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

Lecture - 29
Tungsten Enzymes – I

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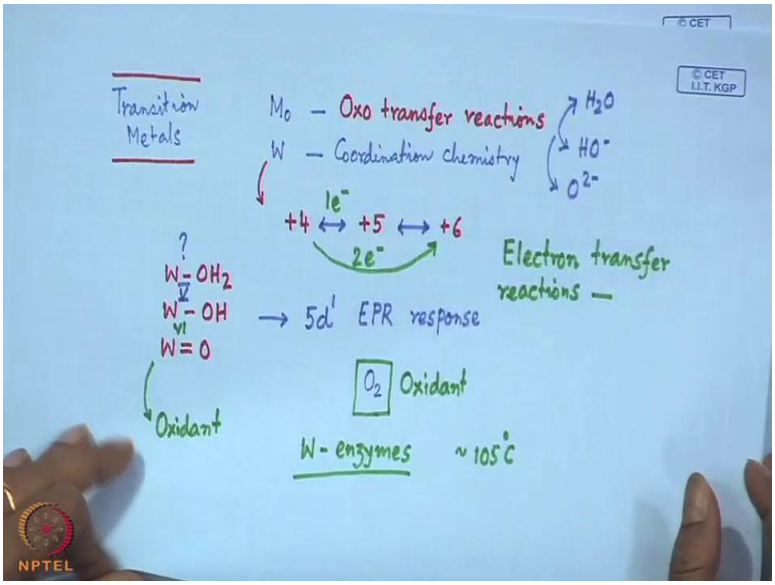

Good morning. So, we will just now we will just continue from the series what we are seeing the transition metals. So, these are we have seen their role in biology the molybdenum then we have seen how both molybdenum and tungsten do participate in biology, and little bit we have discussed about molybdenum, and also tungsten we will discuss about their coordination chemistry. So, how does this part of the inorganic chemistry can help us to understand the very complex biological reactions, because in case of the other congener of the group; that means the molybdenum we have seen it is mostly dominated by the oxo transfer reaction, where the coordination chemistry is also mostly dominated by the formation of the oxo molybdenum complexes.

So, this part of the reactions in (( )), so these second group and second row, and third row metal ions the molybdenum and tungsten when do participate, but they are not much abounded in the biological system. Only few examples are there where the tungsten center can play some important role in all these systems and where these like molybdenum can move from an oxidation state of plus four to plus five to plus six. That means, when we consider these we can immediately think of that there is some electron

transfer between these two oxidation state and also these two oxidation states. So, what we see that along with this oxo transfer reactions which are mostly dominated by the reactivities with water hydroxide iron as well as with oxoanion.

So, these groups basically following simply de protonation, they can give rise to the hydroxido group or the oxido group which can immediately go and bind to that of your tungsten center to give us a tungsten echo bound initially, which can further go for deportation de protonation to give us tungsten hydroxido bound or tungsten oxo bound. And during all these transformations, sometime we do not have any control over the oxidation state on the metal iron; whether the tungsten is in plus four oxidation state or Plus five or plus six is very difficult to predict. So, we always like that of our molybdenum part, we have seen that we rely on some of the useful spectroscopic techniques, such that if this particular one is in plus five oxidation state and if we have one unpaired electron on that, so if that is in the 5 d one level, we do expect to have some EPR responses.

So, EPR response will immediately tell us even in the solution in a very dilute condition where the concentration of this tungsten center is very less, because it is surrounded by huge protein molecule, but this center which is having one unpaired electron in five d level can show some response for its characteristic EPR signal. So, leaving this inter conversation when you move from aqua complex to an oxo complex, we basically go from a plus four to plus five to plus six oxidation state. So, along with oxo transfer reactions what we except that there is also some electron transfer reactions can also take place with that of the tungsten centre. So, during that electron transfer we can have a single electron transfer or we can straight away a case where we can go for two electron transfers.

So, you can have the catalytic processes which can be a either a single electron transfer case or a double electron transfer case. So, very simple or very use full electron transfer reactions we can have which we can get simple for this oxidation by air; that means, the di oxygen present in air can go for some of these transformations, but in the biological system we required; that means, activating this di oxygen molecule is not so easy in the biological system.

So, we take the help of the water molecule attach to the tungsten centre for these electron transfer reactions; otherwise, in normal laboratory environment we except that some of these transformations are simply catalyzing by the presence of di oxygen molecule. So, here that case the di oxygen is the most useful oxidizing agent or oxidant what can be active on the substrate molecule. But in these cases, if this tungsten centre is in plus six oxidation state; that means, the hexa valiant tungsten centre which is attach to some oxo centre is now the oxidant for all these biological transformations instead of the simple di oxygen molecule which is available in the air.

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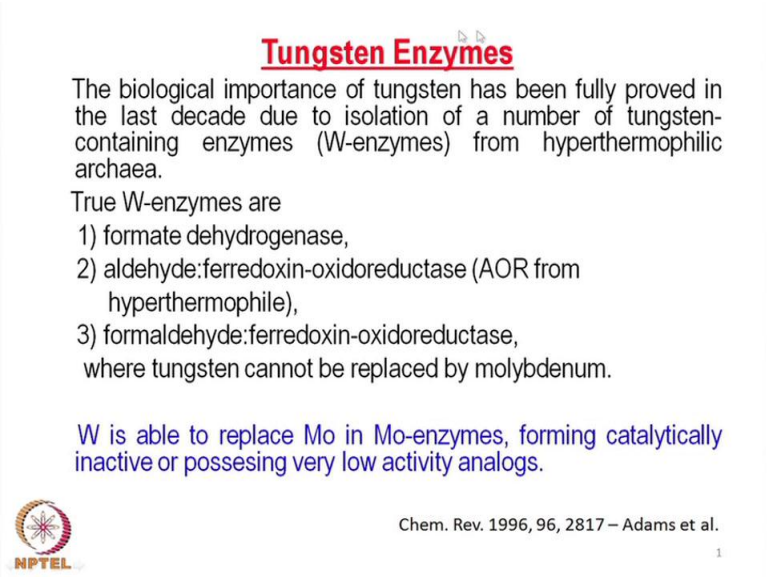

So, in all these tungsten enzymes slowly one after another will discuss little bit on that, because we have discussed already the molybdenum enzymes in detail. So, is a very recent phenomenon. So, only during the last decade or last fifteen years people could isolate a number of tungsten containing enzymes; this we call it as tungsten enzymes in hyperthermophilic archaea.

So, hyperthermophilic archaea is that are stable towards temperature. So, all these tungsten enzymes are thermally very much stable. So, they do not degrade in the range of say hundred and five degree centigrade. They do not degrade otherwise, we know that the biological systems what we can have in our body which is only living tell we have the corresponding temperature range of our body temperature which is thirty seven degree centigrade, but in case of these tungsten enzymes they are very much stable till

the temperature is reaching hundred degree centigrade. So, these particular groups they are known as the hyperthermophilic archaea and these enzymes the first one is of this category is the formate dehydrogenase.

When the substrate is the formate amine and which is important in the redox transfer reactions. So, formate is sometime getting oxidize to carbon di oxide molecule what we have seen in case of molybdenum centers also; that means, the molybdenum enzymes. Then another group molecules which are very important; that means, we are talking something which is nothing but the oxido reductase family; that means, the reversible oxidation and reduction reaction can take place which is mediated by the ferredoxin molecule, and which is acting on the substrate aldehyde. So, it is a little bit complex arrangement where we have the redox enzymes. So, what we have in our hand is our redox enzyme.

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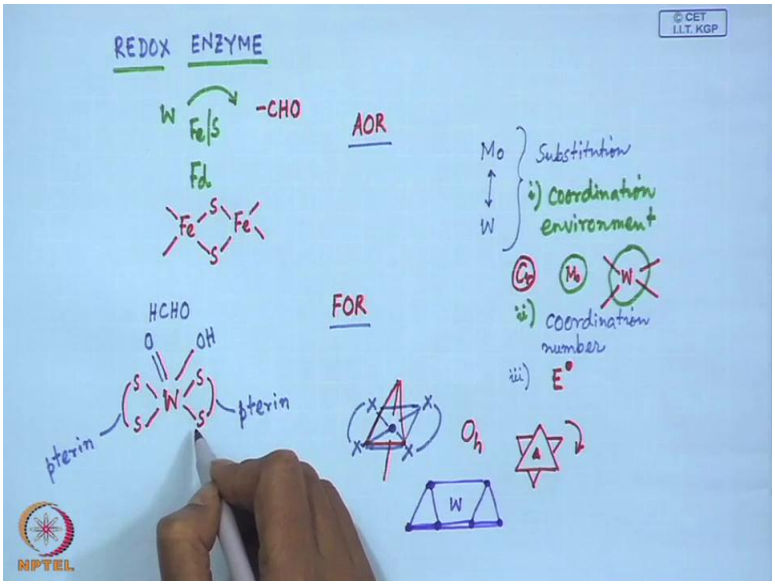

So, as soon as we have some redox enzyme in our hand; obviously, we can think of that there should be some electron transfer from that enzyme part, but in case of these we have that enzymes which is tungsten centered and this tungsten centered functioning as a redox enzyme which is then under the category of oxido reductase family, but which is coupled with some iron sulfur protein molecule which we consider as the ferredoxin molecule; that means, atleast we should have two iron centers connected to two sulfur

groups. So, the basic unit what we can have which is not a redoxing unit, but is a ferredoxin unit.

So, atleast a dymaric unit if not a tetramerric one which is a dymer of dymer thing. So, this ferredoxin molecule is basically can give rise to the electron to the system. So, the electron transfer is mediated through the ferredoxin molecule and we have the aldehyde as our substrate. So, it is working on the aldehyde substrate mediated by the iron sulfur mediator and tungsten is the corresponding catalytic site, and another group is that of your formaldehyde ferredoxin oxido reductase. So, in one group, it is acting on aldehyde; that means, any other aldehyde not that of the formaldehyde. So, it is aldehyde oxido reductase; again from it is thermophilic bacteria archaea. So, this again belongs to the hyperthermophilie.

So, aldehyde oxido reductase is belongs to AOR family, but the other group which is very much specific on formaldehyde; that is why it is very much specific for the substrate which is formaldehyde not any other aldehyde like acetaldehyde or any other group. So, this formaldehyde when acting on this particular tungsten enzyme which is belongs to the class of again oxido reductase and again ferredoxinmidated. So, we have aldehyde oxido reductase which is the AOR family and when we have the formaldehyde oxido reductase, we get FOR family. So, FOR family is little bit different when we have the substrate as formaldehyde.

So, this FOR family and AOR family, reactivity wise or the source wise sometime initial isolation was difficult and once people have isolated that then they went for the corresponding identification of the centre has the tungsten one. So, in case of FOR family, we cannot replace this particular tungsten centers. So, tungsten is very much needed for their reactivity, because the reactivity wise these group of the tungsten enzymes are very much similar to that of our molybdenum enzymes. So, if we can isolate some of these native enzymes from different biological part, we can take and those biological sources can be checked whether we can substitute one particular metal centre by the other.

If we the tungsten enzyme can be replaced by the molybdenum enzymes, because we want check whether the tungsten is mediate for their absolute reactivity for the corresponding transformational molybdenum can have a different catalytic role or

molybdenum can be more reactive. But in this particular one where we truly speaking that they are the true tungsten enzymes and this tungsten cannot be replaced by molybdenum; that means, tungsten metal iron is very tightly bound to that particular center and once tungsten is replaced by molybdenum, the reactivity for that particular centre is also lost.

But in some other cases, we can replace this molybdenum centre in different molybdenum enzymes. So, these are the bigger metal iron compare to the molybdenum one; this is a four D element; this is the five D element. So, five D element can go and remove the molybdenum and take that particular position, but during that transfer we get a catalytically inactive species which is not active at all, and which is not reacting on the substrate if the substrate is our formaldehyde or acetaldehyde, but some other cases if we shows little bit of that reactivity, it shows very low activity analogs.

So, the substitution of these; that means, whether we can substitute a molybdenum centre by a tungsten centre and we just basically check what is the effort for that substitution? So, metal iron substitution is a well known practice for this bioorganic aspects of the different enzymes, because sometimes if we want to know the immediate coordination environment and that particular environment do change, because we are changing one particular size of the metal iron from molybdenum to a bigger one which is tungsten. So, definitely, not only the coordination environment, but also the corresponding coordination number might change.

So, in that particular case the reactivity pattern is also changing if we go for substitution of one metal centre by the other. So, coordination number is also changing. And another important thing which we always should be careful in knowing that thing whenever we go for changing this thing is the corresponding redox electron transfer; that means, the E 0 values what we measure for one particular centre based on molybdenum to that of our tungsten. So, if that centre is on molybdenum and this centre is on tungsten, that E 0 values are also different which is well known to us that if we go down to a group; this particular centre is weakly oxidizing compared to the other congeners in four D and three D series, because in the three d series we have the chromium on the left.

So, whenever we have the chromium which when we stabilize as in terms of the corresponding oxo group; that means, the chromate and dichromate amine which is

highly oxidizing compare to the corresponding molybdenum oxo unit then which is again less oxidizing compare to that of that tungsten centre. So, you should compare always the E 0 values what we get, because all these reactions are dependent on the corresponding E 0 values and the corresponding thermodynamic stability of the corresponding substrate, and the substrate which is giving the corresponding product. So, this low activity analog will basically get when we just simply change the corresponding centre from that of tungsten to molybdenum or molybdenum to tungsten.

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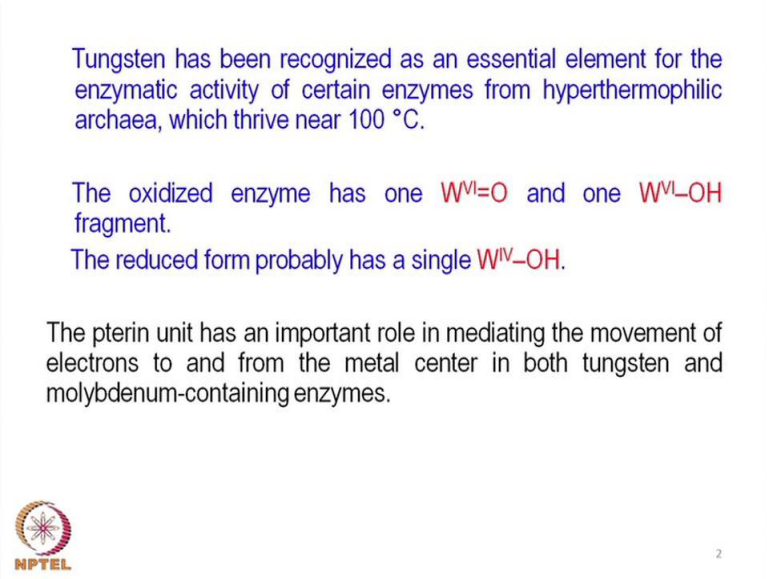

So, it is an essential element in all these enzymatic activity and again we talk that the hyperthermophilic archaea which thrive near hundred degree centigrade; which basically stable and so an activity till will reach a temperature range of hundred degree centigrade. And what I just now told you that the oxidized enzymes has at least one tungsten oxo unit having the tungsten centre in hexa valiant state and one of than is that tungsten in the same oxidation state, but attach to your hydroxide unit.

So, if we have a corresponding tungsten centre and if these two groups are attached to that corresponding tungsten pterin unit which are the sulfur groups. So, these are the sulfur groups. So, four coordination sides are already attached and the size of these tungsten unit is little bit bigger. So, we have like that we are just covering a particular bigger ball or bigger sphere compare to the smaller one. So, four coordination positions are already taken up and two these positions are still vacant for the corresponding

reactivity to the substrate or the other reagent what is coming out as oxo and hydroxide unit.

So, if we see that this is one of them is oxo, the next one can be the corresponding hydroxide unit. So, hexa coordination can be fulfilled around the tungsten centre and depending upon that it basically settle between this water hydroxide and oxide unit to show the reactivity. And the pterin unit which is our source for the bidented S S donor units which is involved from the pterin unit, and which has important role in movement of electrons to and from the metal centre in both the two cases; that means, in case of tungsten as well as in case of molybdenum; this basically the petrin unit; that means, the ligand part. So, these are our pterin unit, it is for tungsten we call it as the tungstopterin unit; if it is from molybdenum, we call it as a molybdpterin unit. So, this pterin unit from both the two sides can hold basically the tungsten site for its catalytic reactivity.

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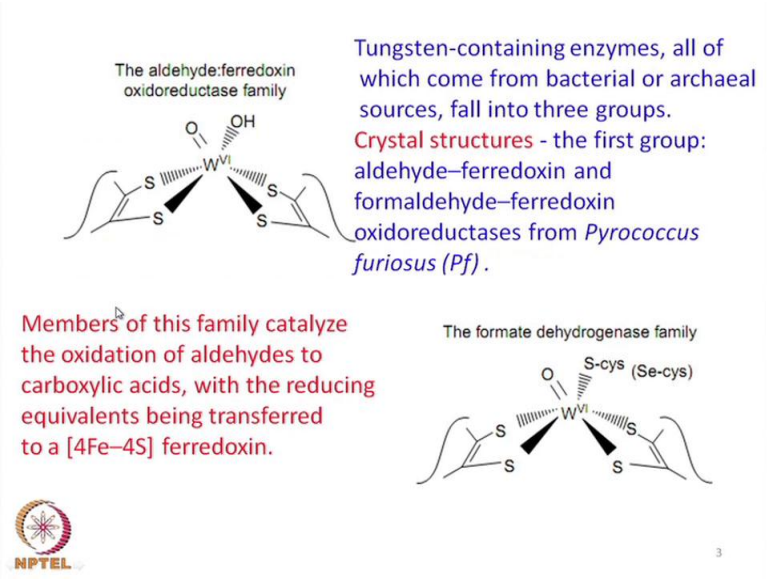

So, these are the two cases. So, in the first case which is the corresponding AOR family the aldehyde ferredoxin oxido reductase family, we have this particular aldehyde ferredoxin oxido reductase family. So, you have this particular S S stable unit in di thyol units. So, this two sulfur groups are the thyol sulfur unit S minus, S minus and the backbone is little bit stabilized in the form of a double bound between these two carbon center. So, is basically a tip little bit of planner unit. So, this entire part what is there is the two plus two four plus five; this five member ring is basically a planner unit with less

distortion related to that of our carbon carbon backbone which is a double bounded one. Similarly, another group is also present on the right which is also from the same pterins unit the pterin bidented sulfur sulfur ligand.

So, bidented S S donor ligand are basically covering something, because this basically giving some important coordination geometry which we are not getting unlike our first transition series elements. Because whenever we find in case of iron, nickel, cobalt etcetera all if the metal center is present over there and if we have one donor group from here; another donor group from here; another donor group here and another donor group here.

So, for the three D elements and which is not biologically connected. So, these are non biological donor groups. So, non biological donor groups they basically prefer for again if this particular individual unit; that means, if this particular ring whatever ring it is, it can be five membered or it can be six membered ring, but if this part is a planner one and depending upon the nature of the metal center, we can have the square planner environment or if this particular five membered ring or six membered ring is perpendicular to the other ring, we get a tetrahedral geometry, but basically it is settling between either a tetrahedral geometry or a square planner geometry.

So, when two of these ligands are attached, we go for the attachment of the fifth and sixth groups, but in this particular case the attachment of the fifth and sixth which is also true for the iron centre which is present in our hemoglobin and the myoglobin molecule. So, with one of these group will come from above the square plane and another from below the square plane making a corresponding octahedral geometry. So, this octahedral geometry what we sometimes draw in the form of the corresponding trigonal plane, because this is one of such trigonal plane and below we have another. So, being along the c three axis which is the threefold axis c three axis, we get some arrangement where we have one trigonal plane.

So, if we can move these two trigonal planes, these are the staggered orientation in typical octahedral geometry; these two planes are in staggered orientation, but this particular one can move from here to here and we get a corresponding eclipse orientation. Between these eclipse orientations, we can have a corresponding geometry which is a prison geometry. So, we can have a corresponding hexagonal arrangement

where the metal centre; that means, tungsten is sitting over there and six coordination sites are available for binding.

So, we can have any kind of distortion particular when we have the bigger metal iron present we can have huge distortion, because we do not have any control or ligand to ligand or donor atom interaction between these which is very much true for smaller metal iron like nickel, iron or cobalt where you can have the corresponding interaction between these things and we do not get a huge distortion and the coordination site. But in this particular case, we have the six coordination sites; this two are fixed bidented fragments are fixed, but these two are mono dented one. So, we can have a corresponding geometry where you find that these dotted coordination sites; this is one of these threefold axis what we have seen just now; this is one threefold axis and including O S S species; another threefold axis.

So, this threefold axis and another threefold axis if these two are the two planes; the C three planes. So, one C three planes and another C three plane they can adjust themselves depending upon the corresponding size of the metal centre based on the corresponding oxidation state; that means, whether our tungsten is in plus four, plus five or plus six oxidation state, we can have these typical arrangements. So, these particular enzymes basically fall into three groups and crystal structure of these three groups are been identified so far, and people have identified the corresponding coordination form; this pterin unit, the tungstopterin units, two such tungstopterine units fulfilling this particular site and the other two sites are occupied by oxido and hydroxido groups. So, this AOR family, the aldehyde ferredoxin and formaldehyde ferredoxin oxido reductases.

So, AOR family and FOR family, these are the two families and they are basically identified from pyrococcus furiosus and is abbreviated as PF. So, this the biological name of the origin for this particular enzyme. So, crystal structure basically tells us that what type distortions we can have, because this particular geometry is not at all and octahedral geometry, but which is in different form and between the catalytic turnovers basically the adjustment of the coordination centre can also take place. And when this particular centre is acting on aldehyde definitely, we accept that this is basically the corresponding oxidation reaction and that oxidation reaction the corresponding aldehydes are getting oxidized.

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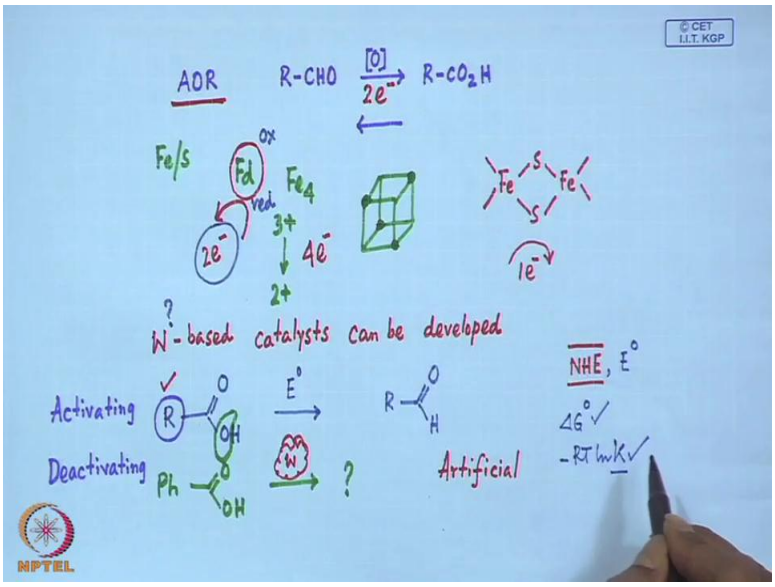

So, in AOR family, the aldehyde oxido reductase family where R is basically the corresponding methyl group we get the acetaldehyde. So, when it is acting on acetaldehyde, we get R C O 2 H in the corresponding carboxylic acid formation. So, this we all know from the knowledge of organic chemistry that this is well known oxidation reaction even if you some bengeldehyde in our hand; the bottles of the bengeldehyde in the laboratory can be oxidized very easily by the di oxygen present in air.

So, di oxygen can be a very good oxidizing agent for all aldehyde like substrate particular the bengeldehyde and acetaldehyde, and this particular conversation of this acetaldehyde to acetic acid what we are seen in case of the corresponding molybdenum based enzymes where you can take care of the corresponding oxidation of ethanol to acetaldehyde. So, this is an oxidation reaction, some electron flow can take place in a reverse direction. So, in the reverse direction, the electron can go for the corresponding transfer; that means, once we oxidized the aldehyde to carboxylic acid, the reducing equivalent are been transferred to a four iron four sulfur ferredoxin.

So, we have seen that this is dependent on iron sulfur ferredoxin molecules and this ferredoxin is now our Fe four unit. So, four sulfur four iron ferredoxin molecule which is we all know is basically a cube type molecule where all the alternate coronets are occupied by iron and sulfur groups. So, if these are the iron other alternative coronets are

occupied by sulfur groups. So, this ferredoxin molecule, the iron centers are settling between plus three to plus two oxidation state; that means, between the ferres and ferric oxidation state.

So, depending upon the number of electron transfer which is being taken off for this particular oxidation reaction whether we are talking about some electron transfer which is single electron transfer or a double electron transfer, we should relay on a two iron ferredoxin molecule or a two iron ferredoxin molecule, because sometime we find that though you can have two iron centers present and all the four iron centers can be reduced to plus two or all the four iron centers can be oxidized to plus three. So, you can extract out if it goes from a typically reduced form where all the iron centers are present in plus two oxidation state to a system where all the iron centers are oxidized to plus three oxidation state; we except to get four electron transfer for this particular system.

But in most cases, we get one particular ferredoxin molecule which can provide us two electron transfer. So, ferredoxin molecule which is based on four iron center which can go for two electron transfer either it can be oxidized by two electron or it can be reduced by two electron which is very much unlike for two iron ferredoxin system, because in two iron ferredoxin system what we have seen just now that we have two iron system and these two can settle between the corresponding oxidation state, and here also it can initially go for a single electron transfer; that means, already the system is in mixed oxidized form; that means, one center is in plus two and another center is plus three.

So, it can reduced for this iron or it can be oxidized for the second iron. So, we get for this corresponding oxidation of the aldehyde to acid corresponding acid, this reducing equivalents being transferred to the four iron four sulfur ferredoxin. So, whatever reducing equivalent we can generate from this particular oxidation reaction that is getting transfer to the ferredoxin molecule. So, these reduced form of the ferredoxin molecule then take part in the corresponding catalytic cycle to the next step.

And this is one particular aldehyde or the in the original form, it is possible for all other aldehyde molecules starting from the acetaldehyde. But for formate, this formate di hydrogen is family is little bit different only towards this particular coordination of O H, because this particular one from the cystin sulfur or cylinocystin selenium, it can be attached to this particular tungsten site and since this corresponding donor atoms are

bigger in size if it is sulfur or if we it is selenium close to another bigger unit which is our tungsten unit. So, very easily from the determination of the crystal structure, we can identify the nature of these donor groups attach to this tungsten unit and that also when a bigger unit is attach to the tungsten site though tungsten is exavaliant state which is the smallest possible among the all three oxidation states available for the tungsten, but this specially this bigger donor atom can also destroy the coordination environment around this tungsten site. So, this coordination centre which is attached to the oxygen and which is attached to the sulfur selenium are different. So, that is why the reactivity pattern for formate dehydrogenase is also little bit different compare to that of your normal original aldehyde.

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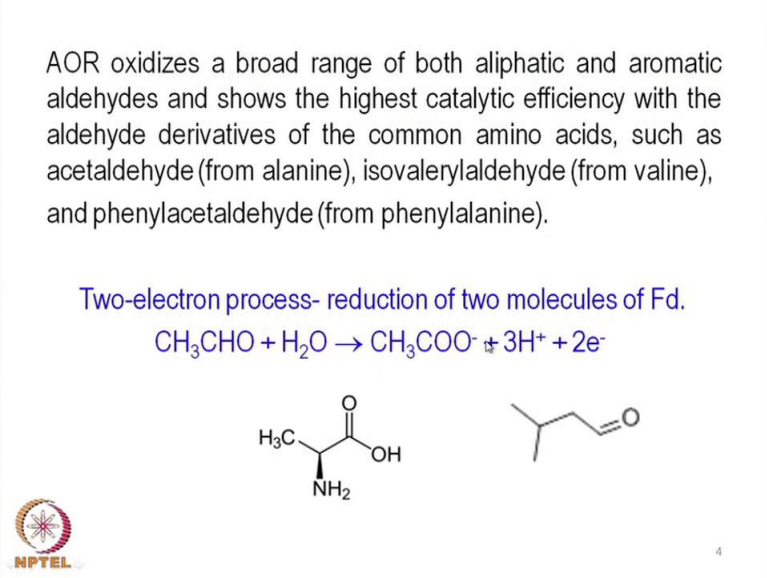

So, this aldehyde oxido reductase, they can reduce or oxidize this two fragment. So, one is the corresponding aldehydes, they can also work on aliphatic and aromatic aldehydes. So, it is very interesting to note that in the biological systems when certain system has been identified and that system when we identify as it is working on some aliphatic unit, this particular aliphatic group is available. So, this aliphatic aldehyde is getting oxidized by AOR family of tungsten enzyme.

We expect whether that particular centre can also be operating on the aromatic aldehydes as well, but the biological substrate what is coming out from the biological system is the aliphatic substrates. So, if we people can isolate that particular enzymes, AOR family of

enzymes, if we can isolate that particular enzyme can be tested for their reactivity on some aromatic aldehyde like bengeldehyde or like any other aldehyde, because the corresponding enzyme pocket is very important to hold the substrate, because some cavities should always be their which can take off the corresponding aldehyde close to that of our tungsten centre which is our catalytic site. And in this particular case, if the aliphatic aldehyde is a biological origin and aromatic aldehyde are of synthetic origin they show equal type of catalytic efficiency towards this two aldehydes.

So, they can also show good efficiency towards other substrates which are our common amino acids such as when it can act on acetaldehyde. So, acetaldehyde which we are getting from alanine; alanine is this one. So, it can basically go for the corresponding transformation. So, alanine can be transferred to acetaldehyde and that acetaldehyde can be utilize for substrate for AOR family of molecules reacting on it to giving rise to corresponding acid function; then isovalerylaldehyde.

So, if we have the valine as his corresponding amino acids, that valine unit can be converted to its corresponding aldehyde which is isovalerylaldehyde; isovalerylaldehyde is this molecule. So, isovalerlaldehyde can also be a good substrate, not only acetaldehyde which we identified. So, a good range of other aldehyde molecules can be tested for this particular reactivity; that means, tungsten can be a very good catalytic site. So, that also tempted us to discover some good catalyst which can be based on tungsten center. So, tungsten based catalysts can be developed with these information's.

Then also this corresponding other aldehyde where you have the corresponding phenyl acetaldehyde is not directly a bengeldehyde, because bengeldehyde corresponding aldehyde function is directly attached to the aromatic carbon of the bengin ring. But if we have a C 6 H 5 series to C H O types of acetaldehyde; that means, the phenylactaldehyde which has a biological origin also it is coming from the amine acid phenylalanine from the deamination reaction, because all these things can go the corresponding deamination reaction; like that of our alymine, because we can go for the corresponding kito function over here and that when goes for the corresponding oxidation leaving behind us; the corresponding de carboxylation for the C O 2 units. So, this unit goes as C O 2 and this part is oxidized to acetaldehyde, and that acetaldehyde can be utilized for substrate for this enzymatic activity.

So, all these molecules which are directly or indirectly supplying some aldehyde based substrate. So, these aldehyde base substrates can be tested for their reactivity which is a very useful two electron redox process; that means, our acetaldehyde molecule in presence of one molecule of water can be oxidized to acetic acid with the liberation of three protons and two electrons. So, these liberation of these protons and electrons can take part in basically some of our well known fact of that electroprotic equilibrium; that whenever we have that electrons transfer side wise you can have the corresponding proton transfer from the system.

And these two electrons are basically taken up by the oxidized form of the ferredoxin molecule. When we have the four iron ferredoxin molecule where the oxidized form of these is giving us that the iron centers in the plus three oxidation state and those plus three oxidized state of the iron centers can take off these two electron, and reduce that to the reduce form of the four iron ferredoxin molecule, and these protons are attach to some of the other side's where we have some basic sides can also be available from there, and those sides can be attach to these protons liberated from these reaction.

So, basically this particular transformation what we are seeing there that is basically a two electron transfer reaction and this two electron transfer reaction already we have and we have thought of that the individual ferredoxin centre can take off those two electrons to change for one form of the ferredoxin; that means, ferredoxin in in the oxidized form, and ferredoxin in the reduced form. So, in the catalytic cycle which direction this particular reaction can go either from the carboxylic acid to aldehyde or aldehyde to carboxylic acid that definitely depends on the oxidation state; that means, the oxidized form of the tungsten centre as well as the state of the ferredoxin; that means, whether the available ferredoxin molecules are in the reduced form or the oxidized form.

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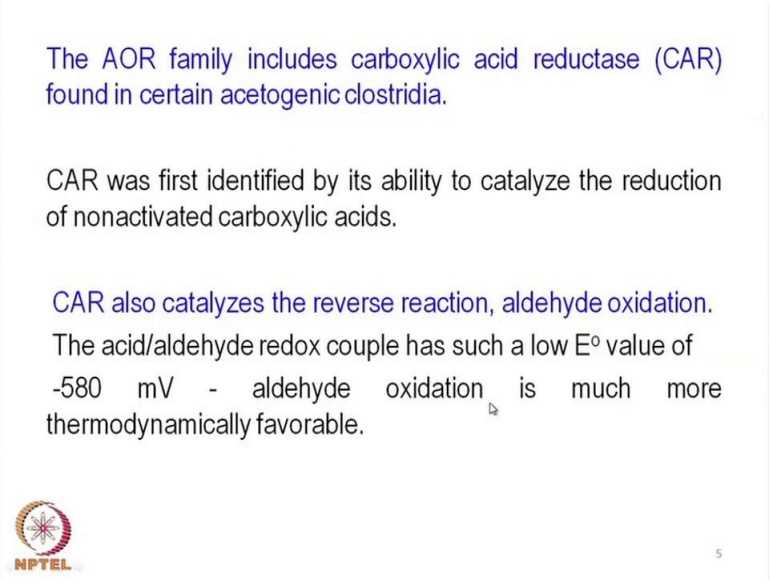

So, knowing this particular type of oxidation based on tungsten then another group of molecule which we immediately fill that once we are able to oxidize that aldehyde; that means, aldehyde oxido reductase family which is acting on the aldehyde molecules what we are producing is the corresponding carboxylic acid. So, this carboxylic acids if they can be reduced back to the aldehyde, we get another group of or another family of corresponding enzymes; those enzymes are known as the corresponding carboxylic acid reductase. So, along with AOR family, we get another family which is CAR family carboxylic acid reductase family and biologically also they can be available from some of the acetogenic clostridia.

So, acetogenic clostridia is the corresponding acetyl function which we can generate; that means, the acetogenic bacteria or the acetogenic corresponding clostridia can develop to get some of these groups as the corresponding acetyl function which can be obtain from the corresponding reduction of the carboxylic acid function. This was first identified and its ability to catalyze the reduction of non activated carboxylic acids. So, if we have some group which is we know that the R group and this R group is attached to the corresponding carboxylic function and the reactivity for this carboxylic function; that means, R is there, and that is going for the corresponding aldehyde function.

So, this particular reactivity that means we are taking away this particular oxygen atom from this particular unit. So, this particular catalytic activity is very much dependent on

how we have the corresponding carboxylic function is activated; that means, if we just for R as the phenyl ring, R is attached to some bengin ring which is also attach to C double bound O H function.

So, what type of reaction based on these enzymes we get? And if we get a different reactivity pattern for this reaction, we immediately can say that this phenol function is basically deactivating the carboxylic function which is deactivating for this short of reaction. Whereas the R group, if they are activating the carboxylic function for the smooth transfer from carboxylic unit to the corresponding aldehyde function, we consider that this particular R function has some role to play for this particular reaction.

So, depending upon of all these substrates if R is equal to methyl function and if it is biological origin definitely, this has some catalytic function and catalytic rate, and we can measure the corresponding rate of the catalysis. Based on that particular substrate which is biologically available for that particular enzyme, but if we just move for some artificial substrate which we are not getting form the enzymatic system. So, this particular artificial substrate can be tested for the role of these R function for this catalytic action and whether this particular enzyme whatever tungsten enzyme we are utilizing this for this reaction can be utilized for other biochemical transformation or bio catalytic transformation where the substrate is utilized from outside.

So, during this particular conversation, we discuss that this typical oxidation reaction or the reduction reaction from the corresponding carboxylic acid to aldehyde is definitely related to some redox couple which can be measured very nicely by bolographic measurement or cyclic voltametric or any other ampermetric measurements for their E 0 values. So, this acetaldehyde acid redox couple has a very low E 0 value which is minus five eighty mille volt. So, minus five eighty mille volt is a quite negative redox potential compare to other standard reference electoral, if we have a reference electoral like normal hydrogen electoral or satiated calomel electoral or any other standard reference electoral, we consider these and this has minus five eighty mille volt is deported with respect to normal hydrogen electoral.

So, how useful this particular potential is? In finding the corresponding redox couple for these transformation we can think this potential is very small the corresponding aldehyde oxidation what we have seen that if we have in a bottle or if it is in a test tube is very

easily oxidized by the oxidation form the di oxygen present in the air; that means, no catalyst is required; nothing is required, only the di oxygen present in air can oxidize nicely these aldehyde to carboxylic acid and the extra oxygen what is their gong to attach the aldehyde function is coming from the di oxygen molecule; the di oxygen which is functioning as an oxidizing agent.

So, E 0 value for the di oxygen is much more positive compare to the corresponding the reduction potential for the corresponding acid aldehyde conversation. So, once we find the corresponding E 0 value, E is with respect to the n H e the E 0 value if we know and this E 0 value can be correlated with the delta G 0 value; that means, the free energy change and that free energy change which can also be correlated with the corresponding minus artificial natural logarithm of K. So, once we find this E 0 value for the any transformation, we can find out the corresponding delta g 0 value and the corresponding k value. So, this k nothing but the equilibrium constant once we determine the equilibrium constant for the reaction, we immediately know the corresponding reaction whether it is an enzymatic reaction or non enzymatic reaction.

How much fossil the reaction is for transferring one side to the other? So, therefore, this aldehyde oxidation is much more thermodynamically favorable. So, immediately by determining the corresponding E 0 value from this reaction, we can talk about the corresponding the thermodynamic driving force for this particular reaction in terms of the corresponding compression with the equilibrium constant and we can comment on that this particular reaction if the K values is high; that means, the equilibrium constant is very high, it immediately goes from one side to the other due to that particular catalytic transformation. But we can have some kinetic barrier related to this particular reaction and the enzyme environment whatever enzyme environment you can have.

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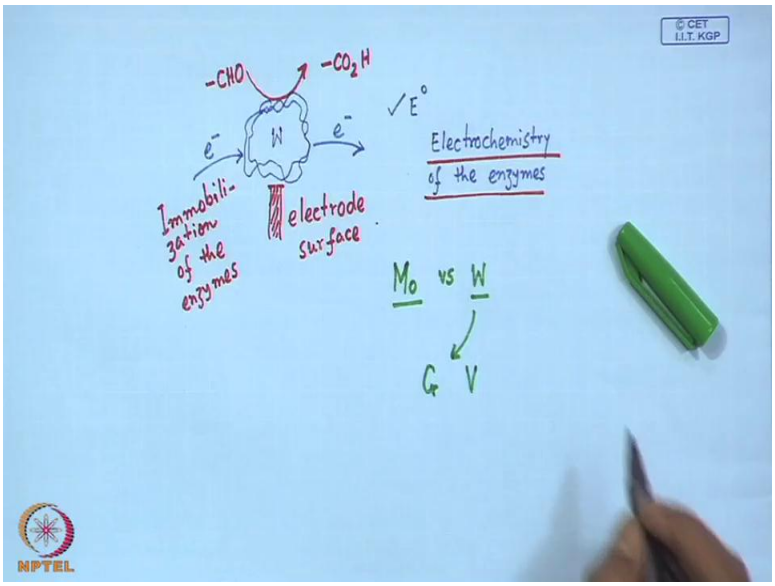

So, if we have the typical enzyme environment and if it is in the huge polypeptial chain, and within that polypeptial chain we have the tungsten unit present, and we are thinking of some electron in and electron out business.

So, electron is entering and electron is leaving from the system for the catalytic reaction, and the E 0 value we have determined for that particular transfer and the corresponding kinetic bearer, we should also determine that the rate of that electron transfer. So, the rate of the electron transfer is also important. So, if we are able to overcome the corresponding kinetic barrier utilizing this enzyme, we also get a very fast reaction based on this particular tungsten centre. So, this determination of E 0 values, because we can some instruments are also available. So, those instruments like the cyclic voltmeter.

So, cyclic voltmeter can immediately determine the corresponding E 0 value for this enzymatic. So, electrochemistry of the enzymes are very important and this electrochemistry on the electrode surface what we do, and which is sometime bound with the immobilized enzyme. So, this enzyme can be bound to the electrode surface. So, we have this electrode surface and on that electrode surface we basically go for the immobilization of the enzymes and we have to see the corresponding substrate what is getting oxidized; that means, you can have the corresponding substrate as the corresponding aldehyde or the acid.

So, all these things basically we can comment on whether we have a very useful enzyme based on tungsten and whether we have a very useful enzyme which is based on the molybdenum. So, these particular things can basically utilized for the compression of this molybdenum verses tungsten. So, next day will just see whether this particular tungsten enzyme can also be useful some other system and in our future classes will just slowly correlate that whether the chromium can have some biological role as well as the vanadium in this particular environment, because we have seen that all these four metal irons can give rise to the corresponding oxo functions very easily.

Thank you.