Advanced Transition Metal Chemistry

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Lecture - 45
Inorganic Reaction Mechanisms

Hello everyone. I once again welcome you all to MSB lecture series on transition metal chemistry. In my previous lecture I was discussing about oxidative addition reactions and reductive elimination reactions and also in the last few lectures I did explain how important these two reactions in coordination chemistry and also in organometallic chemistry. And they give clear information about possible utility of a given metal complex in a homogeneous catalytic reaction.

So, now we shall move on to another interesting topic, very very important that complement what we learned in previous lectures that is inorganic reaction mechanisms. So, under inorganic reaction mechanism I shall elaborate on substitution reactions especially in octahedral complexes and also square planar complexes. And also, I shall tell you about the trans influence in the substitution reactions of square planar complexes.

And also, what are the different type of mechanisms we can think of for substitution reactions in both octahedral complexes and also square planar complexes, and this is again very important from the reaction point of view.

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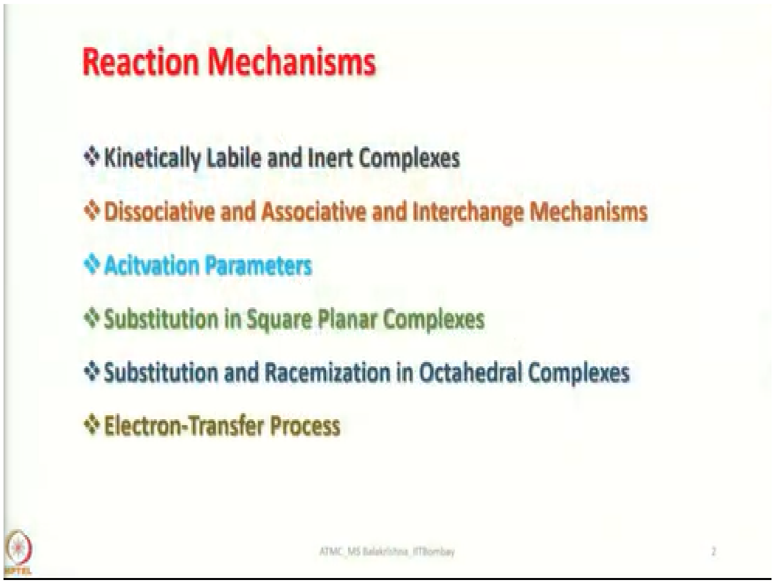

Reaction Mechanisms

- ❖ Kinetically Labile and Inert Complexes
- ❖ Dissociative and Associative and Interchange Mechanisms
- ❖ Acitvation Parameters
- ❖ Substitution in Square Planar Complexes
- ❖ Substitution and Racemization in Octahedral Complexes
- ❖ Electron-Transfer Process

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So, I have given some of these points here, you can see. One has to be very careful when we listen to some terms such as kinetically labile and inert complexes. I shall elaborate more and so under this, we will begin discussion on what are labile and inert complexes, what are stable and unstable complexes, what is stability and instability. Then we shall see what are the different mechanistic pathways we can think of dissociative, associative.

Also, there is one more mechanism that is called interchange mechanism and then we shall look into activation parameters. After this one, let us move on to understanding the substitution reactions in square planar complexes and then substitution reactions and racemization reactions in octahedral complexes. And also, with respect to octahedral complexes, we shall also look into the stereo chemical consequences of substitution reactions in octahedral complexes.

And at the end, let us also look into electron transfer process. So, these are all important topics that I would discuss under inorganic reaction mechanism. Now let us look into kinetically labile and inert complexes, the terms stable and unstable, stability or instability refer to the thermodynamics of complex formation, whereas the terms labile and inert refer to the kinetics of complex formation. We should know how to distinguish these terms without any confusion.

If the complex formation equilibria are established rapidly, the complex is said to be labile, on the other hand, if the complex formation equilibria are established very slowly or relatively slowly, the complex is said to be inert. Metal complexes that undergo reactions with half-life less than one minute are described as kinetically labile. On the other hand, if the reaction takes longer than one minute or if the half-life of a complex in a substitution reaction is much longer than one minute, the complex is called kinetically inert.

So, one should bear in mind that there is no connection between the thermodynamic stability and its lability towards substitution reactions. I repeat again there is no connection between the thermodynamic stability and its lability towards substitution. For example, if we look into the hydration energy associated with chromium 3 plus ion and iron 3 plus ion, they are almost equal but hexaaquachromium 3 plus having d^3 electronic configuration.

Undergoes substitution reaction rather slowly, whereas hexaaquairon 3 plus having d^5 electronic configuration undergoes substitution reactions very rapidly. In a similar way the overall formation constant of tetracyanomercury is greater than that of hexacyanoferrate because Hg^{2+} complex readily exchanges cyanide ions with isotopically labelled cyanide while exchange is very slow in case of hexacyanoferrate.

That means if you consider tetracyanomercurate and also hexacyanoferrate for isotopic exchange of cyanide ions it is very rapid in case of Hg^{2+} complex but rather it is very slow in case of Fe^{3+}. Of course, you should recall the kinetic inertness of d^3 electronic configuration that we come across in hexacyanoferrate. So, that means the kinetic inertness of d^3 in case of chromium 3 plus.

And also, low spin d^6 electronic configuration in case of hexacyanoferrate both are octahedral complexes that is essentially associated with partly with crystal field effects. That means d^3 in case of hexaaquachromium three plus and low spin d^6 electronic configuration in case of iron three plus in hexacyanoferrate are associated partly with crystal field effect as a result we see the difference in their reactivity.

So, that means one should be able to make direct correlation between crystal field stabilizing effects and also the complex ion we are considering for substitution reactions. So, when we perform a reaction, we write a stoichiometric or well-balanced chemical equation but that does not say about the mechanism. For example, if I add A + B or more substrates and reagents and combine, I write the product in a chemical equation that is well balanced.

But the process that occur in a reaction are not necessarily obvious from the chemical equation that means chemical reaction represented in the form of a balanced chemical equation does not say anything about the mechanism. Let us consider the simple reaction here.

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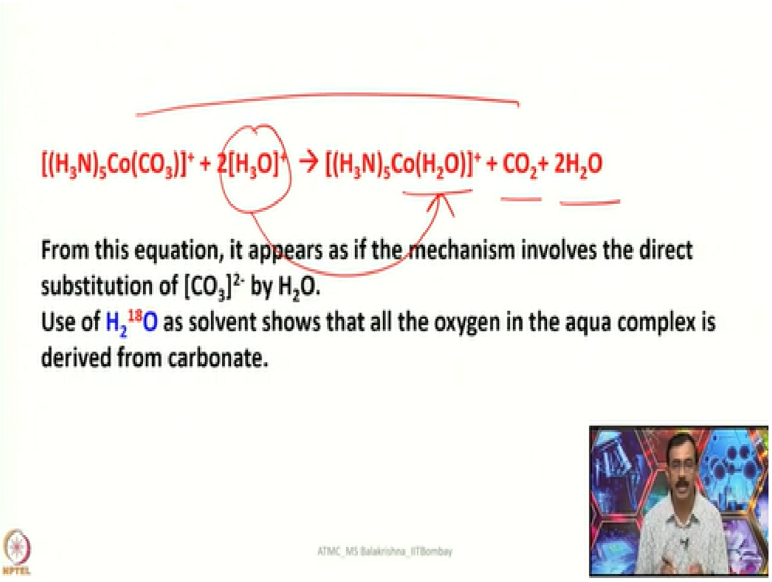

$[(H_3N)_5Co(CO_3)]^+ + 2[H_3O]^+ \rightarrow [(H_3N)_5Co(H_2O)]^+ + CO_2 + 2H_2O$

From this equation, it appears as if the mechanism involves the direct substitution of $[CO_3]^{2-}$ by H_2O.

Use of $H_2{}^{18}O$ as solvent shows that all the oxygen in the aqua complex is derived from carbonate.

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You can take this pentammine cobalt carbonate complex and treat this one with water. Then what happens? Carbonate ion is replaced here to get this aqua coordinated compound with the liberation of CO_2 and $2H_2O$. By looking into the balanced chemical equation, it appears that simply CO_2 has come out in this place; this water has gone, but that is not the case. It appears as if the mechanism involves the direct substitution of carbonate by water.

But if we use labelled water such as $H_2{}^{18}O$ as a solvent that shows all the oxygen in aqua complexes derived from carbonate. So, that is interesting but simply when you look into this equation you can never get this information. So, this is where reaction mechanism and also the mechanistic pathway followed by a particular reaction is very important. From that point of view reaction mechanism and kinetics are very important.

It is essential to understand the sequence of a reaction and also the path followed by that particular reaction. So, now let us look into this reaction, you see, I have given here.

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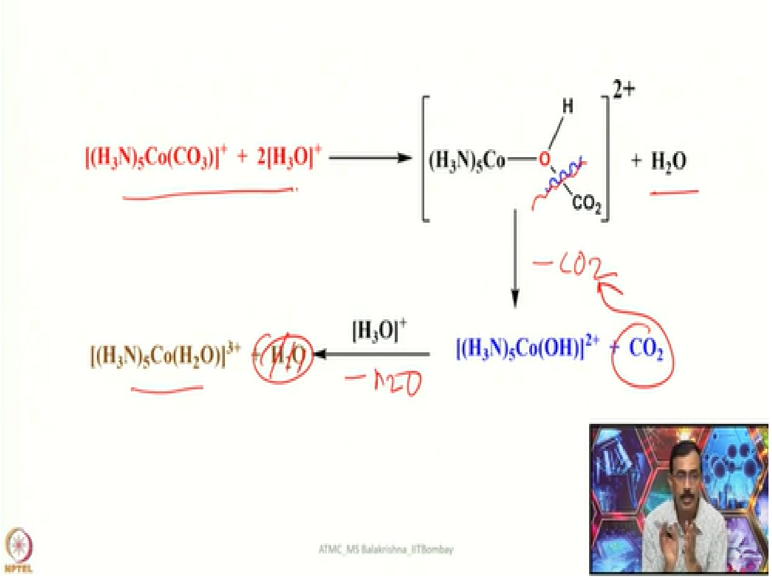

First what happens, a molecule of water of come here as hydronium comes and then it attacks oxygen lone pair and we have a dicatonic species of this type with the H_2O coming out and now this next step this bond goes and here of course CO_2 comes here. This is what I have written here and now it forms a hydroxyl compound and again when this is treated with another mole of water here. So, H_2O comes out, I think it is better to write here now it forms here.

So, this information was confirmed after doing the labelling studies to analyse which oxygen is sitting here whether it is that one or this one. So, this kind of information one can only get from kinetic studies and looking into reaction mechanism, but not simply writing a balanced chemical equation. Often most of the time balanced chemical equation can tell you the kind of products we are getting but it would never tell you the mechanistic path followed in that particular reaction. So, now let us look into the substitution reaction mechanism, we have in inorganic reactions.

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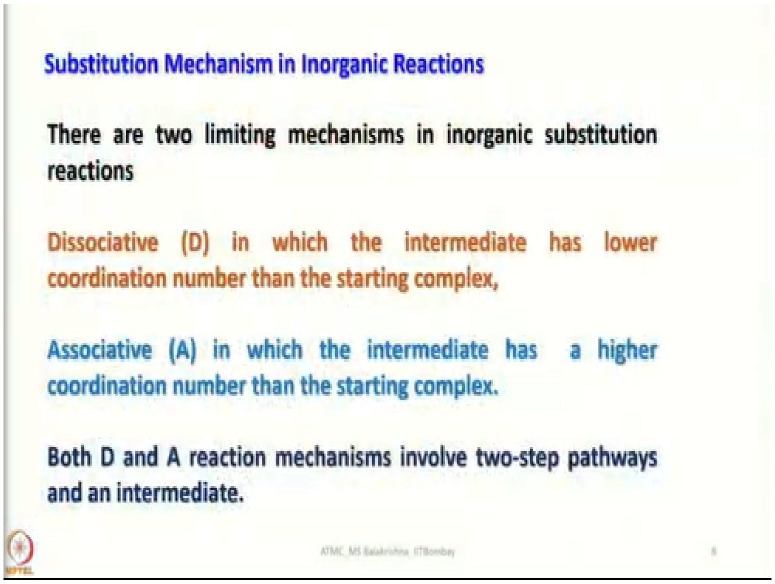

Substitution Mechanism in Inorganic Reactions

There are two limiting mechanisms in inorganic substitution reactions

Dissociative (D) in which the intermediate has lower coordination number than the starting complex,

Associative (A) in which the intermediate has a higher coordination number than the starting complex.

Both D and A reaction mechanisms involve two-step pathways and an intermediate.

So, there are two limiting mechanisms in inorganic substitution reactions. There, one is dissociative, it is denoted by term D. In future if I use term just D instead of dissociative you, please understand that this is a dissociative mechanism, in which the intermediate has lower coordination number than the corresponding complex. The starting complex is say, octahedral compound then we end up with a five membered or five coordinated complex as an intermediate.

So, lower coordination number is there that can be simple square based pyramid or it can be trigonal bipyramid. These things, I shall discuss later and next the second one is associative. It is denoted by term A, associative mechanism in which the intermediate has a higher coordination number than the starting complex. If the starting compound is say, octahedral, the coordination number increases, because in the intermediate the incoming or entering ligand will be added.

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So, that there is an expansion of coordination number. In that case what happens. Begin with octahedral, we have and it can have the entering can come something like this, then this is called capped octahedron or it can simply have pentagonal bipyramidal, something like this. These two are possible especially with octahedral complexes, when they are taking associative path.

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So, that means both D and A reaction mechanisms, involve two step pathways and an intermediate. In case of dissociative, the slow step is elimination of the living group to form the intermediate having coordination number five. In case of associative mechanism, the slow step is addition of the entering ligand to expand its coordination number from 6 to 7 having pentagonal bipyramidal geometry preferably the more symmetric one.

That means whether we consider D or A reaction schemes or reaction mechanisms, both of them involve two step pathways and an intermediate.

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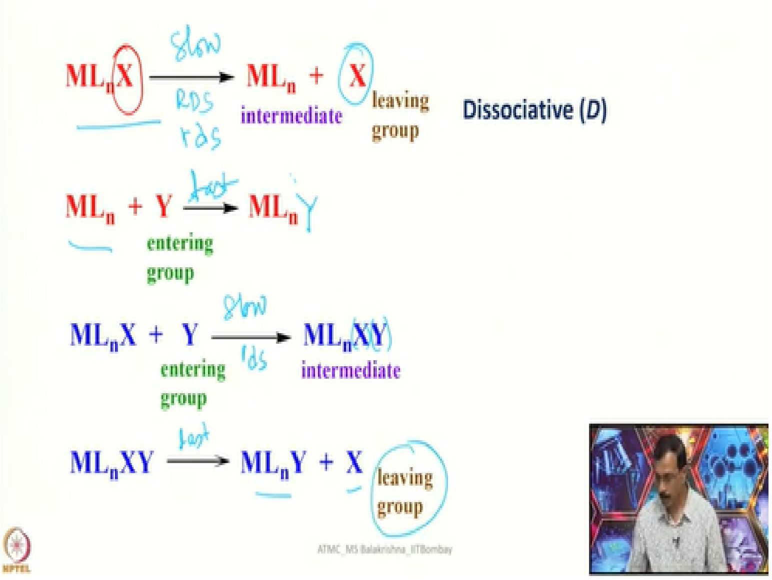

$ML_nX \xrightarrow[\text{RDS}\ \text{rds}]{\text{slow}} ML_n + X$

intermediate

leaving group

Dissociative (*D*)

$ML_n + Y \xrightarrow{\text{fast}} ML_nY$

entering group

$ML_nX + Y \xrightarrow[\text{rds}]{\text{slow}} ML_nXY$

entering group

intermediate

$ML_nXY \xrightarrow{\text{fast}} ML_nY + X$

leaving group

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So, now let us see, for example, ML_nX, I am considering. Let us focus our attention on this one this is the leaving group here. So, this is the leaving group and intermediate would be having the coordination number one less than what we had in case of the starting complex. And this is leaving group this is usually the slow step and hence it is rate determining step. It can be written in capital or small does not matter, sometime one writes like this; rate determining step, this is a slow step.

Then once we have this intermediate here so that is attacked by entering group and then we get the product like this. So, this is called dissociative pathway or dissociative mechanism. The other one is associative. So, in this case, what happens, this is the slow step or rate determining step. In this one the entering group will be added before the intermediate is formed. Now intermediate is there, the expansion of coordination number you can see here.

And now once in the first step, and here this is the first step, so here what happens? X is eliminated and the compound will revert back to the previous geometry with some distortion or whatever that depends upon the nature of steric bulk of the entering ligand Y. So, here it is leaving group. So, this is associative mechanism. So these two are very important. Of course, these dissociative and associative mechanisms are true in case of square planar complexes and even tetrahedral complexes.

But let us see as we progress with that one how we can explain dissociative mechanism or associative mechanism with respect to octahedral geometry as well as square planar geometry.

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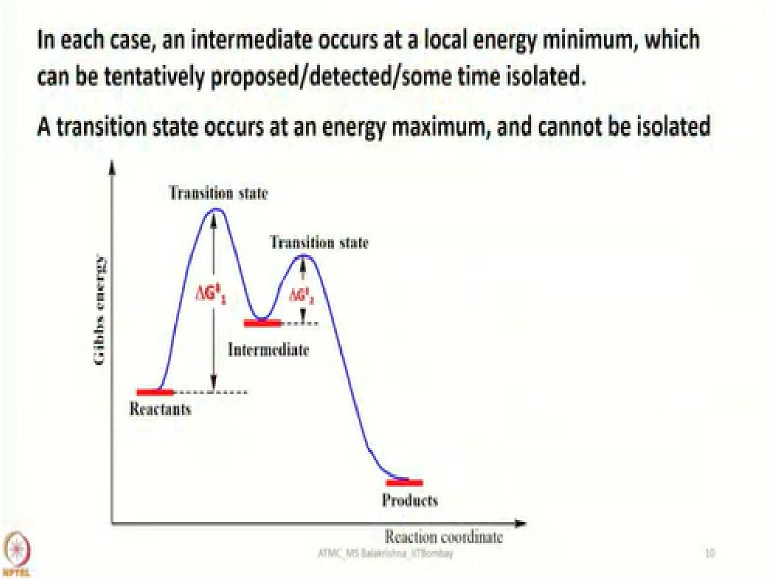

In each case, an intermediate occurs at a local energy minimum, which can be tentatively proposed/detected/some time isolated.

A transition state occurs at an energy maximum, and cannot be isolated

So, in each case, an intermediate occurs at a local energy minimum which can be tentatively proposed, detected or sometime that can be isolated also. That means in each case when we get an intermediate at a local energy minimum which cannot be tentatively proposed. So, when we are performing a reaction as a chemist, we know that what kind of intermediate is formed and where it goes and binds, all this information is there.

So, keeping that information in mind we can propose a tentative intermediate and also tentative mechanism. So, in that case what happens? The intermediate that obtained either theoretically it can be proposed or through some spectroscopic measurements or analytical measurements that can be detected and, in some cases, if it can also be isolated. Provide ideal condition for its isolation.

The transit state occurs at the energy maximum cannot be isolated because it is a high energy transient species, and it is very difficult to isolate, that one. So, in most metal complex substitution reaction pathways, the bond formation between the metal and the entering group and bond cleavage between the metal and leaving group are thought to be concurrent and hence the trans state would have weak interactions with both entering and leaving groups. This is known as interchange or I mechanism.

So, you should remember, apart from D, dissociative and A, associative we come across another pathway or mechanism in inorganic chemistry that is called interchange mechanism. In this one what happens? The entering group and living group are held loosely to the intermediate that means the moment a molecule is set for substitution reaction with entering group, is ready to establish coordination and that happens simultaneously.

So, the leaving group will be preparing to leave from the coordination sphere and the entering group is preparing to enter. In that case what happens? We have an intermediate where both of them are associated with weak bonds to the metal atom. So, that is called interchange mechanism.

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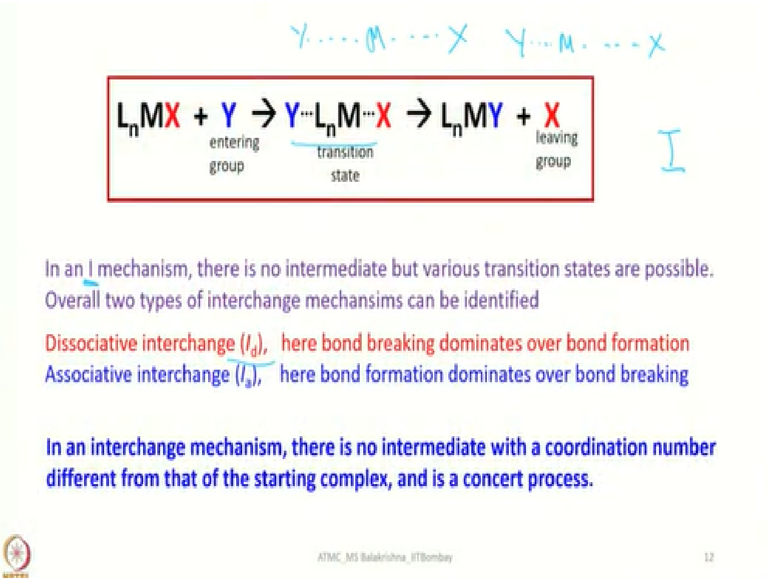

Y····M····X Y···M·····X

$L_nMX + Y \rightarrow Y \cdots L_nM \cdots X \rightarrow L_nMY + X$

entering group

transition state

leaving group

I

In an I mechanism, there is no intermediate but various transition states are possible. Overall two types of interchange mechansims can be identified

Dissociative interchange (I_d), here bond breaking dominates over bond formation
Associative interchange (I_a), here bond formation dominates over bond breaking

In an interchange mechanism, there is no intermediate with a coordination number different from that of the starting complex, and is a concert process.

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You can see in this reaction. For example, this is the starting complex ready for undergoing substitution reaction having X as leaving group. Now Y comes as an entering group and now, we have the transition state where both of them are held loosely and then at the end, in the first step X is eliminated to form the substituted product. So, this is called interchange. In an interchange mechanism, interchange is always represented by I, it should not be confused with any other symbol I.

When we talk about reaction mechanism in chemistry if, I comes, it is for interchange. There is no intermediate. When you are considering an interchange mechanism there is no intermediate but various transition states are possible. Overall, two types of interchange mechanism can be identified. In this kind of mechanism, no intermediate can be looked into but various transition states are possible. So, that means you ask me whether this is not an intermediate, yes, this is not an intermediate, this is a transition state.

It can have different forms, what are different forms? For example, something like this. Both of them can be longer and then what happen? This is the leaving, the entering group, this can come something like this and this this is can get elongated. So, something like this happens. This kind of various transition states are possible but you cannot have any intermediate well defined intermediate in that one.

So, in this context overall, we can come across two types of interchange mechanisms. One is dissociative interchange it is called I_d here bond breaking dominates over bond formation. So, that means within no time X will be moving away before Y can establish a bond with metal that is what it is, dissociate, this is represented by I_d.

Then other one is associative interchange, here opposite is true in this case. Here bond formation dominates or bond breaking, that means it readily establishes weak interactions with the metal before X is getting ready to leave from the metal coordination sphere. So, that means, I can be further classified into two categories, one is dissociative interchange I_d here bond breaking dominates over bond formation and associative interchange mechanism I_a here bond formation dominates over bond breaking.

So, in an interchange mechanism, there is no intermediate with a coordination number different from that of the starting complex and hence it is a concerted process. I am stressing upon this fact in an interchange mechanism, there is no intermediate with a coordination number different from that of starting complex or neither that can be detected nor that can be isolated and hence it is a concert process.

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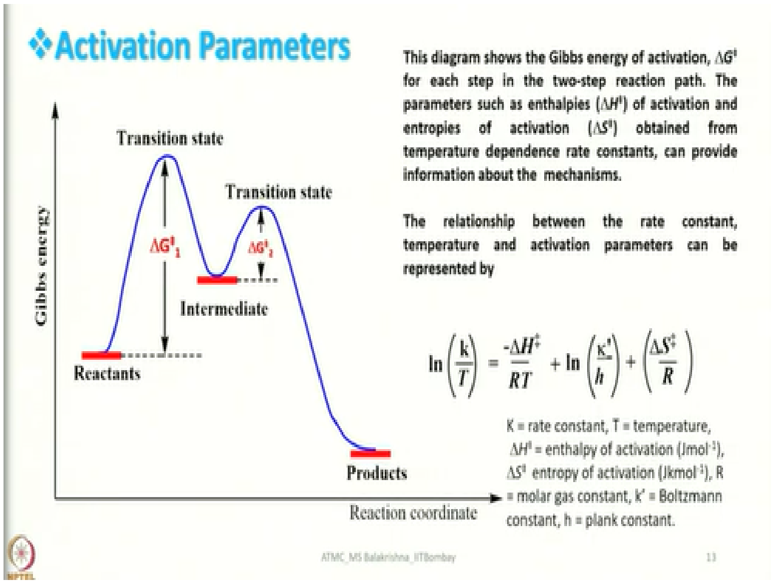

❖Activation Parameters

This diagram shows the Gibbs energy of activation, $\Delta G^{\ddagger}$ for each step in the two-step reaction path. The parameters such as enthalpies ($\Delta H^{\ddagger}$) of activation and entropies of activation ($\Delta S^{\ddagger}$) obtained from temperature dependence rate constants, can provide information about the mechanisms.

The relationship between the rate constant, temperature and activation parameters can be represented by

$$\ln\left(\frac{k}{T}\right) = \frac{-\Delta H^{\ddagger}}{RT} + \ln\left(\frac{\kappa'}{h}\right) + \left(\frac{\Delta S^{\ddagger}}{R}\right)$$

K = rate constant, T = temperature, $\Delta H^{\ddagger}$ = enthalpy of activation ($Jmol^{-1}$), $\Delta S^{\ddagger}$ entropy of activation ($Jkmol^{-1}$), R = molar gas constant, k' = Boltzmann constant, h = plank constant.

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This is the plot I showed you, the coordinates and Gibbs energy related with that one also you can see, transient species. This diagram shows the Gibbs energy of activation for each step in the two-step reaction path. The parameters such as enthalpies that is ΔH and entropy of activation obtained from temperature dependence rate constants can provide information about the mechanism.

That means in order to understand the sequence of the reaction and also the rate of the reaction under ΔG associated with the reaction, what we need is enthalpy of activation and also the entropy of activation. So, how these terms are related, can be seen here to the rate. The relationship between the rate constant, temperature and activation parameters can be represented by this equation $\ln(K/T) = -\Delta H^{\#}/RT + \ln(K^{'}/h) + \Delta S/R$.

And of course, you are all familiar with the terms we are using here, K is rate constant and T is temperature and ΔH is enthalpy of activation in joules per mole, and ΔS is entropy of activation Joules per Kelvin per mole and R is molar gas constant and K’ is Boltzmann constant and of course small h is plank constant.

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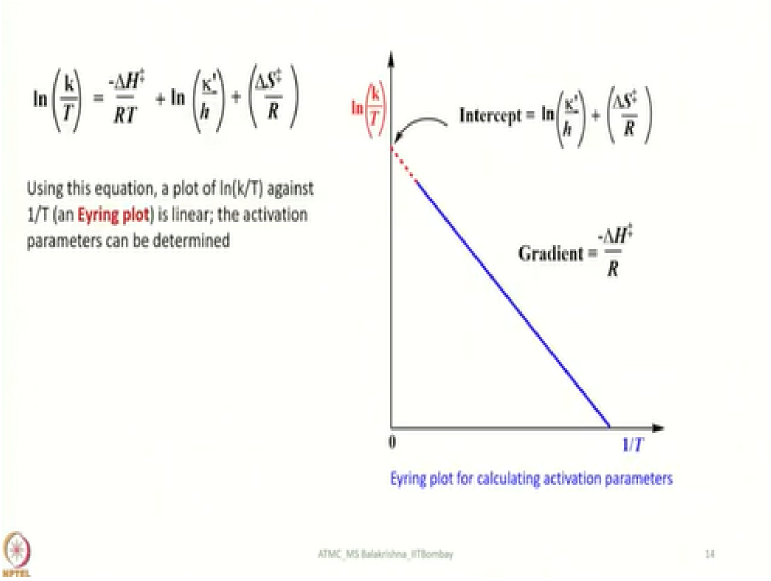

$$\ln\left(\frac{k}{T}\right) = \frac{-\Delta H^{\ddagger}}{RT} + \ln\left(\frac{K'}{h}\right) + \left(\frac{\Delta S^{\ddagger}}{R}\right)$$

Using this equation, a plot of ln(k/T) against 1/T (an **Eyring plot**) is linear; the activation parameters can be determined

Eyring plot for calculating activation parameters

So, using this equation if you plot ln(K/T) versus 1/T this is called Eyring plot. So, plot representing ln(K/T) versus 1/T is called Eyring plot is linear. The activation parameters can be determined. So, the activation parameters whatever I mentioned can be determined from this one. So, for example if you take the intercept that gives you these two terms and, whereas the gradient if you take that gives this term and hence the rate can be calculated.

The values of ΔS are very useful in distinguishing between the dissociative and associative mechanism. Although many times or often, we ignore the term entropy term and its contribution for a reaction to understand the sequence of reactions or intermediates that are you know, coming in a particular reaction. And especially, to distinguish the type of reaction mechanism that is followed whether it is dissociative or associative the value of ΔS is very helpful.

For example, a large and negative value of ΔS is an indicative of associative mechanism as the entering ligand coordinates are associated with starting complex and hence entropy decreases. This is true in case of oxidative addition reaction also, that we saw in my previous lecture. I told you about when we are looking into thermodynamic parameters, I did mention that in a typical oxidative addition reaction ΔS is large and negative.

You looked into that equation I showed you the values of ΔS are very useful in distinguishing between dissociative and associative mechanisms. A large negative value is indicative of associative mechanism as the entering ligand coordinates or associates with the starting complex, entropy decreases. And of course, sometime what happens? It can be misleading also because solvent reorganization can also lead to decrease in entropy even for a dissociative mechanism.

So, one has to be extra cautious by looking into the change in entropy. If ΔS is very large and negative, you can assume the mechanism is always associative.

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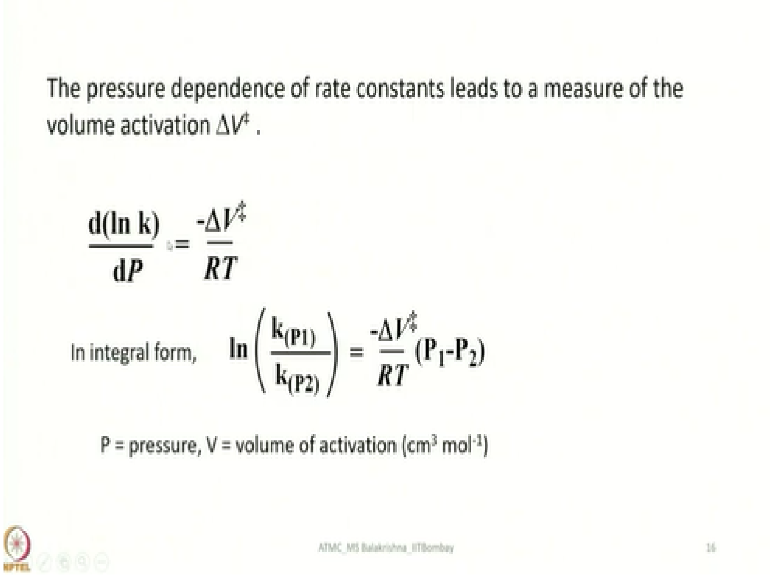

The pressure dependence of rate constants leads to a measure of the volume activation $\Delta V^{\ddagger}$.

$$\frac{d(\ln k)}{dP} = \frac{-\Delta V^{\ddagger}}{RT}$$

In integral form, $\ln\left(\frac{k_{(P1)}}{k_{(P2)}}\right) = \frac{-\Delta V^{\ddagger}}{RT}(P_1-P_2)$

P = pressure, V = volume of activation ($cm^3\ mol^{-1}$)

Now the pressure difference of rate constants leads to a measure of the volume activation that is called ΔV. So, for example ΔV can be related to the rate in this fashion dlnK/dP = -ΔV/RT and this is negative and of course in integral form, one can write something like this. And here P is pressure and V is volume of activation cm^3 per mole. So, a reaction having greater volume in its transition state compared to the initial state shows a positive value for this one.

If the transition state being compressed relative to initial state it will be negative that means ΔV will be negative. So, after allowance for any change in volume of the solvent, the sign of ΔV should distinguish between dissociative and associative mechanism.

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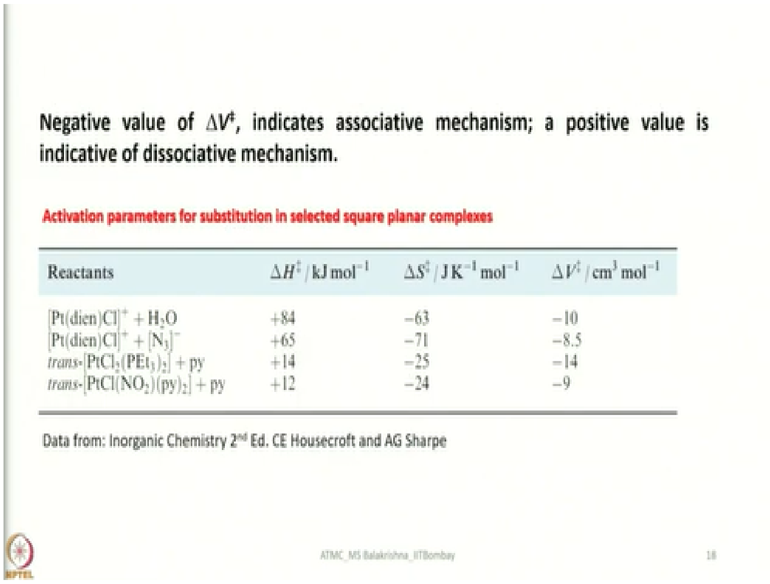

Negative value of $\Delta V^{\ddagger}$, indicates associative mechanism; a positive value is indicative of dissociative mechanism.

Activation parameters for substitution in selected square planar complexes

Reactants	$\Delta H^{\ddagger}$ / kJ mol^{-1}	$\Delta S^{\ddagger}$ / J K^{-1} mol^{-1}	$\Delta V^{\ddagger}$ / cm^3 mol^{-1}
$[Pt(dien)Cl]^+ + H_2O$	+84	−63	−10
$[Pt(dien)Cl]^+ + [N_3]^-$	+65	−71	−8.5
trans-$[PtCl_2(PEt_3)_2]$ + py	+14	−25	−14
trans-$[PtCl(NO_2)(py)_2]$ + py	+12	−24	−9

Data from: Inorganic Chemistry 2nd Ed. CE Housecroft and AG Sharpe

So, you can see here negative value of ΔV indicates associative mechanism, a positive values indicative of dissociative mechanism. So, that means two important parameters we can analyse, one is ΔS. If the ΔS is negative and large, this is associative mechanism. On the other hand, if ΔV is negative that indicates associative mechanism. Because what happen there will be reduction in the volume.

A positive value is indicative of dissociative mechanism, what happens? Another leaving group comes out so volume increases. So, one should remember that, and of course activation parameters for substitution reaction in square planar complexes are given here typically for platinum two complexes. In most of the cases when we talk about substitution reactions in square planar complexes, we are always considering platinum(II).

Because in case of platinum(II) complexes, the rate is relatively slow. And hence all these mechanistic aspects have been established very nicely without any flaw starting from Warner's time. As a result, all these substitution reactions revolving around square planar complexes would also revolve around platinum(II) complexes and you can see here some of these parameters are given here.

If you are curious of course you can take a typical reaction and also try to find out ΔG associated with these reactions, and also using these terms you should be able to even calculate the rate constant for this reaction. Hope you will do it by analysing in a proper way.

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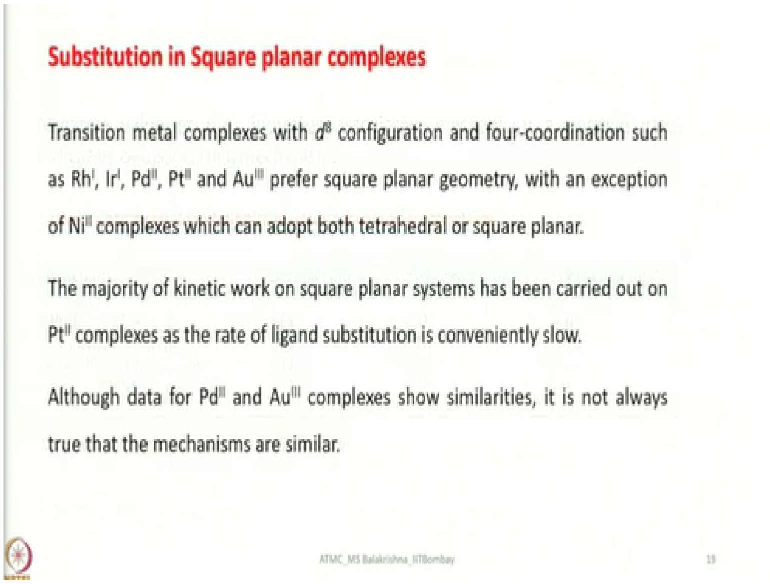

Substitution in Square planar complexes

Transition metal complexes with d^8 configuration and four-coordination such as Rh^{I}, Ir^{I}, Pd^{II}, Pt^{II} and Au^{III} prefer square planar geometry, with an exception of Ni^{II} complexes which can adopt both tetrahedral or square planar.

The majority of kinetic work on square planar systems has been carried out on Pt^{II} complexes as the rate of ligand substitution is conveniently slow.

Although data for Pd^{II} and Au^{III} complexes show similarities, it is not always true that the mechanisms are similar.

Now let us look into substitution in square planar complexes with this information general information also some special information about square planar complexes. Now let us look into exclusively the substitution reactions in square planar complexes. Transition metal complexes with d^8 electronic configuration and four coordinated species such as rhodium and iridium or palladium and platinum in +2 state, rhodium and iridium in +1 state or gold in +3 state.

They all prefer square planar geometry because all of them have d^8 electronic configuration of course with an exception of nickel(II) complexes. Even with strong field ligands sometimes they can adopt tetrahedral and of course square planar geometries. The majority of kinetic work on square planar systems has been carried out on platinum(II) complexes as I mentioned as the rate of ligand substitution is conveniently slow.

So, although data is available for palladium(II) and gold(III) complexes which also show similar behaviour when we compare them to rhodium, iridium and palladium and platinum species. Especially rhodium and iridium and platinum(II) species, it is not always true that the mechanisms are similar. So, they show similar product formation but mechanisms may not be similar and, in some cases, yes, they show some similarities.

With this let me stop this lecture, please look into some of the parameters I discussed and also showed some plots. Just go through it and try to understand. Let me continue in my next lecture further discussion on substitution in square planar complexes. Thank you for your kind attention. Have an excellent time.