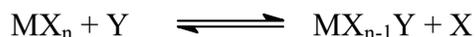


INORGANIC REACTION MECHANISM

Introduction

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



This class of reaction includes complex formation, in which the leaving group, the displaced base X and the entering group, the displacing base Y, is some other ligand (one of the ligands involved is often also the solvent species). The rates of such reactions vary widely, ranging from completion within the time for reactant mixing to years. H. Taube called complexes having substitution half life $t_{1/2} < 30$ sec labile and called those with longer $t_{1/2}$ inert.

Classification of ligand substitution reactions

Ligand substitution reactions of coordination complexes can be illustrated by the general equation,



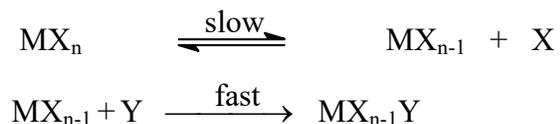
where 'M' is a metal atom or ion and 'X' and 'Y' are any two ligands. For simplicity the charges have been ignored. In keeping with organic chemistry terminology, substitution reactions have been conveniently divided into nucleophilic (S_N) and electrophilic (S_E) substitutions:



Electrophilic substitution mechanisms will not be considered further. For a ligand substitution process, S_N mechanisms are relevant and can be further subdivided into two paths like:

- (i) S_N1 dissociation (substitution, nucleophilic, unimolecular):

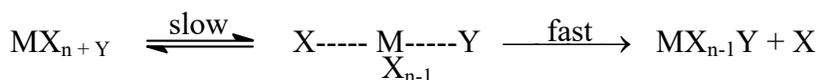
This type of reaction can be illustrated as:



Such reactions are insensitive to the nature of the incoming nucleophile, 'Y', but sensitive to the leaving group 'X' and reach the transition state principally by the internal accumulation of the energy to break the bond to the leaving group. The detection of an intermediate coordination number is the best diagnosis of the S_N1 mechanism.

(ii) S_N2 displacement (substitution, nucleophilic, bimolecular):

This type of reaction involves a bimolecular rate determining step followed by a rapid cleavage of 'X'



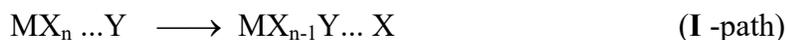
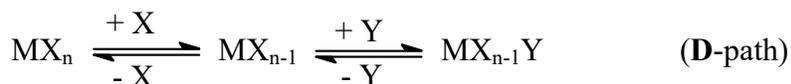
These reactions are affected by the nature of the entering group. Stereospecificity i.e. retention of configuration suggests an S_N2 reaction.

One of the great complicating factors in assigning mechanism of substitution reactions is the existence of borderline mechanism or intermediate mechanism between S_N1 and S_N2. Depending upon the nature of participation of entering ligand in the transition state, it has been suggested to classify ligand substitution reactions into four categories:

- S_N1(lim), where the rate determining state involves only bond breaking and definite evidence for intermediate of reduced coordination number exists;
- S_N1, in which bond breaking is important in the rate determining step but no evidence for the existence of intermediate of reduced coordination can be presented;
- S_N2(lim), in which the rate determining step involves only ligand-substrate bond making and definite evidence for intermediate of increased coordination number exists;
- S_N2, in which the rate determining step involves about equal bond making and bond breaking in the transition state.

An alternative classification has been proposed by Langford and Stengle. According to them the ligand substitution processes can be classified in terms of stoichiometric and intimate mechanism. Stoichiometric mechanism relates to the identification of the sequence of elementary steps involved in a complicated overall reaction. Intimate mechanism is the understanding of the magnitude of the rate constants for the individual steps in terms of rearrangements of atoms and bonds.

Stoichiometric Mechanism: Three paths for ligand substitutions are illustrated below:



In dissociative path (D), the leaving ligand is lost in the first step, producing an intermediate of reduced coordination number. In associative (A) path the entering ligand adds to the complex in the first step, producing an intermediate of increased coordination number. In the concerted path termed interchange (I), the leaving group is moving from the inner to outer sphere while the entering group is moving from outer to inner sphere.

Intimate mechanism: Two categories of intimate mechanism may be distinguished operationally.

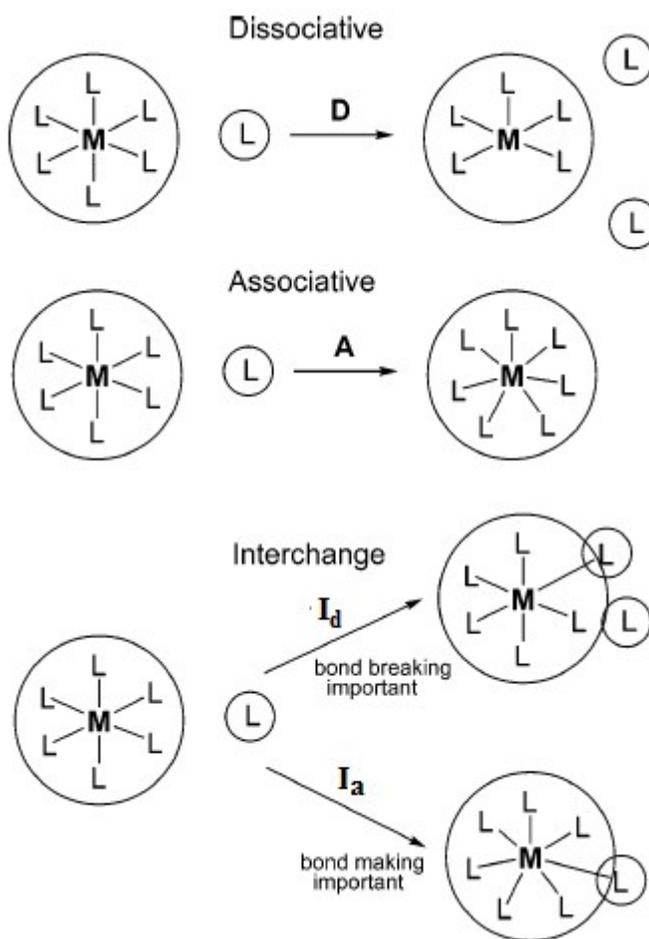
1. Associative activation (a): The reaction rate is approximately as sensitive to variation of the entering group as to variation of the leaving group.
2. Dissociative activation (d): The reaction rate is much more sensitive to variation of the leaving group than to the variation of the entering group.

D mechanism must be dissociative. A mechanism must be associative. 'I' reaction may have a variety of transition states, but two well-defined types will be those resembling the transition state of A and D reactions. The A-like transition in an 'I' process will display substantial bonding to both the entering and leaving groups, and the entering group will display an important part in determining its energy. Such a transition state in an I path will be indicated by adding a notation a (i.e. I_a). The D-like transition state of I reaction is one with only weak bonding to both the entering and leaving groups (the bonding may be very weak indeed). The entering group effect on the reaction rate will be small. Such an 'I' process will be denoted with an added d (i.e. I_d). However, the effect of charge and size of the central metal ion influences the mechanism of a reaction. This can be summarized in Table 1.

Table 1: Effect of size and charge on the rate of reactions involving dissociative (**D**), interchange (**I**) and associative (**A**) mechanism:

| Changes | Effects on rate | | |
|--|------------------|------------------|------------------|
| | D process | I process | A process |
| Increase in positive charge of central atom | Decrease | Little change | Increase |
| Increase in size of central atom | Increase | Increase | Increase |
| Increase in negative charge of entering group | No effect | Increase | Increase |
| Increase in size of entering group | No effect | Decrease | Decrease |
| Increase in negative charge of leaving group | Decrease | Decrease | Decrease |
| Increase in size of leaving group | Increase | Little change | Decrease |
| Increase in negative charge of non-replaceable group | Increase | Little change | Decrease |
| Increase in size of non-replaceable group | Increase | Little change | Decrease |

These processes can be represented as below:

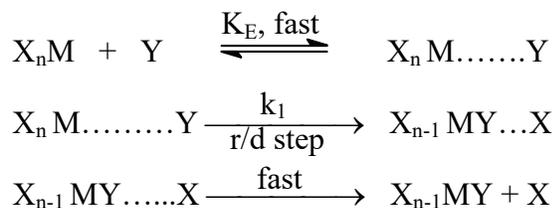


In this scheme, the large circle represents the total coordination sphere of the metal ion and the small circle labelled 'L' represents an (identical) entering and leaving ligand molecule respectively.

Following Basolo and Pearson, a correlation can be drawn between Langford's mechanistic designation and Hughes-Ingold's classification. The **A**-path of ligand substitution processes corresponds to $S_N2(\text{lim})$. The **D**-path corresponds to $S_N1(\text{lim})$. The I_a mechanism would be S_N2 path and the I_d mechanism parallels S_N1 process.

The rate law of ligand substitution reaction by an interchange mechanism is also consistent with an Eigen-Wilkins mechanism in which an encounter complex is formed in the pre-equilibrium steps. The diffusion controlled encounter complex between MX_n and the entering group diffuse together and come into contact. They may also separate at diffusion

limited rates. The next step is the rate determining reaction of the encounter complex to give the final products. This can be represented by Scheme 1:



Scheme 1

Substitution reactions in square planar complexes

General discussion

Metal ions with the d^8 configuration [Au(III), Pt(II), Pd(II), Rh(I) and Ir(I)] usually form four coordinated square planar complexes, especially with strong field ligands. Ligand substitution reactions of square planar geometry are mainly confined to platinum(II) because the reaction occur on a timescale that is very amenable to study. More recently, the availability of methods [18] for following faster reactions has opened the area to study the highly labile palladium(II) and other d^8 systems.

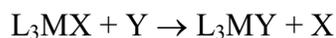
Ligand substitution processes of Pt(II) complexes appear to proceed generally by associative mechanism. This is due to lack of steric crowding and availability of an empty 'p' orbital perpendicular to the molecular plane. In some cases, however, steric requirements demand dissociative path. Another recognized pathway is oxidative addition followed by reductive elimination leading to ligand substitution.

Extensive studies on the ligand substitution of Pt(II) and Pd(II) complexes have shown that:

- (a) sterically uncrowded four coordinated systems have a definite tendency to form five and six coordinated species;
- (b) rates of these reactions are dependent on the nature and concentration of the incoming ligand;
- (c) steric effects, i.e. trans effect and cis effect play an important role in reaction kinetics.

However, Pd(II) complexes differ from Pt(II) complexes in that the trans effect is insignificant in the former systems.

Stoichiometric Mechanism

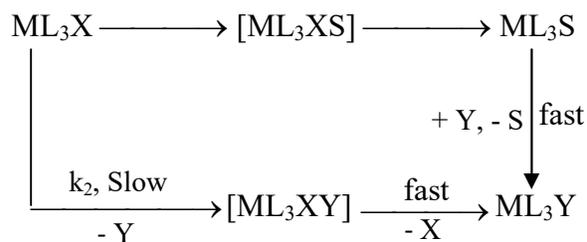


The kinetics of the above type of reaction follows a two term rate law and can be described by rate equation

$$\text{Rate} = k_{\text{obs}} [L_3MX] \quad \text{where, } k_{\text{obs}} = k_1 + k_2[Y].$$

k_1 and k_2 are first and second order rate constants respectively, $[Y]$ is the concentration of the substrate. The two term rate law indicates that the product formation takes place in two parallel reaction paths. These reactions are generally studied under pseudo first order conditions. The rate is measured at several values of $[Y]$ and the rate constant k_{obs} is plotted against $[Y]$. The plot is linear in nature with an intercept. The intercept of the plot gives the value of k_1 , while that of k_2 is obtained from the slope. The values of k_2 differ for different nucleophiles Y , but the value of k_1 remains unchanged for all nucleophiles except for the solvent present in the reaction. Hence the k_1 term originates due to nucleophilic attack of the solvent and k_2 term originates due to nucleophilic attack by Y . k_1 is related to solvento path and k_2 is related to nucleophilic path. The stoichiometric mechanisms involved in different nucleophilic substitutions involving either solvento or nucleophilic or both paths are different and present different rate expressions as different solvento paths are involved.

For the reaction, $L_3MX + Y \rightarrow L_3MY + X$, the possible stoichiometric mechanisms are discussed below. For irreversible solvolysis the Scheme 2 can be used:



Scheme 2

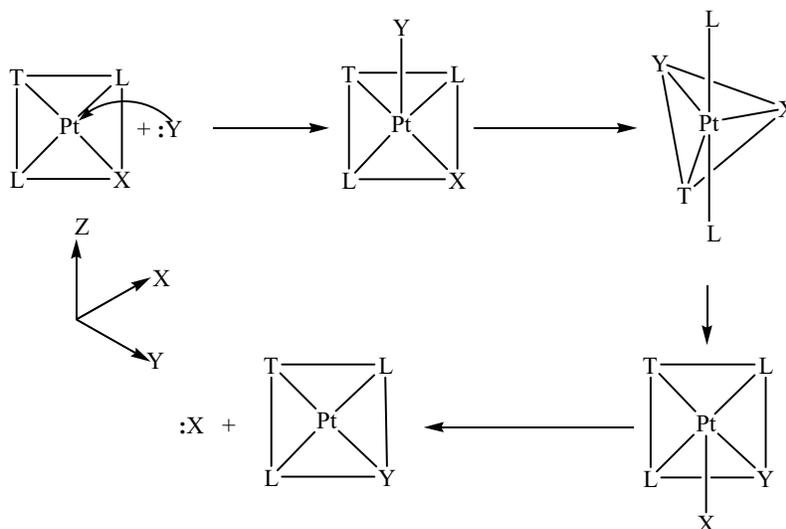
$$\text{Rate} = d[ML_3Y]/dt = d[ML_3XS]/dt + d[ML_3XY]/dt$$

$$\begin{aligned}
 &= k_s[S][ML_3X] + k_2[Y][ML_3X] \\
 &= (k_s[S] + k_2[Y])[ML_3X] \\
 &= (k_1 + k_2[Y])[ML_3X] \quad \text{where } k_s[S] = k_1 \\
 &= k_{obs}[ML_3X] \quad \text{where } k_{obs} = k_1 + k_2[Y]
 \end{aligned}$$

According to the Scheme 2, the substrate may undergo rate determining associative attack either by incoming ligand Y, or by a molecule of solvent S, in steps governed by the rate constants k_2 and k_s respectively. The five coordinated species thus formed (which may be active intermediate or transition state) subsequently decay to products. With weak nucleophiles and polar solvents, the reaction is dominated by the solvento path i.e. the value of k_2 is small or zero.

Intimate Mechanism

The bulk of the evidence indicates that the substitution reactions of square planar complexes are associative in nature (**A** or at least **I_a**). In associative activation, the incoming ligand 'Y' attack the metal either from below or from above the square plane leading to a five coordinated species, which rapidly transforms to trigonal bipyramidal species. From steric considerations, the geometry of the transition state is expected to be trigonal bipyramidal, since this arrangement minimizes mutual repulsions of the five ligands. Moreover, substitution with steric retention can be explained on the basis of the model. The leaving group 'X', the spectator ligand 'T', *trans* to 'X' and the entering ligand 'Y' form the triangular plane while the *cis* ligands lie on the perpendicular C_3 axis. The steric course of the reaction is represented below (Scheme 3).



Scheme 3

Intimate analysis of the five coordinated transition state shows that the three ligands that occupy the trigonal plane in the trigonal bipyramid may take advantage of certain σ - and π -bonding possibilities which are substantially changed from the ground state square planar complex. On the other hand, the bonding situation of the two apical ligands is not appreciably different from the ground state complex. Thus, the assumption of approximate trigonal bipyramidal geometry for the transition state correctly predicts relatively large substituent effects for the ligands in the trigonal plane (the *trans*, entering and leaving groups) and relatively small effects for the *cis* groups.

Factors affecting the rates of substitution reaction in square planar complexes

Effect of ligands

Trans Effect

The spectator ligands that are *trans* to leaving group in square planar complexes influence the rate of substitution. This phenomenon is called *trans* effect. The *trans* effect was first recognized by Werner and elaborated on by Chernuyavev (1926), is very important for better understanding of the kinetic behavior of the planar complexes in particular. It is generally

accepted that the trans effect arises from two separate influences: one arising in the ground state and the other in the transition state itself. Of all the specific ligand effects in substitution reactions, the trans effect is probably the most dramatic, spanning several orders of magnitude in rate ($\sim 10^5$). The effect of the *trans* ligand 'L' on the rate of the reactions in ethanol was studied by Basolo and others.



Although trans effect order of ligands is undoubtedly dependent on the substrate, an average order of trans labilisation is:

$\text{CO}, \text{CN}^-, \text{C}_2\text{H}_4 > \text{PR}_3, \text{H}^- > \text{CH}_3^-, \text{SC}(\text{NH}_2)_2 > \text{C}_6\text{H}_5^-, \text{NO}_2^-, \text{I}^-, \text{SCN}^- > \text{Br}^-, \text{Cl}^- > \text{Py}, \text{NH}_3, \text{OH}^-, \text{H}_2\text{O}.$

This order is approximately the order of increasing overlap of ligand orbitals with either a $\sigma\text{-Pt}(6p)$ or $\pi\text{-Pt}(5d)$ orbital. Greater the overlap, stronger is the trans effect. Depending on the nature of overlap, trans effect can be divided in two classes: $\sigma\text{-trans}$ effect and $\pi\text{-trans}$ effect. $\sigma\text{-trans}$ effect is due to overlap of appropriate ligand p_σ valence orbital with a $\text{Pt}(6p_\sigma)$ orbital. Thus, when the *trans* group is a strong $\sigma\text{-donor}$ ligand, the approximate increasing $\sigma\text{-trans}$ effect order is:



Similarly, $\pi\text{-trans}$ effect is due to overlap between ligand π^* orbital and $\text{Pt}(5d_\pi)$ orbital and the increasing order is:



Generally, a group with greater trans effect is replaced least easily and acts as a powerful nucleophile. This is expected for a trigonal bipyramidal transition state since the trans group and the entering group both are in similar positions with respect to the leaving group in the trigonal plane.

Cis Effect

Studies have also been made for a possible cis effect in square planar substitution, that is, labialization of a group *cis* to a particular group. In contrast to the profound influence of the

trans-group on the rate of substitution, *cis*-groups have only a very small effect. Tucker and coworkers have shown that 'cis effect' can be more important than 'trans effect' when groups of nearly equal trans effect are compared. Thus in the substitution reactions of chloroamine Pt(II) complexes, it was found that the difference in the cis effects of NH₃ and Cl⁻ (NH₃ > Cl⁻) is larger than their trans effect difference (Cl⁻ > NH₃). Therefore, the *cis* ligands determine the relative rates in these complexes.

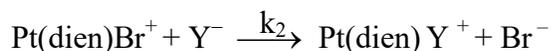
The cis effect series in the decreasing order is:



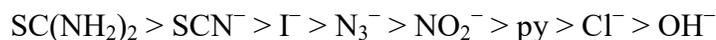
Grinberg has pointed out that pyridine substitutes a little faster in [Pt(py)Cl₃]⁻ than in [Pt(NH₃)Cl₃]⁻. There is also some evidence that Cl⁻ is replaced from Pt(II) complexes when *cis* to NH₃ about 1.2 times faster than when *cis* to NO₂⁻. This gives a cis effect order: py > NH₃ > NO₂⁻ for the substrates involved.

Effect of the incoming group

In an associative mechanism, the incoming group is an important factor in determining the rate of a reaction. The size of the rate constant, k_2 , is a measure of the effectiveness of the incoming group. The quantitative measure of the effectiveness or reactivity of the incoming group is termed nucleophilicity. Comparing the rates of reaction of a series of complexes with different entering groups and the same leaving group e.g. the reaction was carried out in aqueous solution at 25°C establishes the above generalization.



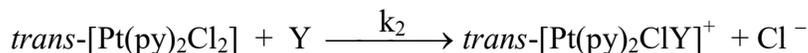
The entering ligands may be arranged in decreasing order of the k_2 values as:



A thorough study of reactions of different ligands especially with *trans*-Pt(py)₂Cl₂ in methanol solution has been reported⁴². The reactivity order is: S₂O₃²⁻ > SC(NH₂)₂, C₆H₅S⁻ > SeCN⁻ >> SO₃²⁻ > SCN⁻ > I⁻ >> C₆H₅SH > Br⁻ > N₂H₄, NH₂OH > N₃⁻ > NO₂⁻ > py > NH₃ > Cl⁻ > MeO⁻.

Nucleophilicity parameter

The effect of entering group on the rate can be exemplified by reaction carried in methanol:



Values of k_2 provide a measure of nucleophilicity towards $\textit{trans}\text{-}[\text{Pt}(\text{py})_2\text{Cl}_2]$. The nature of ‘Y’ affects the rate over a large range $\sim 10^9$ in the series of reactions where Y = NH_3 , pyridine, $^{36}\text{Cl}^-$, Br^- , I^- , SCN^- , thiourea etc. This large range of reactivity is a feature of associative mechanism of Pt(II) complexes.

The nucleophilicity parameter, n_{Pt} , can be defined as $n_{\text{Pt}} = \log \frac{k_2[\text{Y}]}{k_2\text{CH}_3\text{OH}}$

The nucleophilicity parameter depends on basicity of ‘Y’ towards Pt(II) and oxidation potential of ‘Y’. Another feature is that the nucleophilicity of the entering group towards platinum appears to correlate with soft Lewis basicity. The ligands, which are good σ -donor and π -acceptor, have high n_{Pt} values.

However, the reaction rates of platinum(II) complexes depend not only on the nucleophilicity of ‘Y’, but also on the electrophilicity of the platinum complex. In other words, different Pt(II) substrates display different abilities to discriminate among nucleophiles. For reactions of nucleophiles ‘Y’ with other Pt(II) complexes in other solvents (S) besides methanol, the relative reactivity of ‘Y’ and ‘S’ is related to n_{Pt} as:

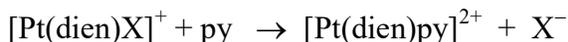
$$\log[k_2(\text{Y}) / k_2(\text{S})] = s \cdot n_{\text{Pt}}$$

The parameter, which characterizes the sensitivity of the rate constant to the nucleophilicity parameter, is called nucleophilic discrimination factor. The large value of ‘s’ indicates that the reaction is more sensitive to changes in nucleophile.

Effect of leaving group

The effect of the leaving group is very difficult to qualify as it is very closely connected with the nature of the incoming nucleophile and the trans ligand. In a dissociative reaction the bond between the leaving group and the metal breaks in the transition state and therefore in these reactions there is a large dependence on the nature of the leaving group. However, for an

associative reaction, the effect of the leaving group is dependent on the degree to which bond breaking occurs in the transition state. Each reaction differs in the extent to which bond breaking occurs in the transition. A fairly extensive study of relative effects of leaving group on rates has been made utilizing the reaction in aqueous medium.



Here the three coordination positions are rendered inert by using strongly complexing ligand dien (diethylenetriamine) and the entering ligand is pyridine in each case. The order of decreasing rate [45, 46] is $\text{NO}_3^- > \text{H}_2\text{O} > \text{Cl}^- > \text{Br}^- > \text{I}^- > \text{N}_3^- > \text{SCN}^- > \text{NO}_2^- > \text{CN}^-$. It has been observed that H_2O departs about 10^5 times faster than CN^- . This indicates that the leaving group has a substantial effect on the rate of the reaction and Pt-X bond breaking make a significant contribution comparable to that of Pt-py bond making. Generally a good attacking group is a poor leaving group with very few exceptions. OH^- is notable, for it is a very poor nucleophile for Pt(II), but is only very slowly replaced.

Steric Effect

The first compelling experimental evidence for associative activation in square planar substitution was demonstration of large rate effects on blocking the entering group attack positions above and below the plane. In a square planar complex two ligands *cis* to the leaving group and one ligand *trans* to the leaving group are inert ligands. Inert ligands may exert steric hindrance to the incoming nucleophile and may affect the reaction rate. Steric retardation observed in several cases provides good evidence in favor of an associative mechanism, since there is no way to rationalize such retardation on the assumption of a dissociative mechanism. The results of a study of the rates of reaction of *cis*- and *trans*- $[\text{Pt}(\text{PEt}_3)_2(\text{R})\text{Cl}]$ complexes with pyridine in ethanol show the variation of rates in the ratio 1 : 5 : 36 (for R = mesityl, o-tolyl and phenyl respectively) in the *trans* complex and the variation of rates in the ratio 1 : 200 : 80,000 (for R = mesityl, o-tolyl and phenyl respectively) in the *cis* complex. Thus *cis*-blocking is more effective than *trans*-blocking in associative mechanism.

Effect of charge on the complex

A classical test for detecting associative or dissociative pathway is the effect of electronic charge on the reaction rates. Martin and coworkers have provided the most conclusive evidence

for an associative solvent path, with the lack of a large rate effect in k_1 path for reactions of complexes which, carry different net charges in aqueous solution. Proceeding from $[\text{Pt}(\text{NH}_3)_3\text{Cl}]^+$ to PtCl_4^{2-} , the k_1 remains roughly constant. This is not consistent with a dissociative path but is reasonable assuming any associative path such as **A** mechanism.

Nature of the Metal Centre

The nature of the reaction centre also affects the rate of substitution of square planar complexes. To ensure that effects are due only to a change in metal centre, only the reactivities of isovalent ions can be compared. Thus, the only d^8 isovalent ions that can be compared are Ni(II), Pd(II), Pt(II) and Co(I), Rh(I) and Ir(I). The general sequence that has been determined is $\text{Ni} > \text{Pd} > \text{Pt}$ in the ratio $10^7\text{-}10^8:10^5\text{-}10^6:1$. There have been no other adequate comparisons made although Tobe predicts that the smaller the effective nuclear charge on the metal, the greater the relative stability of the five-coordinate intermediate and thus $\text{Ir(I)} > \text{Pt(II)} > \text{Au(III)}$.

Effect of pressure

The effect of pressure on the rate of a reaction can be summarized in the simplified expression :

$$\ln(k_2/k_1)_T = -(\Delta V^\ddagger/RT)(P_2 - P_1)$$

Here, ΔV^\ddagger , the volume of activation, indicates the change in molar volume when the reactants are brought from uncombined state to the transition state, k_1 and k_2 are the rate constants at the pressure P_1 and P_2 , usually expressed in megaPascals (Mpa).

Role of activation parameters

The activation parameters such as enthalpy of activation (ΔH^\ddagger), entropy of activation (ΔS^\ddagger) and volume of activation (ΔV^\ddagger) are related to the transition state of a reaction and play an important role to point out the mechanism. The ΔH^\ddagger and ΔS^\ddagger are related by Eyring equation:

$$\ln(kh/k_B T) = -\Delta H^\ddagger/RT + \Delta S^\ddagger/R$$

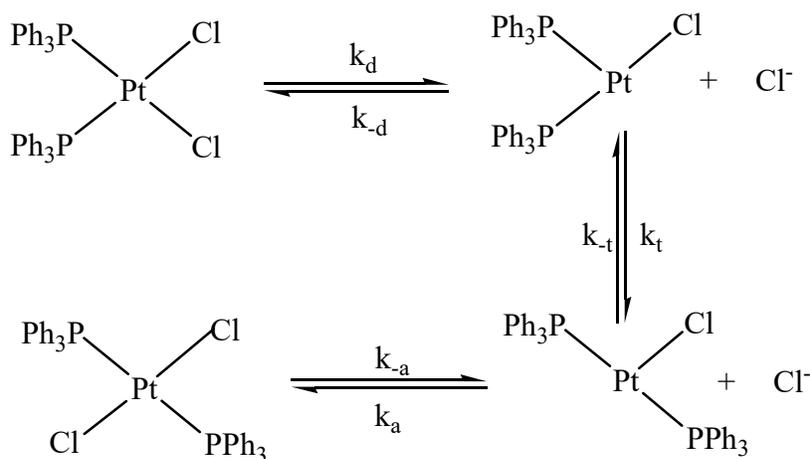
Here, 'k' is rate constant of the reaction, 'h' is Planck constant, 'k_B' is Boltzman constant, 'T' is temperature in Kelvin scale and 'R' is universal gas constant. The values of ΔH^\ddagger and ΔS^\ddagger can be obtained from the slope and intercept of Eyring plot.

Generally for a dissociative activation, ΔH^\ddagger has higher value than for an associative activation. Very often low positive value of ΔH^\ddagger strongly suggests associative activation. The entropy of activation, ΔS^\ddagger , is the difference in entropy between the transition state and the ground state of the reactants. In solution where charged particles are involved, solvation effects often dominate the entropy of activation. For associative activation the transition state is more compact than the ground state and a large decrease in entropy is observed i.e. ΔS^\ddagger shows large negative value.

Dissociative Mechanism

As it has already been discussed, a dissociative mechanism is not the favoured pathway for substitution of square planar complexes; however, it can be encouraged by following one or more of the following methods: promote bond weakening, stabilize the intermediate of lower coordination number or prevent bond formation. In theory this can be done by using either electronic or steric effects.

In case of Pt(II) complexes such a dissociative path operates only when the substrate is so much sterically hindered that the incoming ligand finds no way to approach the metal. Such steric blocking has almost been achieved with the complex $[\text{Pt}(\text{Et}_4\text{dien})\text{Cl}]^+$. The four terminal ethyl groups are above and below the plane and render virtually impossible any access to the central metal. Photochemical isomerisation of the complex *cis*- $[\text{Pt}(\text{PPh}_3)_2\text{Cl}_2]$ proceeds through a dissociative path according to the Scheme 9.



Scheme 5