[PtCl_4]^{-2}$ the bond dipoles to the various ligands will all be identical and cancel (Fig. 11.1(a)). In contrast, if a more polarizable and polarizing ligand, T, is introduced (such as an I^- ion), its polarizability will induce an additional, uncompensated dipole in the metal (*cf.* the mutual polarization of the Fajans' effect, page 91). This induced dipole in the metal will oppose the natural dipole of the ligand *trans* to the polarizing ligand (Fig. 11.1(b)). The polarization theory is supported by the following facts: (1) It should be most important when the central metal atom is large and polarizable, and indeed the ordering of the *trans* effect is $Pt^{II} > Pd^{II} > Ni^{II}$; (2) the *trans* series listed above should also be a polarizability series and, in general, the *trans*-directing groups

- Kinetic Trans Effect (KTE)
  a kinetic phenomenon
- Static Trans Effect → STE → Trans infl.
  a thermodynamic phenomenon

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[2] Whether the static *trans* influence is operative in the dynamic *trans* effect is a moot point. Certainly it is reasonable to assume that a weakening of a *trans* bond may be *one* of the important factors in the latter mechanism.

[3] F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 381 (1962). The symbol T has been substituted for the symbol A used by Basolo and Pearson to make the definition consistent with the symbolism used in the following discussion.

[4] A. Pidcock, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc., A*, 1707 (1966).

[5] A. A. Grinberg, *Acta Physiochim, U.R.S.S.*, **3**, 573 (1935) [*C.A.*: **30**, 4074^6]; B. V. Nekrasov, *Zh. Obshch. Khim.*, **7**, 1594 (1937); for an English translation see A. A. Grinberg, in "An Introduction to the Chemistry of Complex Compounds," 2nd ed., J. R. Leach (transl.), D. H. Busch and R. F. Trimble, Jr., Eds., Pergamon, Elmsford, N.Y., 1962.

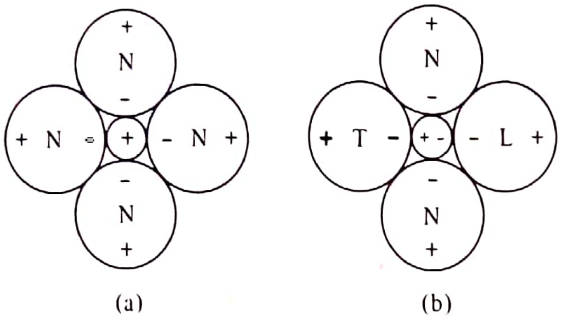

Fig. 11.1 *trans*-Directing in a square planar complex according to the polarization theory. T = *trans*-director, N = non-*trans*-director, L = labilized leaving group. (a) No *trans* effect; (b) *trans* effect operating.

are more polarizable either because they are large (iodide) or multiply-bonded (ethylene, cyanide, carbon monoxide). Nevertheless, the emphasis on *weakening* of the *trans* bond limits its application to the *trans* influence.

A second approach that involves the weakening of the *trans* bond is the static pi-bonding theory. According to this viewpoint, two pi-bonding ligands vying for the *d* orbitals of the metal atom will tend to labilize each other (as opposed to the more stable *cis* isomer where they do not compete), and the stronger pi bonder will dominate, weakening the bonding of the group *trans* to it (Fig. 11.2). Such a theory suffers from a number of difficulties. The emphasis on *weakening* of the *trans* bond presents the same ambiguities between *trans* influence and *trans* effect as Grinberg's polarization theory. In addition, it is difficult to see how the superior pi bonding of cyanide ion or a phosphine molecule could labilize an ammonia molecule *trans* to it inasmuch as *the ammonia is not stabilized by pi bonding either in the presence or absence of the trans director*. Thus pi-bonding olefins exhibit a *trans* influence on halogens but not on nitrogen ligands.[6] Furthermore, ligands such as the hydride ion and alkyl groups which are exceptionally good *trans* directors obviously cannot pi bond. Nevertheless they show a strong *trans* influence toward all ligands.[7]

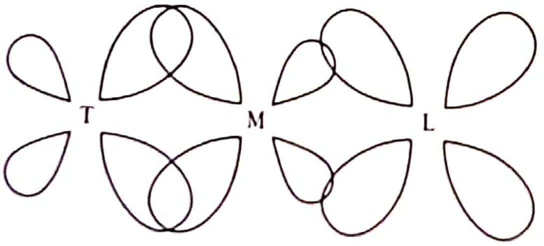

Fig. 11.2 Weakening of pi bonding resulting in a *trans* influence. The two non-*trans*-directing ligands have been omitted for clarity.

Two recent attempts have been made to revive a non-pi-bonding explanation for the *trans* influence. They are, in effect, a restatement of Grinberg's polarization theory in terms of modern molecular orbital theory. Langford and Gray[8] have pointed out that ligands *trans* to each other effectively compete for the *p* orbital of the metal ion that lies along the T—M—L axis. A ligand that competes more efficiently can "monopolize" this *p* orbital to the detriment of the bonding of the *trans* ligand, L. Similar explanations of the *trans* influence and *trans* effect in terms of preferential use of low-energy *ns* and/or $(n-1)d$ orbitals have been offered.[9] The details of these explana-

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[6] J. A. Wunderlich and D. P. Mellor, *Acta Crystallogr.*, **7**, 130 (1954); **8**, 57 (1955); P. R. H. Alderman, P. G. Owston, and M. M. Rowe, *Acta Crystallogr.*, **13**, 149 (1960).

[7] F. Basolo *et al.*, *J. Chem. Soc.*, 2207 (1961); A. Pidcock, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc.*, *A*, 1707 (1966).

[8] C. H. Langford and H. B. Gray, "Ligand Substitution Processes," Benjamin, New York, 1965, p. 25.

[9] Y. K. Syrkin, *Izv. Akad. Nauk S.S.S.R. Otdel. Khim. Nauk*, 69 (1948); A. Pidcock, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc.*, *A*, 1707 (1966); L. M. Venanzi, *Chem. Brit.*, **4**, 162 (1968); R. S. Tobias, *Inorg. Chem.*, **9**, 1296 (1970). The views in these papers are not all the same but represent a spectrum of "sigma-only" approaches to the problem.

tions are beyond the scope of this discussion but the basic premise is the same in all: The formation of an extraordinarily strong sigma bond by T will cause the hybrid orbital directed to T to be optimized to the detriment of the group *trans* to it.

All static theories suffer from the fact that the stress on the *weakening* of the *trans* bond implies (but does not necessitate) a *dissociative mechanism*[10] which is not found. In contrast, we might expect from what we have seen previously of 5-coordinate complexes that the most ready transition state would be one in which a square pyramid or trigonal bipyramid was formed (*associative mechanism*)[10] followed by elimination of the leaving group. Experimentally this has been verified in that those reactions that have been studied are second order, depending upon the concentration of both the complex and the attacking ligand:

$$[\mathrm{PtX_4}]^{-2} + \mathrm{E} \xrightarrow{\text{slow}} [\mathrm{PtX_4E}]^{-2} \xrightarrow{\text{fast}} [\mathrm{PtX_3E}]^{-} + \mathrm{X}^{-} \qquad \textbf{(11.12)}$$

Cardwell[11] has suggested that by consideration of the activated complex,[12] the *trans* effect can be explained in terms of the electronegativity of the substituents. This approach is related to the polarization theory of Grinberg which is basically electrostatic, but is a dynamic or kinetic explanation. Cardwell suggested that the activated complex consisted of a trigonal bipyramid (Fig. 11.3). The most electronegative substituents will tend to assume axial positions in such a trigonal bipyramid (see page 145). Loss of the leaving group, L, from the transition state will re-form the square complex with the entering group, E, *trans* to the least electronegative group, T, in place of the former group L. Substituents of high electronegativity such as F, O, N, *etc.*, will tend to assume the axial positions preferentially and will not act as *trans* directors. It should be pointed out that the relative position of the chloride ion is consistent with the high electronegativity of chlorine if it is recalled that the ligand in question is the chloride anion, the electronegativity of which is considerably lower than that of the

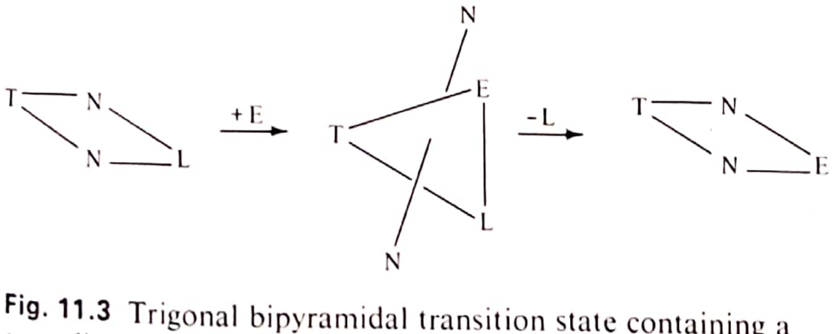

Fig. 11.3 Trigonal bipyramidal transition state containing a *trans*-directing group (T) of low electronegativity; two non-*trans*-directing groups (N) of high electronegativity; and the entering (E) and leaving (L) groups.

[10] Although the terms *dissociative* ($\approx S_{N1}$) and *associative* ($\approx S_{N2}$) are used for simplicity, it should be realized that most often the mechanisms are not so clear-cut. The terms represent two extremes and the actual mechanisms may lie somewhere between, in effect resulting in a *concerted* reaction. See discussion, page 502.

[11] H. M. E. Cardwell, *Chem. Ind.* (*London*), 422 (1955).

[12] The *activated complex* refers to the configuration of the reactants and products at the peak of the reaction profile energy curve (transition state). The term *intermediate* implies that the species has some stability (although perhaps slight) with respect to an activated complex leading from the reactants and an activated complex leading toward the products. In the present discussion the distinction is rather finer than warranted since it is not known whether the proposed species occur as pictured, much less whether they occur at the peak of the curve or in a minor minimum.

neutral atom (pages 168–170). However, the estimation of the effective electronegativities of various ligands in complexes is difficult and this reduces the usefulness of this approach. This factor, together with the evidence that other factors must be involved, has tended to reduce the popularity of this theory.

Chatt[13] and Orgel[14] independently pointed out that consideration of the activated complex improves the pi-bonding theory. These workers assumed a trigonal bipyramidal intermediate or activated complex and proposed that a pi-bonding ligand would stabilize such an intermediate. Chatt and co-workers suggested that a strong pi-bonding ligand would remove electron density from the metal through back-bonding and hence the more positive metal could more readily accept the entering, fifth ligand. Orgel pointed out that the *d* orbital involved in pi bonding on the metal will lie in the trigonal plane formed by T, E, and L (Fig. 11.4). We have already seen (page 437) that pi-bonding (and hence *trans*-directing) ligands will preferentially assume equatorial positions in a trigonal bipyramidal molecule and stabilize the 5-coordinate intermediate. The correlation of the *trans*-directing series with the amount of pi bonding expected on other grounds is generally quite good. The best *trans* directors are the same ones encountered in other cases where pi bonding is thought to be important: CN^-, CO, NO, and to a lesser extent, phosphines and sulfides.

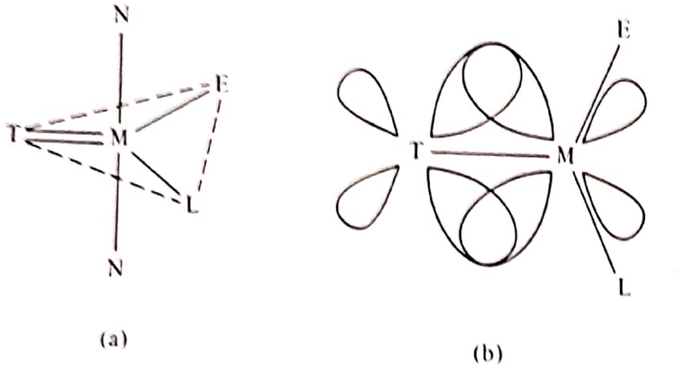

Fig. 11.4 (a) Pi-bonding transition state according to Orgel. (b) The pi-bonding acceptance of T removes electron density from the region of E and L (viewed down the N—M—N axis).

Currently, the best interpretation of the *trans* effect is uncertain. The presence of the hydride ion and methanide ion high in the *trans*-directing series even though they are incapable of pi bonding indicates that in some cases, at least, a sigma-bonding mechanism must be important. Some workers would support a sigma-only theory whereas others believe pi bonding to be important, especially in ligands such as the cyanide ion. The entire controversy is reminiscent of the pi-bonding argument presented earlier (pages 400–411). As in that argument, the sigma- *vs.* pi-bonding viewpoints are not mutually exclusive since in ligands such as cyanide, pi bonding could act synergistically to enhance a sigma effect.[15]

Kinetics of square planar substitution reactions

As we might expect, the rate of a substitution reaction in a square planar complex depends upon the nature of the *trans* ligand, and good *trans* directors behave as

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[13] J. Chatt, L. A. Duncanson, and L. M. Venanzi, *J. Chem. Soc.*, 4456 (1955).

[14] L. E. Orgel, *J. Inorg. Nucl. Chem.*, **2**, 137 (1956).

[15] See F. R. Hartley, *Chem. Soc. Rev.*, **2**, 163 (1973) and R. G. Wilkins, "The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes," Allyn and Bacon, Boston, 1974, pp. 223–233.

activating groups and increase the rate of reaction. Although this is perhaps the most obvious factor in these reactions, there are several other variables that will affect reaction rate.

The nature of the entering group and the nature of the leaving group are two properties which will affect the rate of reaction. Both can be rationalized in terms of an intermediate of the structure shown in Fig. 11.4 and the same pi-bonding arguments that were discussed above. A general ordering of entering groups that enhance the reaction is $R_3P > tu > CN^- > SCN^- > I^- > Br^- > N_3^- > OH^-$. An entering group that can come in and assume a strongly pi-bonding equatorial position (E) can stabilize the intermediate and promote the reaction. The leaving groups can act in the same way to retard the reaction. Although strongly pi-bonding ligands can stabilize the intermediate, they will be poor leaving groups (L) and thus will retard the reaction unless the sum of sigma and pi bonding is not great. The important thing here is not type of bonding but bond strength. Thus CN^- and SCN^- are poor leaving groups because they form strong sigma and pi bonds, whereas the halides form weaker bonds and are good leaving groups in complexes as they are in organic compounds.

A closer look at mechanisms

In the above discussion the simplifying equalities S_{N2} = "associative" and S_{N1} = "dissociative" mechanisms were made. Many chemists prefer to avoid the labels S_{N1} and S_{N2} and to speak of a spectrum of possibilities of associative (*A*) mechanisms ranging from an S_{N2} limit through a variety of possibilities to an interchange (*I*) mechanism consisting of a concerted process with simultaneous action of entering and leaving groups through a variety of dissociative (*D*) mechanisms to a "pure" S_{N1} limit. For the limited discussion of mechanisms in this book we need not worry unduly over these distinctions, but it should be kept in mind that the classification of reaction mechanisms is not a clear-cut, "pigeonhole" process and that no two reactions probably proceed with exactly the same interplay of these mechanisms.[16]

Lability, inertness, stability, and instability : more examples

The *trans* effect illustrates the importance of the study of the mechanisms of complex substitution reactions. Before continuing with a discussion of these, the differentiation of the thermodynamic terms *stable* and *unstable* from the kinetic terms *labile* and *inert* should be made. As indicated, stability refers to *thermodynamic stability*. Consider the following cyano complexes: $[Ni(CN)_4]^{-2}$, $[Mn(CN)_6]^{-3}$, and $[Cr(CN)_6]^{-3}$. All of these complexes are extremely stable from a thermodynamic point of view,[17] yet kinetically they are quite different. If the rate of exchange of radiocarbon-labeled cyanide is measured, we find that despite the thermodynamic stability, one of these complexes is extremely *labile* kinetically, a second is moderately so, and only

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[16] For a more nearly complete discussion, see F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed., Wiley, New York, 1967; C. H. Langford and H. B. Gray, "Ligand Substitution Processes," Benjamin, New York, 1965; R. G. Wilkins, "The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes," Allyn and Bacon, Boston, 1974.

[17] Note that for the one complex for which there are reasonably accurate data, the equilibrium constant corresponds to less than *one free* Ni^{+2} *ion per liter* for a solution of 0.01*M* Ni^{+2} in 1*M* NaCN! The other complexes are probably even more stable.

23 $[Cr(CN)_6]^{+3}$ can be considered to be *inert*:

$$[Ni(CN)_4]^{-2} + 4\,{}^{14}CN^- \rightarrow [Ni({}^{14}CN)_4]^{-2} + 4CN^- \qquad t_{1/2} = ca.\ 30\ \text{sec} \qquad \textbf{(11.13)}$$

$$[Mn(CN)_6]^{-3} + 6\,{}^{14}CN^- \rightarrow [Mn({}^{14}CN)_6]^{-3} + 6CN^- \qquad t_{1/2} = ca.\ 1\ \text{hr} \qquad \textbf{(11.14)}$$

$$[Cr(CN)_6]^{-3} + 6\,{}^{14}CN^- \rightarrow [Cr({}^{14}CN)_6]^{-3} + 6CN^- \qquad t_{1/2} = ca.\ 24\ \text{days} \qquad \textbf{(11.15)}$$

The terms *labile* and *inert* are obviously relative and two chemists might not use them in identical ways. Taube[18] has suggested that those complexes which react completely within about *one minute* at 25° should be considered *labile* and those that take longer be considered inert.

The tetracyanonickelate ion is a good example of a thermodynamically stable complex which is kinetically labile. The classic example of the opposite case, that is, the kinetically inert complex which is thermodynamically unstable, is the hexaamminecobalt(III) cation in acid solution. One might expect it to decompose:

$$[Co(NH_3)_6]^{+3} + 6H_3O^+ \longrightarrow [Co(H_2O)_6]^{+3} + 6NH_4^+ \qquad \textbf{(11.16)}$$

The tremendous thermodynamic driving force of *six* basic ammonia molecules attaching to six protons results in an equilibrium constant for reaction (11.16) of *ca.* 10^{25}. Nevertheless, acidification of a solution of hexaamminecobalt(III) results in no noticeable change and several days are required (at room temperature) for degradation of the complex despite the driving force of favorable thermodynamics. The inertness of the complex results from the absence of a suitable low-energy pathway for the acidolysis reaction. The difference between stable and inert can be expressed succinctly: Stable complexes have large positive free energies of reaction, ΔG; inert complexes merely have large positive free energies of activation, ΔG^*. To anticipate the following discussion somewhat, the lability of Ni^{+2} complexes can be associated with the ready ability of Ni^{+2} to form 5- or 6-coordinate complexes. The additional bond energy of the fifth (or fifth and sixth) bond in part compensates for the loss of ligand field stabilizing energy. In contrast, the reaction for $[Co(NH_3)_6]^{+3}$ must involve either an extremely unstable 7-coordinate species (note the reluctance of 7-coordinate complexes to form) or the formation of a 5-coordinate species with concomitant loss of bond energy *and* LFSE.

KINETICS AND REACTION RATES OF OCTAHEDRAL SUBSTITUTION

Although it is probable that if the reaction rates were known for all possible complexes a continuous series could be formed, it is still convenient to classify metal ions in four categories based on the rate of exchange of coordinated water. Gray and Langford[19] have suggested the following classification (compare also Fig. 11.5).

Class I. The exchange of water is extremely fast. In general, even the fastest kinetic techniques cannot follow the reaction. First-order rate constants are of the order of 10^8 sec^{-1}. The complexes are bound by essentially purely electrostatic forces and include the complexes of the alkali metals and larger alkaline earth metals. The Z^2/r ratio for these ions ranges up to about 10 C^2 m^{-1} (see Table 7.1).

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[18] H. Taube, *Chem. Rev.*, **50**, 69 (1952).

[19] H. B. Gray and C. H. Langford, *Chem. Eng. News*, April 1 (1968), p. 68.

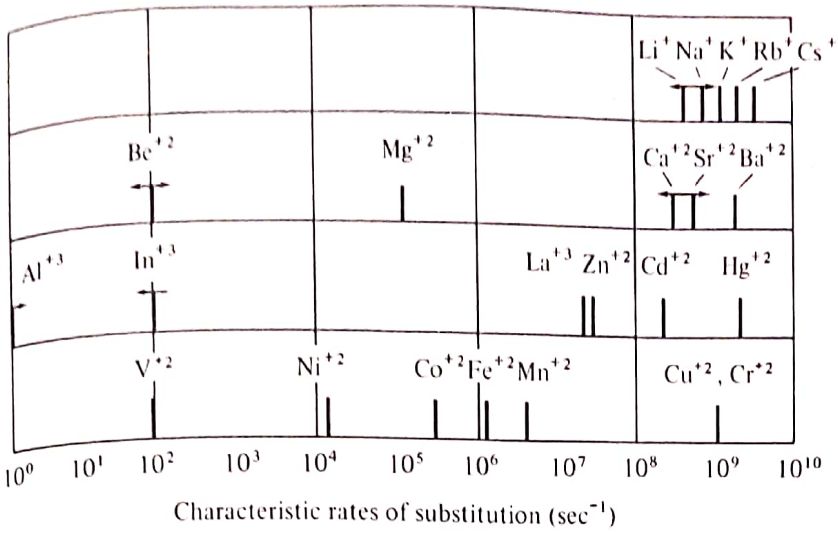

Fig. 11.5 Comparison of the rates of exchange for various metal aquo complexes. [From M. Eigen, *Pure Appl. Chem.*, **6**, 105 (1963). Reproduced with permission.]

Class II. The exchange of water is fast. First-order rate constants for water exchange range from 10^5 to 10^8 $\sec^{-1}$. Such reactions can be studied by the fastest kinetic techniques such as relaxation techniques. In these methods, the system at equilibrium is perturbed by a fast variation of a physical parameter such as pressure (ultrasonic or "P-jump" methods) or temperature ("T-jump" methods) and the response of the system used to estimate rates of reaction.[20] Metal ions belonging to this group are the dipositive transition metals, Mg^{+2}, and tripositive lanthanides. These may be considered as ions in which the bonding is somewhat stronger than in Class I, but LFSE's are relatively small. The Z^2/r for these ions ranges from about 10 to 30 $C^2\ m^{-1}$.

Class III. The exchange of water is relatively slow compared to Classes I and II, although fast on an absolute scale with first-order rate constants of 1 to 10^4 $\sec^{-1}$. The reaction can be followed, however, by more or less conventional kinetic techniques if they are augmented by flow techniques so that the fast reaction times can be related to the rate of flow. The metal ions of this group are most of the tripositive transition metal ions, stabilized to some extent by LFSE, and two very small ions Be^{+2} and Al^{+3}: The Z^2/r ratios are greater than about 30 $C^2\ m^{-1}$.

Class IV. The exchange of water is slow. These are the only inert complexes. First-order rate constants may range from 10^{-1} to 10^{-9} $\sec^{-1}$. These ions are comparable in size to Class III ions and exhibit considerable LFSE: Cr^{+3} (d^3), Co^{+3} (low-spin d^6), Pt^{+2} (low-spin d^8).

Ligand field effects and reaction rates

The complexes of metal ions in Class IV are typically stabilized to a great extent by LFSE: Co^{+3} ($24Dq$, low-spin) and Cr^{+3} ($12Dq$). Of course it is not the absolute LFSE that prevents reaction but the loss upon formation of the activated complex. The difficulty here is, of course, to assign the LFSE of the activated complex without exact knowledge of its structure. In the absence of such knowledge, approximations

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[20] K. Kustin, Ed., "Methods in Enzymology," Vol. XVI (Fast Reactions), Academic, New York, 1969; K. Kustin and J. Swinehart, *Progr. Inorg. Chem.*, **13**, 107 (1970), J. O. Edwards, Ed., Wiley (Interscience), New York; R. G. Wilkins, "The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes," Allyn and Bacon, Boston, 1974, pp. 122–177.

can be made on the basis of likely structures. Basolo and Pearson[21] have presented values for strong and weak fields for square pyramidal (C.N. = 5) and pentagonal bipyramidal (C.N. = 7) intermediates. The values are listed in Table 11.1. The experimental results, in general, correlate rather well with this simple picture. For tripositive metal ions, lability is expected to increase in the order Co(III) < Cr(III) < Mn(III) < Fe(III) < Ti(III) < Ga(III) < Sc(III). The comparison of dipositive with tripositive species is difficult since the rate is also affected by the charge on the central metal ion which strengthens the metal–ligand bonds. For example, in the non-transition metal series $[AlF_6]^{-3} > [SiF_6]^{-2} > [PF_6]^- > SF_6$, the lability decreases in the order shown with SF_6 being exceptionally inert.

Table 11.1 Change in LFSE (units *Dq*)[a] upon changing a 6-coordinate complex to a 5-coordinate (square pyramidal) or a 7-coordinate (pentagonal bipyramidal) species

	High spin		Low spin	
System	C.N. = 5	C.N. = 7	C.N. = 5	C.N. = 7
d^0	0	0	0	0
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	−8.52
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
d^{10}	0	0	0	0

[a] The common convention is used: Negative quantities refer to *loss* of LFSE and destabilization of the complex.

Source: Modified from F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed., Wiley, New York, 1967. Used with permission.

As a result of the generally greater lability of dipositive metals, octahedral Ni(II) is considerably more labile than corresponding tripositive ions in line with the exchange rates shown in Eqs. (11.13) to (11.15). When considering dipositive metals only, however, it is found that other ions such as Mn(II), Fe(II), Co(II), and Cu(II) that possess less LFSE are even more labile.

The difference in lability between Ni(II) complexes and Pt(II) complexes can be related to effects of ligand fields as well. Ni(II) is a Class II metal whereas Pt(II) belongs to Class IV. The explanation parallels that provided for Cu(II) *vs.* Au(I)–Au(III) systems (see page 387). In contrast to odd electrons being oxidized in the latter, the Ni(II) *vs.* Pt(II) comparison involves the availability of the antibonding d_{z^2} orbital for occupancy by a fifth, attacking group in an associative mechanism. Pt(II) will lose proportionately more energy in such a transition since the LFSE is considerably greater for the heavier metal (see pages 362–363).

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[21] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed., Wiley, New York, 1967. For a more recent discussion, see Footnote 35.

The study of substitution mechanisms has occupied many workers for a long time and continues to be an active area of investigation. Only a brief outline of the results of such work can be given here.[22] Consider a reaction of the type:

$$[N_nML] + E \longrightarrow [N_nME] + L \tag{11.17}$$

where $n = 3$ for a square planar complex, $n = 5$ for an octahedral complex, N = a "noninvolved" ligand, L = the leaving ligand, and E = the entering ligand. We have seen that for square planar complexes the reaction has an associative (A or S_{N2}) mechanism:

$$[N_3PtL] + E \longrightarrow [N_3PtLE] \longrightarrow [N_3PtE] + L \tag{11.18}$$

Octahedral complexes conceivably can react via either an associative, dissociative (D or S_{N1}), or intermediate (I) mechanism:

$$[N_5CoL] + E \longrightarrow [N_5CoLE] \longrightarrow [N_5CoE] + L \tag{11.19}$$

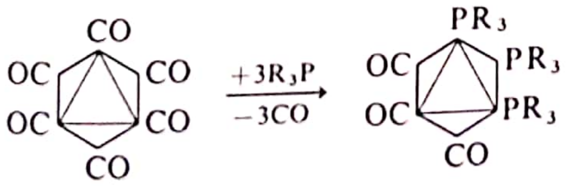
$$[N_5CoL] \xrightarrow{-L} [N_5Co] \xrightarrow{+E} [N_5CoE] \tag{11.20}$$

involving 7-coordinate and 5-coordinate intermediates, respectively.

It is likely that most reactions will be found not to fall cleanly into the extreme mechanism of the first two types but will involve to a certain degree a concerted mechanism.

Substitution in octahedral complexes

One might expect the *trans* effect to be operable in octahedral complexes as well as in square planar complexes. Evidence for its presence in octahedral complexes is not abundant, however. There is definite evidence for a *trans influence* on the ground state of cobalt(III) complexes of the type $[Co(NH_3)_5X]^{+2}$. Significant lengthening is found in the Co—N bond *trans* to the nitrosyl group and shortening *trans* to a chloride ion.[23] In metal carbonyls the *trans* effect seems to be operative to the extent that substitution proceeds readily as long as there are carbonyl groups *trans* to each other (and presumably activating each other):



(11.21)

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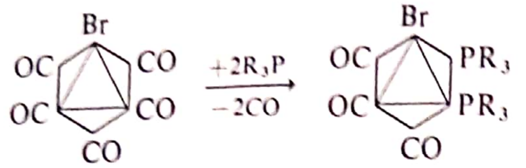
[22] For more nearly complete discussions of reaction mechanisms, see D. Benson, "Mechanisms of Inorganic Reactions in Solution," McGraw-Hill, New York, 1968; F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed., Wiley, New York, 1967; C. H. Langford and H. B. Gray, "Ligand Substitution Processes," Benjamin, New York, 1965; R. G. Wilkins, "The Study of Kinetics and Mechanisms of Reactions of Transition Metal Complexes," Allyn and Bacon, Boston, 1974.

[23] For a complete discussion of *cis* and *trans* effects in cobalt(III) complexes, see J. M. Pratt and R. G. Thorp, *Adv. Inorg. Chem. Radiochem.*, **12**, 375 (1969), H. J. Emeléus and A. G. Sharpe, Eds., Academic, New York.



(11.22)

These products are almost invariably *facial* if trisubstituted or *cis* if the reaction is stopped at the disubstituted product. If steric hindrance exists between the *cis* substituents, isomerization to a *trans* product may occur. Otherwise greater stability is found with the carbonyl groups *trans* to the weaker pi-bonding phosphines.[24]

Substitution in octahedral cobalt(III) complexes

The best-studied systems have been those involving Co(III) because of the stability of the complexes and their availability. As we shall see, other systems sometimes parallel those of Co(III) and sometimes not. For example, in common with most octahedral complexes, those of Co(III) do not show a *trans* effect. Apparently this is because substitution reactions at an octahedral Co(III) center occur via a dissociative mechanism (*D* or S_{N1}):

$$[N_5CoL]^{+n} \xrightarrow[\text{slow}]{-L^-} [CoN_5]^{+n+1} \xrightarrow[\text{fast}]{+E^-} [N_5CoE]^{+n} \qquad (11.23)$$

or a concerted interchange mechanism tending towards the dissociative side (I_d or $S_{N1}\,IP$) with ion pair formation prior to reaction so that the entering group can enter as soon as the leaving group departs[25]:

$$[N_5CoL]^{+n} \xrightarrow[\text{fast}]{+E^-} [N_5CoL]^{+n}E \xrightarrow[\text{slow}]{} [N_5CoE]^{+n}L \xrightarrow[\text{fast}]{-L^-} [N_5CoE]^{+n} \qquad (11.24)$$

There is considerable evidence for mechanisms of this sort, but only a few examples will be given. First, the rates of such reactions correlate fairly well (inversely) with the thermodynamic bond strength of the Co—L bond, indicating that the Co—L bond is broken initially. We might expect that this bond between the metal and an anion would be broken more readily if electron density were increased on the metal. Electron-donating ligands should therefore assist the replacement of L. This proves to be true as shown by the data for the acid hydrolysis of chloride complexes in which various pyridines are present:

$$[Co(en)_2(X\text{-}py)Cl]^{+2} + H_2O \longrightarrow [Co(en)_2(X\text{-}py)H_2O]^{+3} + Cl^- \qquad (11.25)$$

It is found that increasing the basicity of the pyridine (and hence increasing the electron density on the metal) *does* indeed increase the rate of the reaction (Table 11.2).[26]

Increasing the total negative charge on the complex facilitates the reaction by more readily allowing the departure of the leaving ligand. If the reaction were an associative one, increasing the negative charge would be expected to *repel* the incoming ligand.

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[24] R. B. King, "Transition-Metal Organometallic Chemistry," Academic, New York, 1969, pp. 73–75.

[25] The distinction between these mechanisms is a rather fine one and need not concern us here. Basically, it revolves around whether there is a 5-coordinate intermediate with a finite lifetime that can discriminate among potential entering groups.

[26] F. Basolo *et al.*, *J. Am. Chem. Soc.*, **78**, 2676 (1956).

Table 11.2 Rate constants for the acid hydrolysis of $[Co(en)_2(X\text{-}py)Cl]^{+2}$ at 50°C

X-py	pK	Rate constant, k (sec^{-1})
Pyridine	8.82	1.1×10^{-5}
3-Methylpyridine	8.19	1.3×10^{-5}
4-Methylpyridine	7.92	1.4×10^{-5}
4-Methoxypyridine	7.53	1.5×10^{-5}

Further evidence for the proposed mechanism comes through operation of the *cis* effect in certain reactions. The nature of the *cis* effect can be seen from Table 11.3. Certain ligands such as the thiocyanate and hydroxide ions greatly accelerate the hydrolysis of a complex when *cis* to the leaving group as compared to the analogous reaction in which the leaving group is in the *trans* position. For example, consider the reaction:

$$[Co(en)_2CCl]^{+n} + H_2O \longrightarrow [Co(en)_2C(H_2O)]^{+n+1} + Cl^- \tag{11.26}$$

where C represents a *cis*-activating ligand such as hydroxide ion. When the hydroxide ion is *cis* to the leaving chloride ion the reaction rate is about ten times as great as when it is in the *trans* position. The reaction rates for the acid hydrolysis of *cis* and *trans* isomers are listed in Table 11.3 together with the ratio of the reaction rates k_c/k_t. Those ligands that exhibit a strong *cis* effect are those that have unshared pairs of electrons (in addition to the pair used in the sigma dative bond). Pearson and Basolo[27] have suggested that this electron pair is available to be donated to the metal in a *p–d* pi bond (Fig. 11.6). Such pi bonding by a *cis*-substituent can stabilize a square pyramidal activated complex by lowering the positive charge on the metal. This also allows the reaction to proceed without extensive rearrangement and the product is 100% *cis* isomer. When these same ligands are in the *trans* position there is no orbital available for overlap unless the complex rearranges to a trigonal bipyramidal structure (Fig. 11.7). This raises the energy of activation and makes substitution reactions more difficult and results in mixtures of isomers in the product. Those ligands which

Table 11.3 Rate constants and isomeric products for the acid hydrolysis of chlorobis(ethylenediamine)(ligand)cobalt(III) complexes at 25° C

	cis isomer		*trans* isomer		
Ligand, C	Rate constant, *cis* isomer, k_c (sec^{-1})	% *cis* isomer in product	Rate constant, *trans* isomer (sec^{-1})	% *trans* isomer in product	k_c/k_t
NCS^-	1.1×10^{-5}	100	5.0×10^{-8}	30–50	220
OH^-	1.3×10^{-2}	100	1.4×10^{-3}	25	9.2
Cl^-	2.4×10^{-4}	100	3.2×10^{-5}	65	7.5
N_3^-	2.5×10^{-4}	100	2.4×10^{-4}	80	1.04
NH_3	5.0×10^{-7}	84	4.0×10^{-7}	17	1.25
NO_2^-	1.1×10^{-4}	100	1.0×10^{-3}	100	0.11

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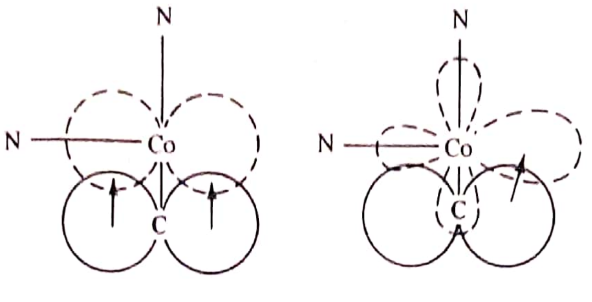
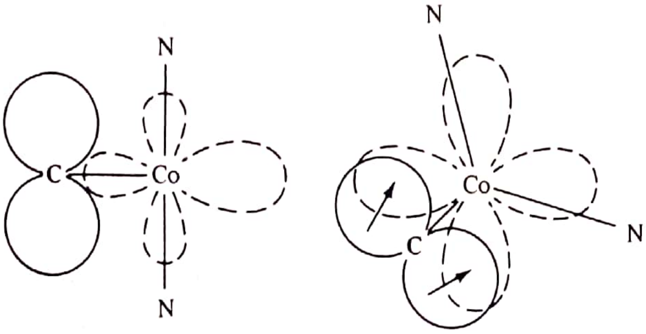
[27] R. G. Pearson and F. Basolo, *J. Am. Chem. Soc.*, **78**, 4878 (1956).



(a) (b)

Fig. 11.6 Overlap of filled *p* orbital of C with vacant (a) *p* orbital or (b) d^2sp^3 hybrid orbital of cobalt in a 5-coordinated square pyramidal activated complex resulting from the dissociation of X from *cis*-[CoN_4CL]. The two N ligands not shown are above and below the plane of the paper. [From F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 381 (1962), F. A. Cotton, Ed., Wiley (Interscience), New York. Reproduced with permission.]



(a) (b)

Fig. 11.7 (a) No overlap of filled *p* orbital of C with vacant d^2sp^3 hybrid orbital of cobalt in the square pyramidal activated complex resulting from the dissociation of X from *trans*-[CoN_4CX]. (b) Efficient overlap with vacant $d_{x^2-y^2}$ orbital if there is rearrangement of a trigonal bipyramidal structure. The two N ligands not shown are above and below the plane of the paper. [From F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 381 (1962), F. A. Cotton, Ed., Wiley (Interscience), New York. Reproduced with permission.]

fail to exhibit a positive *cis* effect are of two types: (1) those that lack another lone pair to donate to the metal such as ammonia; (2) those ligands that are *pi acceptors* such as the nitro group.[28] The latter tend to withdraw electrons via pi bonding and hence cannot operate through the mechanism outlined above.

In acid hydrolysis the reaction rate is independent of the nature or the concentration of the entering group which is further evidence for a dissociative mechanism. The only anion that has been shown to have an appreciable effect upon the rate of hydrolysis is the hydroxide ion. The rate constant for hydrolysis in basic solution is often a million times that found for acidic solutions. Furthermore, the reaction rate is found to be second order and dependent upon the hydroxide ion concentration[29]:

$$\frac{-d[\text{complex}]}{dt} = k_B[\text{complex}][\text{OH}^-] \qquad \textbf{(11.27)}$$

The dependence upon hydroxide ion concentration can be taken as evidence of an associative (S_{N2}) mechanism:

$$[(NH_3)_5CoCl]^{+2} + OH^- \longrightarrow [(NH_3)_5CoCl(OH)]^+ \longrightarrow [(NH_3)_5CoOH]^{+2} + Cl^- \qquad \textbf{(11.28)}$$

---

[28] The azide ion, N_3^-, can potentially behave as either a pi donor or a pi acceptor. It does not appear to act strongly in either capacity.

[29] Equation (11.27) is not precisely accurate. The complex continues to hydrolyze by the dissociative (or "acid") mechanism even at high pH values, so a more accurate expression would be: $-d[\text{complex}]/dt = k_A[\text{complex}] + k_B[\text{complex}][\text{OH}^-]$. Since k_B is from 10^5 to 10^8 times as great as k_A, Eq. (11.27) is adequate if the $[\text{OH}^-]$ is sufficiently high.

5.18 INTERPRETATION OF LABILITY AND INERTNESS IN TERMS OF THE VALENCE BOND THEORY (VBT) AND CRYSTAL FIELD THEORY (CFT) OF OCTAHEDRAL METAL COMPLEXES

5.18.1 Application of VBT in Explaining the Kinetic Behaviour of Octahedral Complexes

(a) Outer and inner orbital octahedral complexes: Valence bond theory (VBT) classifies the octahedral complexes as the **outer orbital complexes** (sp^3d^2) and **inner orbital complexes** (d^2sp^3). The involved d–orbitals in hybridisation are $d_{x^2-y^2}$ and d_{z^2}. Thus in the outer orbital complexes, the nd orbitals participate along with the ns and np orbitals for hybridisation while in the inner orbital complexes, the $(n-1)d$ orbitals participate along with the ns and np orbitals for hybridisation.

The inner orbital complexes are formed only when at least two $(n-1)d$ orbitals are available for d^2sp^3 hybridisation. Thus the situation is straight-forward for the d^0, d^1, d^2 and d^3 configurations. For d^n $(n > 3)$ configuration, it needs rearrangement of electrons through pairing and/or excitation of d–electrons for inner orbital complex formation.

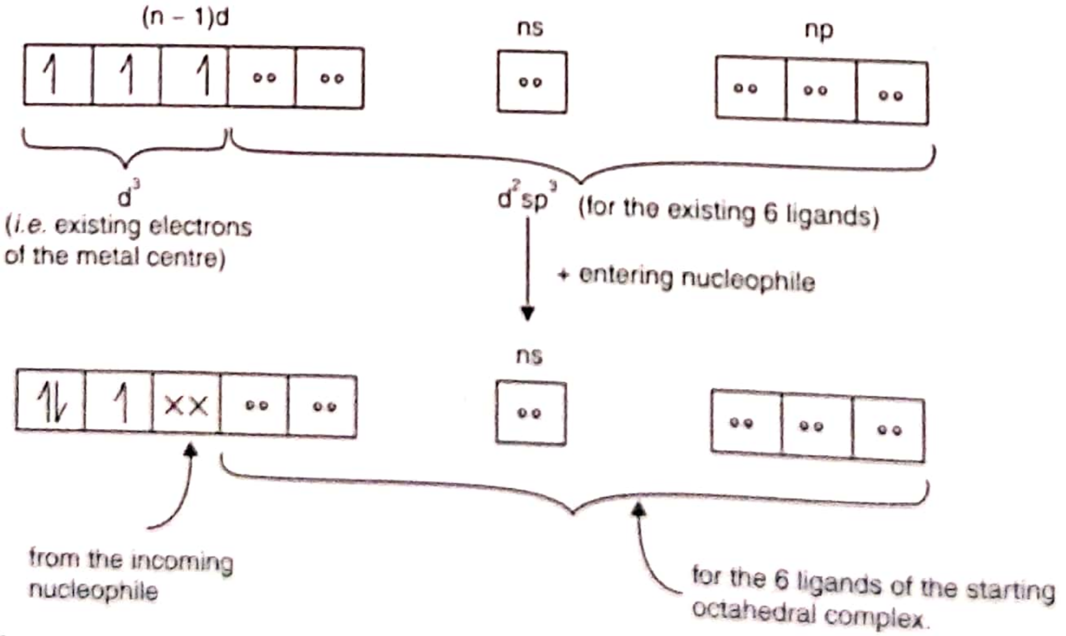
(b) Kinetic behaviour of the outer orbital octahedral complexes: In terms of VBT, the outer orbital complexes are considered to be labile. The outer orbital complexes formed by $Mn^{2+}(3d^5)$, $Fe^{2+}(3d^6)$, $Co^{2+}(3d^7)$, $Ni^{2+}(3d^8)$, $Cu^{2+}(3d^9)$, $Zn^{2+}(3d^{10})$, etc. are labile. In the same way, the complexes of Cd^{2+}, Hg^{2+}, Al^{3+}, Ga^{3+}, In^{3+} are expected to be labile because they form the outer orbital complexes.

The nd orbitals are of higher energy than the (n−1)d orbitals. This is why, the outer orbital complexes (sp^3d^2) are **considered to be relatively less stable** than the inner orbital complexes. Such complexes follow the **dissociative path** (*i.e.* bond breaking mainly contributes to the activation energy) and the process gets kinetically favoured due to the low bond dissociation energy.

However, if the charge on the metal centre increases, the metal-ligand bond becomes stronger and consequently the dissociative path gets disfavoured. *Thus the lability of the outer orbital complexes decreases with the increase of the positive charge on the central atom.* It explains the lability sequence:

$$AlF_6^{3-} > SiF_6^{2-} > PF_6^- > SF_6$$

In fact, the outer orbital complexes (using the $3d$, $3s$ and $3p$ orbitals in sp^3d^2 hybridisation) like SF_6, PF_6^- are very much inert because of the very high positive charge on the central atom.



Scheme 5.18.1.1 Associative path for the d^3 system through the rearrangement of electrons.

(c) Kinetic behaviour of the inner orbital octahedral complexes: The *d*-orbitals d_{xy}, d_{yz} and d_{xz} (*i.e.* t_{2g} set in terms of CFT) of the $(n-1)$ shell are kept out of hybridisation. *Participation of the inner* $(n-1)d$ *orbitals in hybridisation is considered to make* **the relatively stronger bonds** (compared to those of the outer orbital complexes). Because of this stronger metal-ligand bond in the inner orbital complexes, *the dissociative pathway is expected to be disfavoured but the* ***associative pathway will be favoured*** *through the formation of a new metal-ligand bond by the entering nucleophile to produce an intermediate of higher coordination number.*

If the substitution process is argued to pass through an **associative path** to produce a 7-coordinate intermediate from the starting octahedral complex, then the ease of formation of the intermediate depends on the **availability of a vacant *d*–orbital.** ***It indicates that at least one of the d–orbitals*** d_{xy}, d_{yz}, d_{xz} ***which do not participate in bonding in the starting octahedral complex, must remain vacant to accommodate the nucleophilic attack by the entering nucleophile.*** This situation is prevailing for d^0, d^1 and d^2 systems.

Sometimes, the rearrangement of the electrons may be required to make one such *d*-orbital vacant. For example, in the inner orbital complexes of the d^3 and d^4 electronic configurations, as such there is no vacant *d*–orbital to accommodate the incoming nucleophile in the associative process. However, redistribution of these electrons through pairing can make one *d*–orbital vacant for the incoming nucleophile. It is illustrated for the d^3–system in Scheme 5.18.1.1.

Thus we can conclude as follows:

- **Labile inner-orbital complexes**

d^0, d^1, d^2: vacant *d*–orbital is already available to accommodate the entering nucleophile; and these are labile.

- **Inert inner-orbital complexes**

d^3, d^4: redistribution of electrons through pairing can provide a vacant *d*–orbital for the entering nucleophile; the process is relatively disfavoured compared to the cases of d^0, d^1, d^2 systems and consequently, the d^3, d^4 centres are less labile.

d^5, d^6: to provide a vacant *d*-orbital for the entering nucleophile, it needs the promotion of existing *d*–electrons to some higher energy orbitals, and thus the process is highly disfavoured and it introduces the inertness.

(d) Limitations of the VBT in explaining the kinetic behaviour of the octahedral complexes: The important drawbacks are given below.

(i) The **outer orbital complexes** have been suggested to participate in a **dissociative path** based on the argument that the bonds in the outer orbital complexes are weaker than in the inner orbital complexes. But the assumption of weaker bonds in the outer orbital complexes is not experimentally justified. For example, the hydration energies of the metal ions having the d^7, d^8, d^9 and d^{10} configurations (*i.e.* outer orbital hexaaqua complexes) are much higher than those of the d^0, d^1 and d^2 configurations forming the inner-orbital hexaaqua complexes. This fact weakens the argument of VBT.

(ii) In VBT, it was suggested that the inner orbital complexes participate in an **associative path** based on the argument that the bonds in the inner orbital complexs are stronger. However, the argument is not really justified.

Thus, the ***basic assumptions: dissociative process for the outer orbital complexes and associative process for the inner orbital complexes are not justified.***

(iii) The serious objection against the VBT treatment is that it cannot predict anything regarding the order of lability. Thus it is purely a qualitative treatment.

For example, the difference in lability among the inner orbital complexes of the d^0, d^1 and d^2 configurations cannot be predicted and these are lumped into a group provided they do not differ significantly in charge. Similarly, all the inner orbital complexes of d^3, d^4, d^5 and d^6 are lumped into a group described as the inert complexes.

5.18.2 Application of Crystal Field Theory (CFT) in Explaining the Kinetic Behaviour of the Octahedral Metal Complexes (*cf.* Sec. 5.30.10 for CFAE of the square planar complexes)

Activation energy controls the reaction rate. To the activation energy, loss of cfse (crystal field stabilisation energy) in attaining the activated complex from the starting complex contributes. This contribution is described as **crystal field activation energy** (CFAE), more correctly **ligand field activation energy** (LFAE). This CFAE or LFAE mainly contributes to $\Delta H^{\neq}$.

CFAE = loss of cfse in forming the activated complex
= cfse of the starting complex – cfse of the activated complex.

Calculation of cfse of the starting complex whose geometry is known is straight-forward. But calculation of cfse of the activated complex is a difficult task without the exact knowledge of the structure. Without this knowledge, some approximation may be considered as suggested by Basolo and Pearson. For the **associative path,** the activated complex may be considered to be **seven coordinate** of two

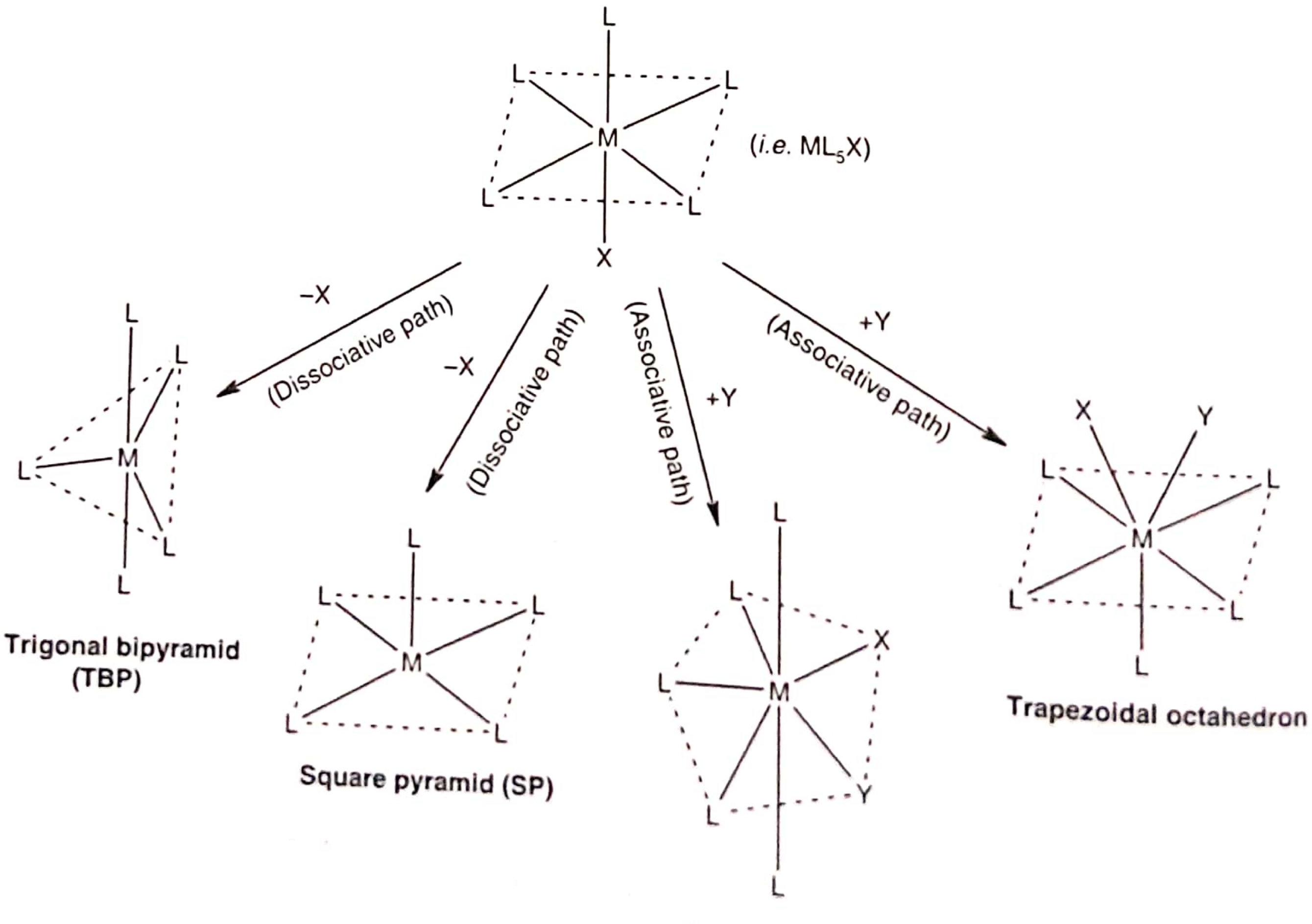


Fig. 5.18.2.1 Structures of the intermediates/activated complexes in dissociative (D) and associative (A) paths of ligand substitution in the octahedral ML_5X complexes: $L_5M—X + Y \rightarrow L_5M - Y$.

probable geometries: *pentagonal bipyramid* (*i.e.* the entering ligand approaches towards the midpoint of an edge of the octahedron) and *trapezoidal octahedron* or *capped octahedron* (*i.e.* the entering ligand approaches towards the centre of a trigonal face of the octahedron). The cfse of such geometries like pentagonal bipyramid or capped octahedron may be calculated easily. Similarly, for the **dissociative path** the activated complex may be approximately considered to be **five coordinate** of two probable geometries: *square pyramid* and *trigonal bipyramid.*

D-path:

$$\underset{(O_h)}{X{-}ML_5} \xrightarrow{(rds)} \underset{(TBP \text{ or } SP)}{ML_5} + X$$

$$\text{CFAE} = \text{cfse of } ML_5X - \text{cfse of } ML_5$$

The 5–coordinate intermediate formed from the octahedral geometry through the rupture of $M — X$ bond is a square pyramid (SP) which may change into a trigonal bipyramid (TBP). In presenting the CFAE in Table 5.18.2.1, the TBP geometry has not been considered.

A-path:

$$X - ML_5 \xrightarrow{+Y,\,(rds)} ML_5XY \quad \text{(pentagonal bipyramid or trapezoidal octahedron or capped octahedron)}$$

$$\text{CFAE} = \text{cfse of } ML_5X - \text{cfse of } ML_5XY$$

Based on the above arguments, Basolo and Pearson have presented the CFAE values (Table 5.18.2.1) for both the dissociative and associative paths for the strong and weak field ligands.

- Thus the **positive value of CFAE** indicates the loss of *cfse* in forming the activated complex or transition state and the rate becomes slow. The more positive value of CFAE indicates the slower reaction.

Table 5.18.2.1 Crystal field activation energy (CFAE) for reactions of octahedral complexes.

System	*Calculated values of CFAE (in Dq_o)**					
	Strong field cases			*Weak field cases*		
	D	*A*	*A*	*D*	*A*	*A*
	Square pyramid	*Pentagonal bipyramid*	*Trapezoidal octahedral*	*Square pyramid*	*Pentagonal bipyramid*	*Trapezoidal octahedral*
d^0	0	0	0	0	0	0
d^1	–0.57	–1.28	–2.08	–0.57	–1.28	–2.08
d^2	–1.14	–2.56	–0.68	–1.14	–2.56	–0.68
d^3	2.00	4.26	1.80	2.00	4.26	1.80
d^4	1.43	2.98	–0.26	–3.14	1.07	–2.79
d^5	0.86	1.70	1.14	0	0	0
d^6	4.00	8.52	3.63	–0.57	–1.28	–2.08
d^7	–1.14	5.34	–0.98	–1.14	–2.56	–0.68
d^8	2.00	4.26	1.80	2.00	4.26	1.80
d^9	–3.14	1.07	–2.79	–3.14	1.07	–2.79
d^{10}	0	0	0	0	0	0

See Sec. 5.30.10 for CFAE of the square planar complex. * The negative values of CFAE are essentially zero.

- The **negative value of CFAE** indicates that the *cfse* of the activated complex is more than that of the starting complex. It implies that the transition state is more stable (in terms of *cfse*) than the reactant but it is improbable. In fact, the negative value of CFAE arises in the cases where the additional *cfse* due to the J.T. distortion in the starting complex is ignored in estimating the CFAE. It may happen so for Cr(II) (d^4), Cu(II) (d^9), etc. For the sake of simplicity, the negative values of CFAE are considered as zero and such complexes react very fast.

Based on the CFAE, the **major conclusions** regarding the lability orders for the reactions of octahedral complexes are given below.

(a) **Dissociative (D)–pathway (square pyramid activated complex)**

(i) **Lability sequence for the strong field ligand:**

$$\underset{\longleftarrow\text{ labile }\longrightarrow}{d^0, d^1, d^2, d^7, d^9, d^{10}} >> \underset{\longleftarrow\text{ inert }\longrightarrow}{d^5 > d^4 > d^3,\ d^8 > d^6}$$

(ii) **Lability sequence for the weak field ligand:**

$$\underset{\longleftarrow\text{ labile }\longrightarrow}{d^0, d^1, d^2, d^4, d^5, d^6, d^7, d^9, d^{10}} >> \underset{\longleftarrow\text{ inert }\longrightarrow}{d^3,\ d^8}$$

(b) **Associative (A)–pathway (Pentagonal bipyramid activated complex)**

(i) **Lability sequence for the strong field ligand:**

$$\underset{\longleftarrow\text{ labile }\longrightarrow}{d^0, d^1, d^2, d^{10}} >> \underset{\longleftarrow\text{ inert }\longrightarrow}{d^9 > d^5 > d^4 > d^3,\ d^8 > d^7 > d^6}$$

(ii) **Lability sequence for the weak field ligand:** $\underset{\longleftarrow\text{ labile }\longrightarrow}{d^0, d^1, d^2, d^5, d^6, d^7, d^{10}} >> \underset{\longleftarrow\text{ inert }\longrightarrow}{d^4, d^9 > d^3,\ d^8}$

(c) **Associative (A)–pathway (Trapezoidal octahedron activated complex)**

(i) **Lability sequence for the strong field ligand:**

$$\underset{\longleftarrow\text{ labile }\longrightarrow}{d^0, d^1, d^2, d^4, d^7,\ d^9, d^{10}} >> \underset{\longleftarrow\text{ inert }\longrightarrow}{d^5 > d^3,\ d^8 > d^6}$$

(ii) **Lability sequence for the weak field ligand:**

$$\underset{\longleftarrow\text{ labile }\longrightarrow}{d^0, d^1, d^2, d^4, d^5, d^6, d^7,\ d^9, d^{10}} >> \underset{\longleftarrow\text{ inert }\longrightarrow}{d^3,\ d^8}$$

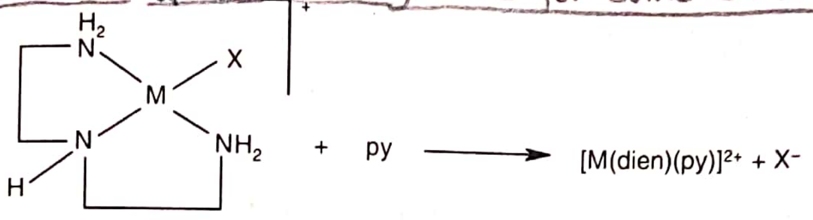
Thus it is evident that **irrespective of the reaction pathway,** the octahedral complexes react as follows:

- d^3, d^8 and d^6 (low spin) centres are **inert**;
- d^3, d^8 and low spin complexes of d^4, d^5 and d^6 are **inert** and the reactivity order is: $d^5 > d^4 > d^3$, $d^8 > d^6$
- d^0, d^1, d^2, d^7 (except strong field ligand, A-path through the pentagonal bipyramidal activated complex), d^9 and d^{10} centres are **labile**;
- high spin complexes of d^4, d^5, d^6 and d^7 are **labile**.
- d^4 (high spin) and d^9 centres are labile because of the J.T. distortion.
- the lability decreases for the **heavier congeners** because of the increase of CFAE.

d^5 *vs.* d^4: The above conclusions have been verified experimentally. Generally, the d^5 system reacts faster than the d^4 system **for the strong field ligands**. However in the case of **exchange of CN$^-$ ligand in [M(CN)$_6$]$^{n-}$** (n = 3, 4), the lability order runs as: $d^4 \rangle d^5 \rangle d^3 \rangle d^6$. It indicates that the process goes

Reactivity Order in different d^8 systems for some examples :

(b)



[M(dien)X]$^+$

k_{py} (dm^3 mol^{-1} s^{-1}), 25°C, in aqueous media

X^-	M = Pd(II)	Pt(II)
I^-	3.5×10^{-2}	1.0×10^{-5}
SCN^-	0.31	3.0×10^{-7}
NO_2^-	6.5	5×10^{-8}

(c) The rate constant (24°C) for the exchange of $^*CN^-$ with $[M(CN)_4]^{2-}$ follows the following sequence.

	Au(III)	Pt(II)	Pd(II)	Ni(II)
$k_{ex}\left(\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}\right)$:	3.9×10^3	26.0	1.2×10^2	5×10^5

(ii) **Reactivity order in terms of the energy of the vacant orbital (*i.e.* LUMO) to receive the nucleophilic attack:** The observed reactivity order can be explained by considering the ease of formation of a 5–coordinate activated complex by using the vacant (non-bonding in nature) $(n + 1)p_z$–orbital in the associative pathway assuming the starting square planar complex to lie in the xy-plane. For Ni(II), Pd(II) and Pt(II), the said orbitals are $4p_z$, $5p_z$ and $6p_z$ respectively. Obviously, for Pt(II), it is energetically most disfavoured while it is energetically most favoured for Ni(II). For Au(III), it is $6p_z$ but its energy is decreased significantly because of higher positive charge. It causes the enhanced reactivity for Au(III) compared to that for Pt(II) which also uses the $6p_z$ orbital.

In an alternative view in terms of MOT, it may be argued that in the associative path, the incoming group will occupy the vacant d_{z^2} orbital having some antibonding character. Due to the higher crystal field splitting for the heavier congeners, this d_{z^2} orbital becomes less easily available for the incoming ligand in the case of heavier congeners.

(iii) **CFAE and reactivity order:** The reactivity of square planar complexes in ligand substitution process can be better understood in terms of *crystal field activation energy* (CFAE). In the associative

path act. Com. may be TBP & SP. CFAE shows $d^{10} \gg d^9 > d^8 > d^7$. Lability $Zn^{2+} > Cu^{2+} > Ni^{2+}$

Table 5.30.10.1 Crystal Field Activation Energy (CFAE) for the ligand substitution reactions of square planar complexes (assuming the strong field ligands). d

d^n	*cfse (Dq)*			*CFAE (Dq)*	
	Square planar (a)	*Trigonal bipyramidal (b)*	*Square pyramidal (c)*	*(a) – (b)*	*(a) – (c)*
d^7	26.84	13.34	19.14	13.50	7.70
d^8	24.56	14.16	18.28	10.40	6.28
d^9	12.28	7.09	9.14	5.19	3.14
d^{10}	0	0	0	0	0

As Dq increases down the group, lability Seq. $Ni^{2+} > Pd^{2+} > Pt^{2+}$