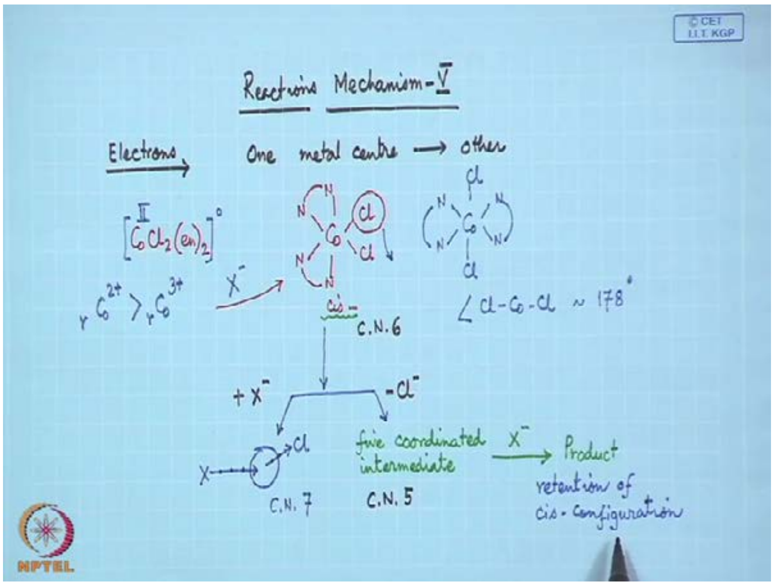
Coordination Chemistry
Prof. Debashis Ray
Department of Chemistry
Indian Institute of Technology, Kharagpur

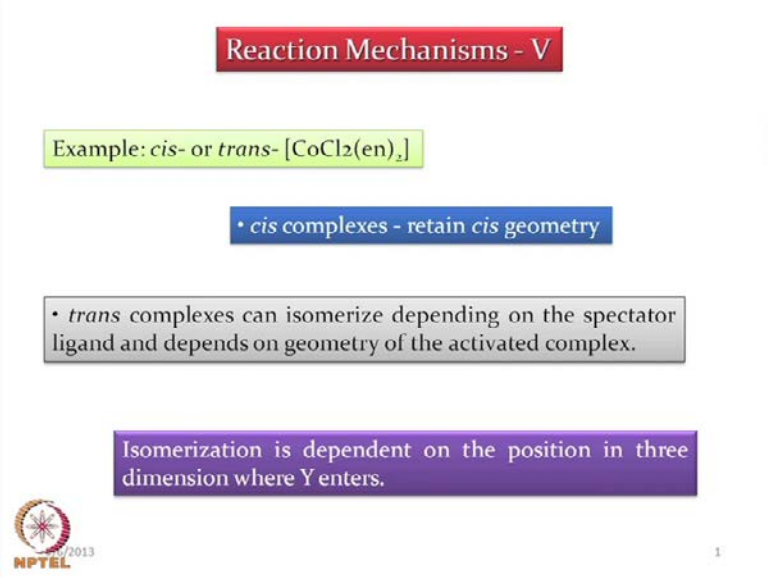
Lecture - 39
Reaction Mechanism – V

(Refer Slide Time: 00:26)



Good evening everybody. So, we will still continue with some of these aspects of reaction mechanisms in part V, where we will mainly discuss about the fate of the molecules when it goes for certain type of reactions particularly when we consider their electron transfer behavior when electrons are moving from one metal centre to the other.

(Refer Slide Time: 01:16)



Reaction Mechanisms - V

Example: *cis*- or *trans*- [$CoCl_2(en)_2$]

- *cis* complexes - retain *cis* geometry

- *trans* complexes can isomerize depending on the spectator ligand and depends on geometry of the activated complex.

Isomerization is dependent on the position in three dimension where Y enters.

NPTEL /2013

So, what will happen in that particular case along with the other one where we will find the different stereochemistry of these complexes can play some important role such as in case of this cis and trans compound of this chloride complex of cobalt where we have this two chlorine atoms to the cobalt centre. So out of the 6 positions, two of them are occupied by chlorine in cis geometry; when these two ethylenediamine groups bind to the cobalt in this particular fashion, and this one also gives us the corresponding trans geometry where the cobalt centre will show the corresponding binding of the chlorine atoms to the corresponding trans fashion; that means we have a corresponding angle of Cl-Co-Cl in the range of say sometime is 178 degree to 180 degree. Here these two ethylenediamine relating ligands remain in this particular fashion.

So, when these two molecules basically react with some substitution, and if we just consider that one of these Cl atom is replaced by some other incoming group; that means this can go for the removal; that means the Cl can go out and some new group, say X minus can enter and take the position of either this Cl or something is happening on the coordinates and sphere of this particular environment. So what basically goes for there, we can have two options from there; one is if this particular centre if it is a centre where we see that if we consider the corresponding charge neutralization by the ligands as well as the other chloride atoms, we find that this particular molecule is electro neutral. So, the oxidation number on the cobalt can be assigned as plus 2; so this plus 2. So, cobalt 2; that means two plus and it is corresponding radius will be greater than cobalt 3 plus radius. So, these are little bit higher; the atomic radius or the ionic radius or cobalt 2 plus will be higher than that of our cobalt 3 plus.

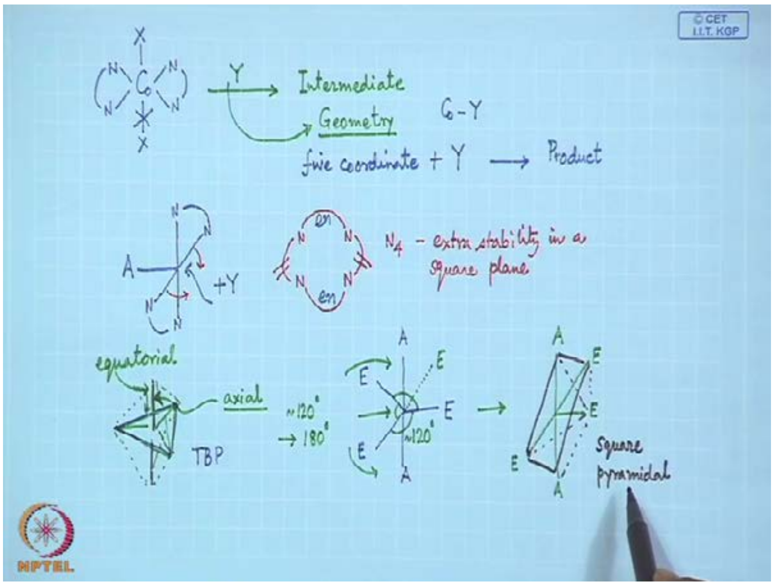
So, when we go for these we only expect that if the corresponding size of the atom which is present over there which can accommodate something; that means this Cl can go away and our incoming X is coming to attach to the cobalt centre. So, this is one particular situation where our coordination number can be increased to 7 where these two bonds are pretty weak; one is going to decay or going to break, another is going to form. So, this we can consider at the corresponding dotted line for this longer bond distances with that of our cobalt X and cobalt Cl and another situation which can have which is based on the corresponding coordination number less than what we have here because here the coordination number is 6 and here after removal of the Cl minus. So, minus Cl minus and this is plus X minus. So, we can have a situation where the coordination number is 5.

So, a penta-coordinated intermediate we can assume is forming at this particular point and how this penta-coordinated species can give rise to the product that will tell us whether we have the different type of geometry where from we are starting our journey from the cis complex. So, it is a 5 coordinated intermediate which basically can in the next step can react with this X minus to give the corresponding product and by analyzing the corresponding nature of this product, we consider that in case of cis geometry; that means when we start from the cis complex, the journey is going completely from the cis compound we get the retention of cis configuration; that means when we have this particular intermediate whether it can be a square pyramidal one or trigonal bipyramidal one, we find that the site where basically Cl has been removed is now simply occupied by the incoming X minus to give rise to the corresponding original configuration; that means the cis configuration attend is not going for any other configuration like that of our trans one.

So, these cis complexes therefore we can say that this basically responsible for retention of the corresponding cis geometry. So, this is one such example for these cis complexes of this cobalt which can retain its corresponding cis geometry; that means no other form is forming over there but what about the corresponding trans complex. In case of this trans complexes the situation is completely different, because in this particular case it can isomerize and how this isomerization can take place that will depend on the spectator ligand; that means the ligand which is present and depends on the geometry of the activated complex; that means the transition state.

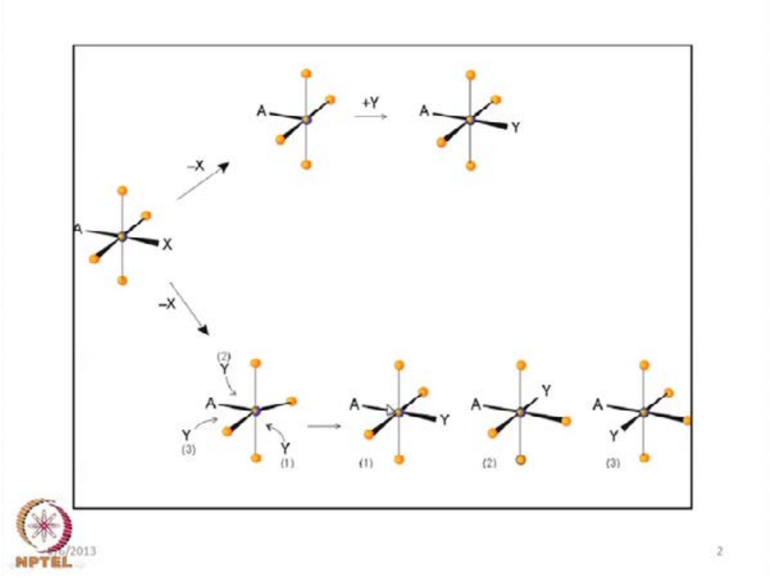
So, the ligands which are still present around the cobalt centre, those ligands we are considering as the spectator ligands and those spectator ligands when they consider for the corresponding geometry we can have again two different options; that means either it can be a squar pyramidal one or a tribunal bipyramidal one. So, in case of this trans complex what we find that isomerization will take place unlike the cis form. In this case, the isomerization will take place and is dependent on the position in three dimension where Y enters.

(Refer Slide Time: 09:37)



So, now we will consider this as X is removing; we are removing X from the centre. So for the trans one, we have the ethylenediamine and we considered this now as the presence of this two X groups. So, we will just see now this Y will enter by replacing this X groups. So the intermediate or the transition state what is forming, it has a particular geometry and that geometry is important; if it has more than one positions to attack where Y can attack this particular geometry and if it has more than one particular position, then depending upon this positions of attachment or position of attack to the cobalt centre by Y forming new cobalt Y bond where we just deleted one of the cobalt X bond; that means it is again a five coordinated one. It is a five coordinate intermediate and new cobalt Y bond will form depending upon the intermediate geometry and where from the Y will enter the corresponding geometry; that means in this particular step, we have the five coordinated one and is basically the corresponding addition of Y and Y is added to give rise to the corresponding product.

(Refer Slide Time: 11:38)



So, what will see from there? So, we have these situations. So, this particular one if we have both of them as A X or one as A, another as X. So, X will go and Y will enter. So, how this cobalt X bond is being cleaved that is important. So, when a trans geometry is present; that means these two ligands along this A cobalt X bond which is closed to 180 degree. So, X is removed. We get from an octahedral geometry, a corresponding square pyramidal geometry where A is forming the pyramidal side of the square plane forming by these four yellow orange spheres.

So, these yellow orange spheres in this particular case are chelated by one ethylenediamine molecule and here another ethylenediamine molecule and then if Y is again entering from that side where X has departed the molecule X has left the molecule from that particular side; that means this particular side where we do not have any kind of reorganization of this thing; that means this N-N cobalt bond, this is cobalt N and this is another cobalt n bond along with these cobalt A bond they are forming a T-shaped structure, but this T-shaped structures are not all the time very much stable until and unless we have a special stabilization for the square pyramidal geometry.

Otherwise, these two basically A and the nitrogen of this ethylenediamine at A and the other part of the nitrogen of the ethylenediamine, they ripple each other and they try to reorganise in a trigonal plane. But when it is not happening; that means this particular square plane; that means the cobalt N four plane. So when we have these, we basically see that this is the thing where we have these two nitrogen's forming one such chelation and this one is our A. So, this particular square plane has some extra stabilization; that is why these two bonds are not moving from this side to that side.

So, this particular plane if it is only a bis-bidentate chelation is not that we have something related to that of our porphyrin or chorin type of macrocyclic coordination where we know that all the four nitrogen's are attached and we have a macrocyclic environment. In that particular case the N 4 ligand has some extra stability in a plane. So, it has extra stability in a square plane. So, that thing is also happening where we do not have this connection and we have do not have this connection is only ethylenediamine units present. So, this is our en and this is also our second en. So the incoming Y, so plus Y; this incoming Y will attack from this side and we get the corresponding retention of the configuration even for the trans compound that we are getting for the cis compound.

So, this particular Y is coming from this side and attacking this particular cobalt centre giving the corresponding original compound where the geometry is same, only the position of X is now occupied by Y. But if the second thing is happening; that means some rearrangement is taking place between this particular plane A N N plane, A N N plane trigonal plane rearranges and rearranges means we should have sufficient flexibility for this bidentate chelation. This is N N bidentate chelation and this side also N N bidentate chelation. If we have little bit of flexibility for this rotation we just basically get trigonal bipyramidal geometry, where this A N N this is the trigonal plane and this is the first pyramidal side and this is the second pyramidal side in the down side.

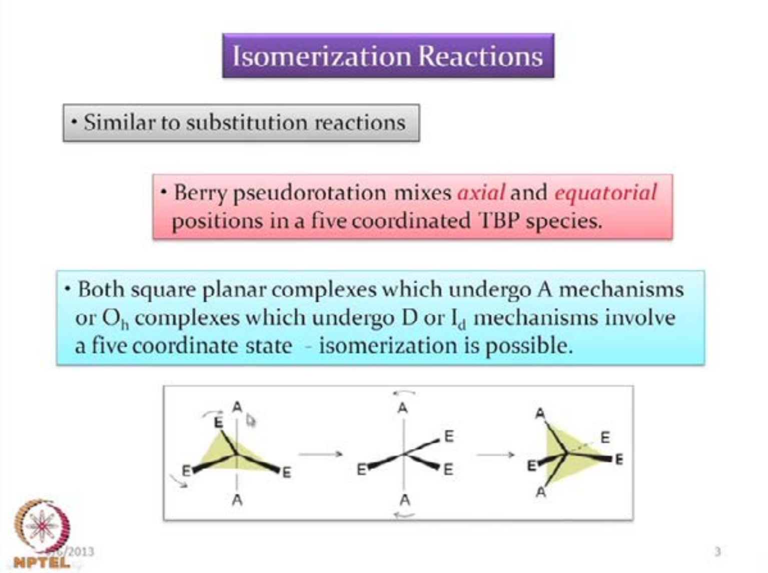
So, now clearly we find that if we consider that we are not touching anything related to the bipyramidal part; that means these two nitrogen's we are not touching but within the triganol plane; that means the triangle, this is the triangle. So, you have a triangular side. So, the triangle has three sides. So, it is side one; when Y is attacking side one, it is also giving the possibility the second possibility. In second possibility we have Y is attacking from side two. This is the side and this is the third possibility, where Y is attacking from this side.

So, when Y is attacking the cobalt centre to get back the original octahedral structure; that means attack of Y will take place from this side which is marked as side number one giving rise to the product which is the same product with the change in X by Y only which here we also get; that means the retention of configuration; that means the trans configuration of the complex. But if Y is attacking from side two; that means from this side and if it is attacking this side, this nitrogen is getting pushed to the trans position of A; that means towards the trans position of A. So, the nitrogen will come here and Y will take this particular position which was originally occupied by the nitrogen of the ethylenediamine.

So, we get one form where A and Y groups are in cis position; that means we have another form. We are getting starting from the trans configuration that A form which is a cis form. Similarly we can attack from side three; that means this side; that means between this A and nitrogen. So between this nitrogen, so nitrogen again will be pushed towards this side and Y will try to take the position cis to A. So like attack two, here also Y will occupy a position where A and Y will remain in cis position towards this particular cobalt centre. So, we get the corresponding cis configuration for this particular system.

So depending upon which particular side, depending upon the steric crowding and the size of this A and it is electronic nature of this A which is there; that means we are considering this as the corresponding spectator ligand. Depending upon this nature of A also, we get both the trans configuration as well as cis configuration if the attack of Y is equally probable from these three sides; that means side one, side two and side three will get the corresponding two isomers; that means the trans and cis isomers in one is to two ratios; that means one part of trans isomer and two parts of cis isomer we will get. That is the thing like other organic chemistry reactions we will find that one of the isomer will be forming in axis compared to the other if the all three path ways; that means all three attacking sides are equally probable.

(Refer Slide Time: 20:12)



Isomerization Reactions

- Similar to substitution reactions

- Berry pseudorotation mixes *axial* and *equatorial* positions in a five coordinated TBP species.

- Both square planar complexes which undergo A mechanisms or O_h complexes which undergo D or I_d mechanisms involve a five coordinate state - isomerization is possible.

So, that gives rise to the two forms where we can get the corresponding things and next we will see how the typical isomerization reactions can take place. So, one particular part; that means if it is forming from completely one isomeric form to the other isomeric form, so this isomerization reaction can give rise to similar to that of the substitution reactions. So, so far we were talking about a substitution of one particular group; that means a replacement of X by Y, X is removing from the system first, then Y is entering to the system. In a similar fashion the isomerization of the molecules can also take place where the substitutions of the reactions are also similar to the corresponding isomerization. So, one type of such thing can happen if we have a pseudorotation type of thing where Berry proposed this particular type of pseudorotation and Berry pseudorotation mixes the axial and equatorial positions of five coordinated trigonal biyramidal species.

So, if straightway we get is complex which is intermediate; that means which is giving rise to the corresponding transition state for our discussion where the geometry is trigonal bipyramid and in this geometry we know that we have a typical triangular plane and this triangular plane is responsible for giving three bonds and these bonds are we consider at axial bonds. So, depending upon the nature of the donor atoms present over there, it can be nitrogen or it can be chlorine for this type of compound what we are discussing in this class and the other one which is above the triangular plane which is on the other side that gives rise to the pyramidal structure of these. This is basically the corresponding one; this is axial and this particular one this is axial and this three are equatorial which is in the axis; that means which is in the perpendicular position which is axial and in the plane; that means the basal plane what we have they are the equatorial.

Similarly on the other side, we have another axial bond on the other side of the trigonal pyramid. So, Berry proposes some kind of pseudorotation of this; that means this particular geometry this trigonal bipyramidal geometry can rearrange and that gives rise to some situation where both square planar complexes which undergo associative mechanisms or octahedral complexes which undergo dissociative mechanism or intimate dissociative mechanisms involve a five coordinated state. If we get a five coordinate state; that means the five coordinate intermediate, then isomerization is possible from there. So, we have the octahedral complex gives rise to for a dissociative mechanism; that means one particulars group is leaving the octahedral complex giving rise to a five coordinate intermediate and that five coordinated intermediate can undergo some isomerization reaction. So, we have this.

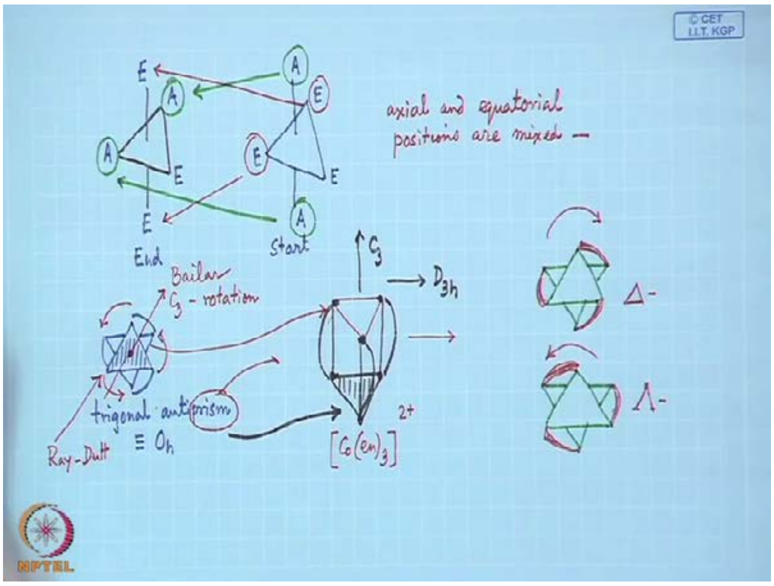
So, this A means the corresponding axial bonds and E means their corresponding equatorial bonds. So, this is basically the corresponding trigonal bipyramidal geometry and this trigonal bipyramidal geometry if we have and if these two E moves from this side to that side, we get basically a typical square pyramidal geometry where this A E and this A and this E make the square plane. So, basically what will be getting over there is something where we can consider these three arcs the corresponding bonds in the equatorial plane. These are the equatorial bonds. So, we level them; the donor atoms also are in the equatorial plane and we have the axial one. So, this is one axial one and this is the second axial one. So, now what is happening over there due to this pseudorotation, so rotation can take place where originally what we have this is closed to 120 degree, all three angles.

These three angles are closed to 120 degree because we have a triangle and if E is moving from this side and this E is moving; that means we try to increase this particular bond. So, due to that rotation what is happening? This bond which is at also 120 degree can go for 180 degree; that means this can go for straightway this position; that means E will go to this position. And as a result what we get from there is basically a structure like this where this is the A A, and this is the new positions of these two E. So, this E has moved and this is the other E. So, as a result what we are getting there is basically a square pyramidal one where this is the square plane and this is the pyramidal side where this one is forming. So, due to this rotation a TBP geometry which is this TBP geometry is giving rise to a square pyramidal one.

So, this particular one; so within this five coordinate species which is also true for typical five coordinated compounds, they can have the different geometry and they can also undergo some kind of racemization or isomerization reaction due to this movement. So once this group is forming, this can again further go for this kind of rotation along the same direction. So, what is happening in the next stage that once these two E groups have been moved, we get this one where we know the position of this E, this E, this E and this positions of A and A. Now these two A groups are moving instead of these two A groups because these two A groups have moved sufficiently and they reached to some equilibrium position. Now once they reached to this position these two A groups, this axial groups; so this particular one.

So, axial groups will start moving. So, pseudorotation basically mixes the positions for these bonds; that means, the axial bonds and the equatorial bonds are no longer distinguishable once we have some intermediate structure. So, if we consider that then if these are moving; that means this is basically this A cobalt A bond angle is 180 degree now and if these two are moving; that means this A cobalt A bond angle will try to reach from again 180 to 120 degree; that means these two will give us this two A along with this E which is in the pyramidal side because these two E's are in a line along 180 degree which is perpendicular to that this E, this A this E and this A will next form a new triangular plane. So, a triangular plane is forming with this A; the other A those two are moving and the E which was originally present in the pyramidal side. So, we have A A E as the new trigonal plane and E E will still remain in the 180 degree site will then therefore the corresponding pyramidal sides. So, this will be below the trigonal plane and this is above the pyramidal a triangular plane.

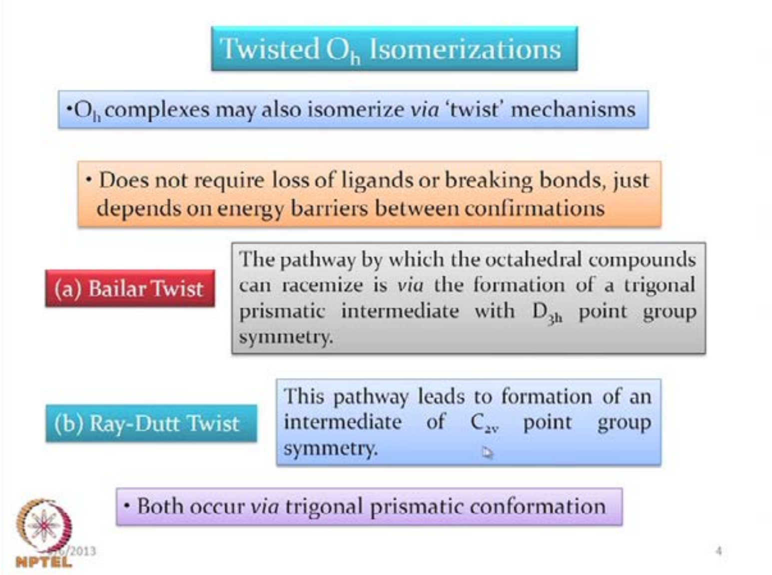
(Refer Slide Time: 30:25)



So, what is happening there; therefore, from there we get something some arrangement we will get where we will have a new triangular plane with two groups which are in the pyramidal site. So, these new groups will be presenting therefore as one as A one as A, another as E also and these E are the original E groups. So, basically what we find that we have moved from a situation where the starting molecule, say it can be the typical trigonal bipyramidal one or it after dissociation of one group to this particular situation from the octahedral geometry where we have all the equatorial groups are there and the axial groups are this side. So, we find therefore that Berry pseudorotation can give us some situation where these axial bonds that the axial groups for the molecule; this is the start, we have started from this molecule and this is the end product.

So these two groups, these two axial groups which were present in the axial direction of the molecule; so these axial groups will now go to the equatorial sides, these two A groups moving from here to here and is moving from here to here. So, axial groups have changed their positions to the new positions where they are occupying the equatorial positions. Similarly these E groups which were present in this particular case; that means they were in the equatorial plane that is one of the E group is still present in the equatorial positions, but two other. So, two other equatorial positions, say, this position and this position they are moving. So, this E is basically moving here and this A is moving here. So, these equatorial positions are now changed to the axial positions. So, these basically tell us that it is possible to mix the axial and equatorial position. So, we consider that axial and equatorial positions are mixed. So, this is basically the result of the Berry pseudorotation. So, this can be considered as one kind of pseudorotation where we get the change from this particular side to the other side.

(Refer Slide Time: 33:39)



Twisted O_h Isomerizations

- O_h complexes may also isomerize *via* 'twist' mechanisms

- Does not require loss of ligands or breaking bonds, just depends on energy barriers between confirmations

(a) Bailar Twist

The pathway by which the octahedral compounds can racemize is *via* the formation of a trigonal prismatic intermediate with D_{3h} point group symmetry.

(b) Ray-Dutt Twist

This pathway leads to formation of an intermediate of C_{2v} point group symmetry.

- Both occur *via* trigonal prismatic conformation

Now we will consider that how we get the corresponding octahedral isomerization where a different kind of twisting is taking place. So, what type of twisting we can have that we will see for this kind of isomerization reaction on octahedral molecules. So, where we see that the octahedral complexes can also possible to isomerize via 'twist' mechanism unlike the Berry pseudorotation what is forming for the five coordinated species. But in case of octahedral situation a different kind of twist mechanism is operating and that twisting can give rise to the isomerization in octahedral complexes. So, how it takes place that we see that it does not require loss of ligands which is very interesting that in previous cases we see that the octahedral complex is giving one ligand giving rise to a penta-coordinated situation and in that penta-coordinated situation, we get a corresponding geometry of either a square pyramidal one or a trigonal bipyramidal one.

But in this particular situation the bidentate ligand if they are present like acetyl acetone or ethylenediamine, they basically strictly attach to the metal centre, they are not giving rise to any kind of bond breaking process. But they basically go for some twisted formation. So, depends on the energy barrier between the confirmations. So, if we have one confirmation on the left and other confirmation on the right and if the energy barrier is not very high, we can move from one barrier crossing the barrier to one form to the other. So, it is Bailar who proposed this J C bailar the scientist J C Bailar proposed one kind of twist which is known as Bailar twist. It is a particular type of twisting mechanism for this situation where the pathway which can be taken away by the octahedral compound is that the racemization; that means 50 percent goes from the one form and the other 50 percent for the other form is via the formation of a trigonal prismatic intermediate because we know now that a typical octahedral geometry is nothing but a trigonal anti-prismatic geometry.

So, if that anti-prismatic geometry can move to a prismatic intermediate with D 3h symmetry; the symmetry of the point group after the distortion is D 3h, then we get something which is the result of the corresponding Bailar Twist. Then another form of twisting is also possible which is now known as this corresponding Ray-Dutt twist. It is due to the Ray-Dutt rays, ray is there and there is Dutt who they proposed this twist which is little bit different from this but on the same line, but the twisting process is different. In this pathway we get the corresponding formation of the intermediate which is of lower symmetry compared to the D 3h, it is of C 2v point group symmetry. So, what we basically get out of these that, we have these triangular phase this octahedral triangular phase we know and in a star structure in a start fashion if this is bidentate one, all three are bidentate one, we get this as a corresponding trigonal anti-prismatic structure.

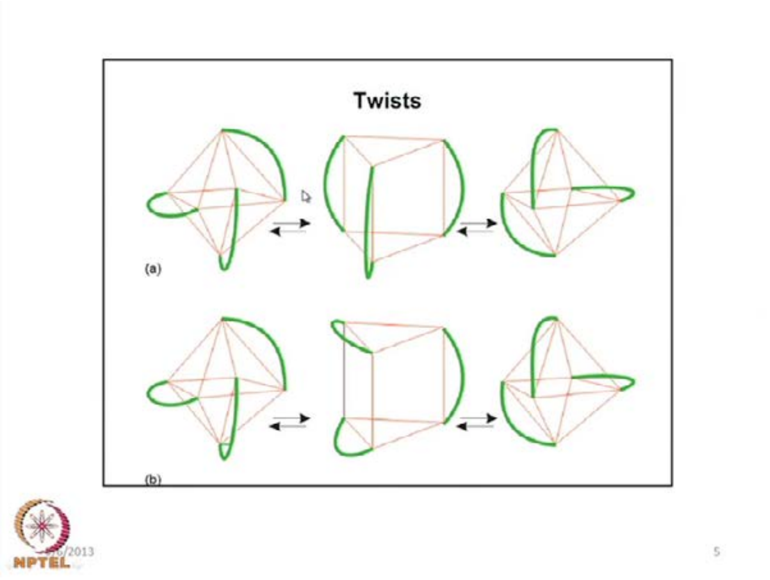
So, it is trigonal anti-prism because this is one particular triangular phase of the prism and the back is the other one which is equivalent to our corresponding octahedral geometry. So, when this movement is taking place we get this anti-prismatic one to a prismatic one; that means if we just move these two planes; that means if we just move this point, this point overlapping to this, this point overlapping to this and this point overlapping to this. So, along this particular axis this is our C 3 axis. So, along this C 3 axis, if the rotation is taking place; so that rotation will move basically one plane to over the other. So, what we will get? We will get this particular one the back one. So, this back one is still in this form but the front one this one this above one which is in the shaded proportion which is also moving in this direction. So, this is the shaded one of.

So, this is basically the corresponding prism structure and we have the corresponding C 3 axis which is also passing through it and since we have the perpendicular C 2 axis also and sigma h groups for also there. So, therefore the point group is D 3h. So, this triangular phase the movement of this particular triangular phase which is above the other one will give rise to the corresponding trigonal prismatic geometry. So, what we have there. So, how we get this structure which is important and how the binding is also changing; when we are moving this, basically this particular form we are moving. So, our chelation is also changing; that means where from this connectivity is going for this particular points. So, we get this particular point and how these chelations are there.

So, these chelations are nothing but since we have this particular D 3h symmetry. So one ligand will be here, second ligand will be here and the third ligand will be like this. So, this is the corresponding geometrical form for the tris-chelates. So, it can also form any compound like it can be cobalt, tris-ethylenediamine compound which can remain in this particular form for this distortion. So, what about this particular other twist that we will see for this other type of distortion and these two are therefore forming or going through the corresponding trigonal prismatic conformation. So, the trigonal prismatic conformation is there in both these two cases.

But if we look at these things we can think of why they both have the trigonal prismatic conformation, but in one case the point group symmetry is D 3h, but in the other case the point group symmetry is C 2v. This is due to the connectivity of these vertices which are for this particular trigonal prismatic arrangement. So, the vertices are connected differently when they are symmetrically connected along the c 3 axis, the point group what we are getting what we have shown just now is D 3h. But in other case the twisting is little bit different and we are leading to a lower symmetry point group and the point group is therefore there is C 2v.

(Refer Slide Time: 42:10)



Twists

So, how these two are coming let us see. So, in this particular case when we get this, so this is the thing; this is the octahedral geometry and these are the bidentate chelation. If it is around cobalt, cobalt is sitting over here. So, with that particular cobalt centre this is the bidentate chelation one, another bidentate chelation and this is the third bidentate chelation and when along the C 3 axis, the movement is taking place. So, we get the trigonal prismatic arrangement and this prismatic arrangement along these three edges which are parallel to the C 3 axis.

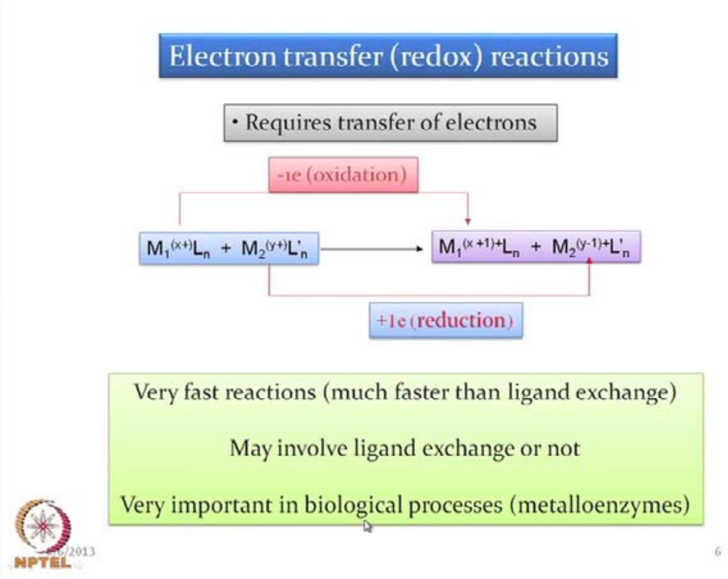
So, this is the C 3 axis which is passing through this triangular plane and this triangular plane also connecting towards this and this is going up and the other side is going down for the C 3 axis and symmetrically these three bidentate ligands are covering the C 3 axis and we basically get that the corresponding geometry where we go for the other one. So, it is racemization is taking place for the movement from this particular form to the other form. But in case of the other type of twist the rise of the twist we get this particular conformation; that means we take this other axis; that means we take this one particular plane as this triangle and this is also the other triangle binding in this fashion, but these two binding are in this other form. So, this is not for this particular axis because for this case we have four C 3 axis and along one C 3 axis we have shown the distortion if the movement is taking place for the other C 3 axis which were there.

So, for the other C 3 axis which is taking place; that means this particular plane where we have this triangular plane where these two positions of these triangular plane are connected by this one ethylenediamine molecule and another triangular plane which is there for the connecting of these two groups are by this bidentate ligand, then only we can give rise to the corresponding symmetry of this is different compared to the previous one. And there also if the movement is continuous one; that means from the trigonal prismatic arrangement to anti-prismatic arrangements; that means this is moving further and that movement if it goes we get the other form. So, in these two cases what we get; these two forms what we are able to get is that in one case how these racemization we can assess that due to this movement what we find for these molecules, the two structural arrangements are possible.

So, this is weaving through one particular axis for this only say because the other one is from the other axis this is not perpendicular to this plane, because we can have the other C 3 axis are there and along these other C 3 axis we get the other twist. So, when it is showing from these, this is the Bailar twist and from the other which is the corresponding Ray-Dutt twist by taking the other C 3 axis which is also equally probable for the twisting. So, when we get this connectivity; that means the bidentate chelation is from this site and from this also and from this also. So, this is basically giving; that means if we move from top phase to the down, this is in clockwise direction. So, the isomer is the delta isomer but if we go for this one; that means if it is in the other direction from top to bottom; this is from top to bottom, this is the top face. So, it is on the other direction that is in the anti-clockwise direction which is therefore the lambda isomer.

So due to all these things, we are basically ending up with getting these two isomers nicely. So, this twisting basically giving rise to the corresponding two isomers; one is the delta isomer, another is the lambda isomer and racemization thus take place due to simple twisting. Because in no point we basically go for the cleavage of this bidentate chelation; bidentate chelation remain intact for all these six positions but some internal distortion; that means this particular connectivity is not very much facile for this distortion, they remain it and they result in basically for the other form which is the corresponding racemized form. So, that basically gives us for the corresponding racemization in the octahedral complexes.

(Refer Slide Time: 47:30)



Electron transfer (redox) reactions

- Requires transfer of electrons

-1e (oxidation)

$M_1^{(x+)}L_n + M_2^{(y+)}L'_n \rightarrow M_1^{(x+1)+}L_n + M_2^{(y-1)+}L'_n$

+1e (reduction)

Very fast reactions (much faster than ligand exchange)

May involve ligand exchange or not

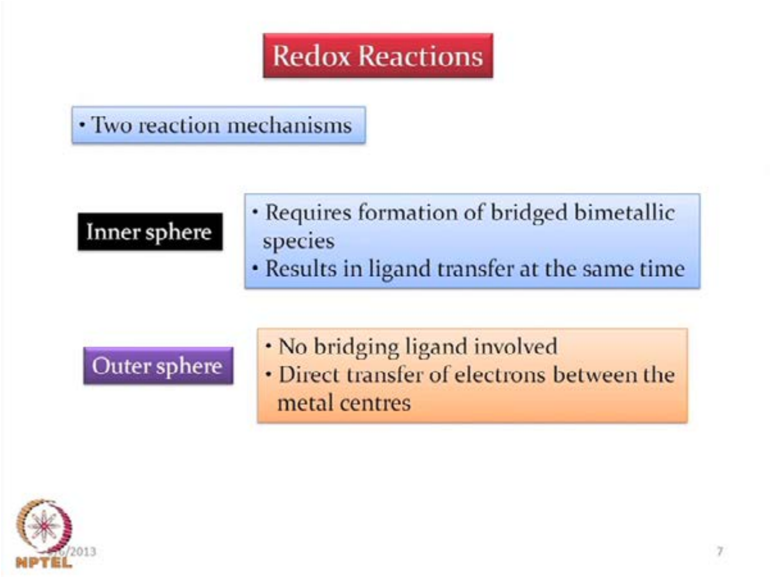
Very important in biological processes (metalloenzymes)

And then we just see that what type of reactions we can follow for the different electron transfers. So, the electron transfer reactions what we know that they are basically responsible for the different types of redox reactions and these redox reactions are basically responsible for electron transfer from one species to the other and this particular is also responsible for the transfer from one side to the other. So, they all require the transfer of electrons and when we see that this transfer of electrons can take place through the involvement of some species where this particular metal centre we considered as M 1 and the other one we are considering as M 2. So, when they are reacting they can be different also; that means one particular centre can be a cobalt centre and the other centre can be a chromium centre.

So, if we see that this has an oxidation number of X plus and this has an oxidation number of Y plus. So, what is happening therefore, the electron is moving from one to the other; that means in this particular case if we have the pair; that means if it is cobalt in the plus three oxidation state, then this is a one more higher oxidation state. So, it is at plus two oxidation state for. So, one electron oxidation will take place on this particular state. So, this is therefore a centre where it can consider as a chromium centre which is going for one electron oxidation to a chromium three centre. In a similar fashion if this is the centre where it is in the Y; that means if it is in the plus three state it will be reduced to plus two state; that means it is Y plus and it will be Y minus 1 plus; that means it will follow some of one electron reduction.

So, in this particular case what type of oxidation reduction can take place through this electron transfer is very important not only for these different types of metal complexes but also for biological system. Because it is a very central process for many systems where we have the metal-biocides are responsible for this sort of electron transfer processes. So, we see here that how we get some of these electron transfer reactions apart from the transfer we get for the different types of ligand exchange; ligand is moving from one metal centre to the other. But in this particular case very first reaction which are much faster than ligand exchange can take place. In that particular case it may involve some ligand exchange but sometime not and very important in biological processes which I just told you that it is also important for metalloenzymes, different cytochromes, the blue copper proteins and all were very fast electron transfer reactions can take place from one protein side to the other.

(Refer Slide Time: 50:47)



Redox Reactions

- Two reaction mechanisms

Inner sphere

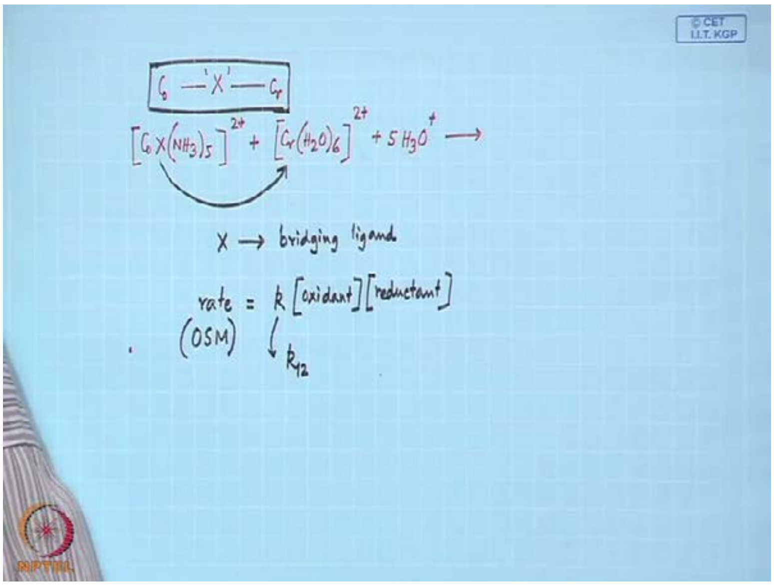
- Requires formation of bridged bimetallic species
- Results in ligand transfer at the same time

Outer sphere

- No bridging ligand involved
- Direct transfer of electrons between the metal centres

So, what we see here that for a particular type of redox reaction, we can have two reaction mechanisms; one is the inner sphere mechanism where we get a particular type of reaction requires formation of bridged bimetallic species and which results in ligand transfer at the same time; that means if we can have a ligand such as that of the corresponding X which can consider it as a X is there.

(Refer Slide Time: 51:19)



$\boxed{Co - 'X' - Cr}$

$[Co\,X(NH_3)_5]^{2+} + [Cr(H_2O)_6]^{2+} + 5\,H_3O^+ \longrightarrow$

X → bridging ligand

rate = k [oxidant] [reductant]

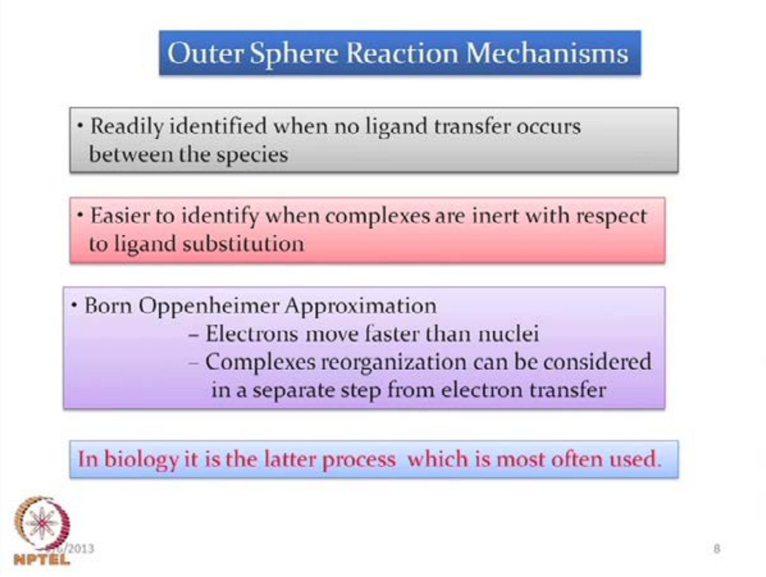
(OSM)

k_{12}

So, X is the unique ligand and that unique ligand can bridge two metal centres; one is the corresponding case, it can be a cobalt centre or it can be a chromium centre. So, if we get the species like that, if we have a cobalt X pentamine compound X pentamine whole 5 two plus which is reacting with chromium H 2O whole 6 two plus with the presence of 5 water molecules in protonated form that gives rise to the corresponding transfer of these X from here to here. So, how this is happening? So, this must go through an intermediate where X is the typical bridging ligand. So, we must have this X; that means X should be our bridging ligand.

So, in that particular case the ligand transfer is also taking place from one side to the other; that means it can move from the cobalt side to the chromium side and another one; that means another type of mechanism what can take place over there is the outer sphere type of mechanism where this sort of bridging is not required and there is direct transfer of electrons between the metal centers. So, metal centers are involved and there will be a direct transfer of electron, and through a outer sphere mechanism though inner sphere mechanism is not required and inner sphere mechanism the bridging is important.

(Refer Slide Time: 53:24)



Outer Sphere Reaction Mechanisms

- Readily identified when no ligand transfer occurs between the species

- Easier to identify when complexes are inert with respect to ligand substitution

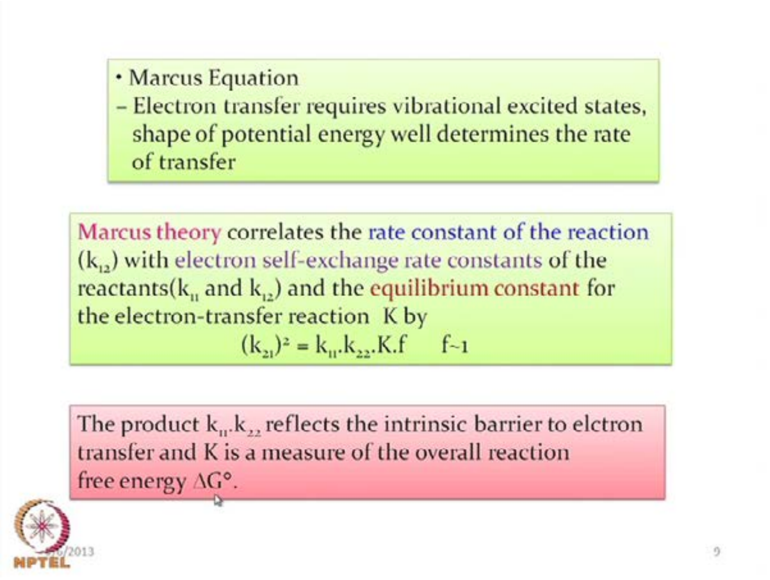
- Born Oppenheimer Approximation
  - Electrons move faster than nuclei
  - Complexes reorganization can be considered in a separate step from electron transfer

In biology it is the latter process which is most often used.

So, we find that in outer sphere reaction mechanism when this is outer sphere reaction mechanism is taking place that electron exchange can take place between two separate and full coordination spheres is readily identified when no ligand transfer occurs between these species. So, the bridging ligand is not involved for the transfer and it is easier to identify when complexes are inert with respect to ligand substitution; that means we are not allowing any kind of ligand substitution, but in case of inner sphere mechanism we see that bridging is taking place; that means at the same time we have the corresponding ligand substitution reaction. But in case of outer sphere mechanism therefore, we do not have any kind of such ligand substitution reaction.

So, in this particular case the Born Oppenheimer Approximation is applicable because the electrons are moving at a faster rate than the nuclei. So, nuclei cannot react adjust themselves nicely. By that time electron will take place in a very fast way and rate of thus outer sphere reaction mechanism can take place is dependent on the product of the oxidant as well as the reductant and the corresponding k value and the complexes reorganization can be considered as a separate step from the electron transfer. So, reorganization step is different one. It also takes some time to reorganize or that is why it is also dependent on the corresponding rate of the reaction. And in biology it is this form; that means the outer sphere reaction mechanism is therefore useful which is most often used for this type of electron transfer reaction.

(Refer Slide Time: 55:16)



- Marcus Equation
  - Electron transfer requires vibrational excited states, shape of potential energy well determines the rate of transfer

Marcus theory correlates the rate constant of the reaction (k_{12}) with electron self-exchange rate constants of the reactants(k_{11} and k_{12}) and the equilibrium constant for the electron-transfer reaction K by

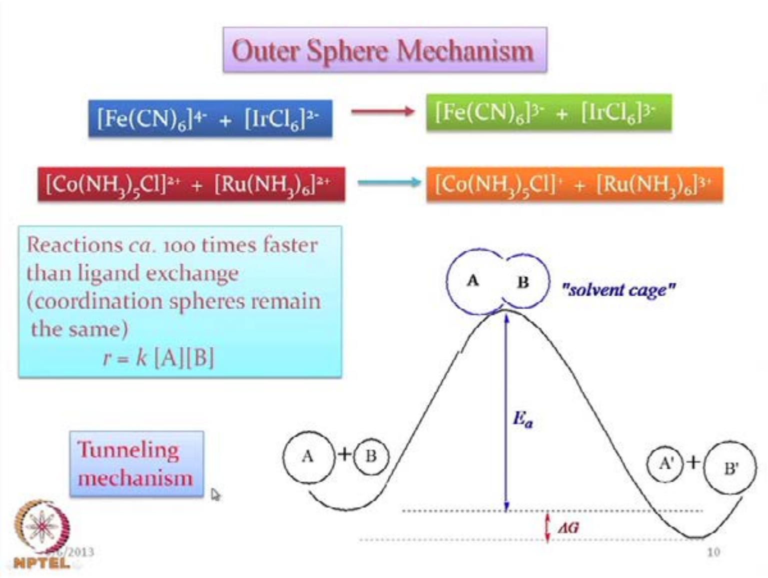
$$(k_{21})^2 = k_{11}.k_{22}.K.f \qquad f\sim 1$$

The product $k_{11}.k_{22}$ reflects the intrinsic barrier to elctron transfer and K is a measure of the overall reaction free energy $\Delta G°$.

So, what we see there is that Marcus equation is also applicable in this kind of transfer and electron transfer requires vibrational excited states and the shape of the potential energy will determine the rate of the electron transfer. So, Marcus equation it proposes one particular reaction rate which can tell us that what type of electron transfer can take place and different thermodynamic and kinetic parameters can be derived by using this particular equation and the theory which basically predicts and correlates the rate constant of the reaction. So, whenever we have a rate we basically find that rate for this outer sphere mechanism which is can be considered as OSM; the rate for the outer sphere mechanism is dependent on the concentration of the oxidant into the concentration of the reductant.

And this particular rate constant for the reaction this can be considered as k 12 for species one and species two and this particular rate we find that k 12 is the electron self-exchange rate constant of the reactants k 11 and k 12 and the equilibrium constant for the electron transfer reaction k. So, there is some equilibrium constant for the electron transfer k. So, this k multiplied by k 11 and k 12 will give raise to k 21 which is the self-exchange rate constant. So, self-exchange rate constant can be determined by knowing this particular equation. So the product of these two, this k 11 and k 22 reflects the intrinsic barrier to electron transfer and k is a measure of the overall reaction free energy; that means delta G 0.

(Refer Slide Time: 57:30)



Outer Sphere Mechanism

$[Fe(CN)_6]^{4-} + [IrCl_6]^{2-} \rightarrow [Fe(CN)_6]^{3-} + [IrCl_6]^{3-}$

$[Co(NH_3)_5Cl]^{2+} + [Ru(NH_3)_6]^{2+} \rightarrow [Co(NH_3)_5Cl]^{+} + [Ru(NH_3)_6]^{3+}$

Reactions *ca.* 100 times faster than ligand exchange (coordination spheres remain the same)

$r = k[A][B]$

Tunneling mechanism

So, this basically tells us some idea that how these things can be useful for the outer sphere mechanism. If we just see that these two species are involved for that particular outer sphere reaction, we find that this can go for the corresponding electron transfer; one is getting oxidized and other is getting reduced for this transfer. Similarly, the cobalt centre as well as the ruthenium centre can have and this can go for the corresponding transfer of electron between these two. And in all these cases the coordination environment is not changing; coordination environments are remaining intact and we can have a corresponding solvent cage for these two.

So, these two are basically trapped inside the solvent cage and within that particular solvent cage, the electron transfer is taking place and from this we can basically get the corresponding delta G 0 value depending upon the corresponding energy state for the reactant as well as the corresponding products. So, in this particular case the reactions which are about 100 times faster than ligand exchange rate reaction, the coordination sphere remains the same and what we just now told you that the rate; that means this r value is dependent on the k and the concentration of A and B. So, these basically tell us that in this particular case there is something which can be considered as a tunneling mechanism. So, outer sphere mechanism which is also true for biological electron transfer, a tunneling type of mechanism is operating for that biological electron transfer also. Thank you; thank you very much.