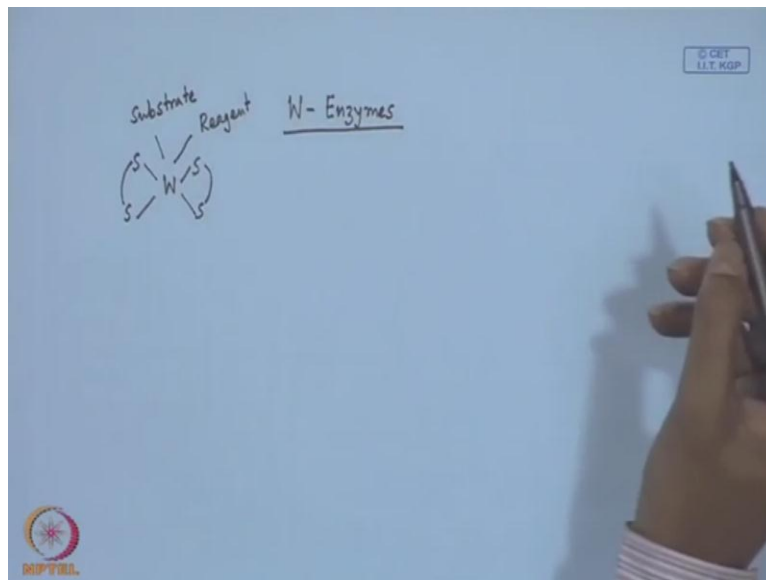


Bioinorganic Chemistry
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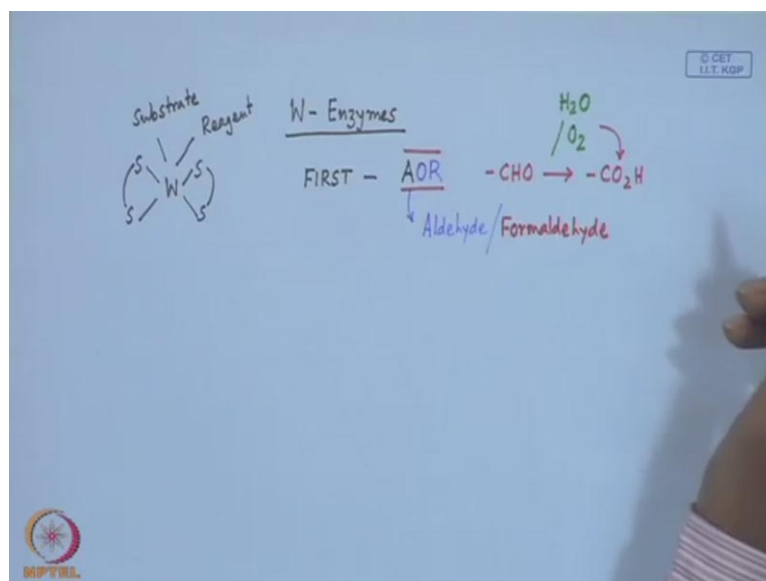
Lecture - 30
Tungsten Enzymes-II

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Hello and good morning to everybody. So, today we will still continue with the tungsten enzymes and today we will see some more examples, where this tungsten can function as a very useful catalytic site. Where this particular 1 that means site is attached to the ligand donor atoms so, s donor atoms are present and there are 2 positions is not that is exactly it is a coordinated octahedral geometry but, is highly distorted geometry. Where the substrate can approach to the metals site in search of the reagent to be attached to the substrate for a typical conversion.

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And for the first group of those molecules what we have seen the first group of molecules was dealing with aldehyde and this aldehyde when they are involved in some form of oxidation and reduction reaction that means a family of these metalloenzymes. What is known as AOR family aldehyde oxido reductase family and that family basically used for handling, will the oxidation of aldehyde and in some special cases a tungsten center can be utilized for the handling the corresponding oxidation of formaldehyde also, and during that redox process that means if we just consider that aldehyde is getting oxidized to carboxylic acid and we are just interested to know how this particular oxygen coming to convert this particular substrate molecule. Which are our aldehyde molecule and whether these oxygen atoms are coming from water molecule or the di oxygen present in air?


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Tungsten Enzymes - II

The second family of W-containing enzymes consists of the formate and N-formylmethanofuran dehydrogenases, both of which function physiologically to reductively fix CO_2 (into acetate and N-formylmethanofuran, respectively).

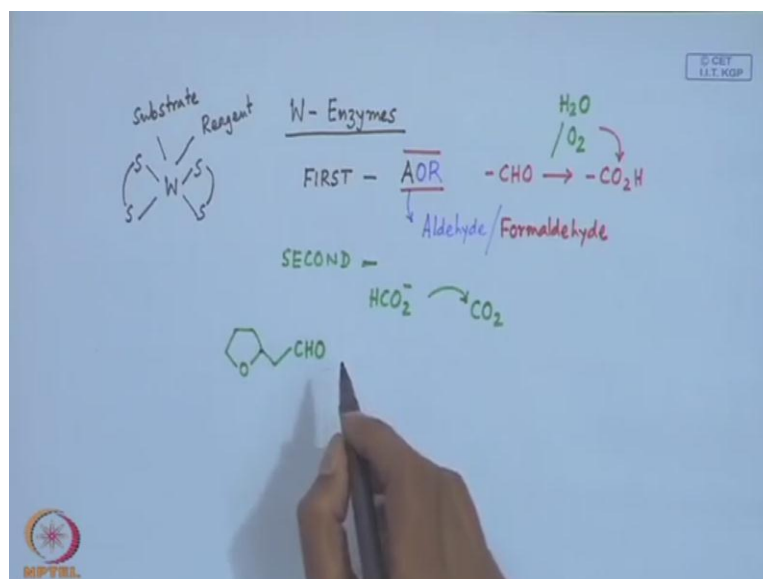
Methanofuran describes a family of chemical compounds found in methanogenic archaea.

Methanofuran converts to formylmethanofuran in an early stage of methanogenesis. The enzyme formylmethanofuran dehydrogenase formylates methanofuran using CO_2 , the primary C1 source in methanogenesis.



So, this particular thing when we go for the second one that means this second family of this tungsten bearing enzymes these is the second family consists of the formate and N-formylmethanofuran dehydrogenases. So, the second group basically will be working on formate.

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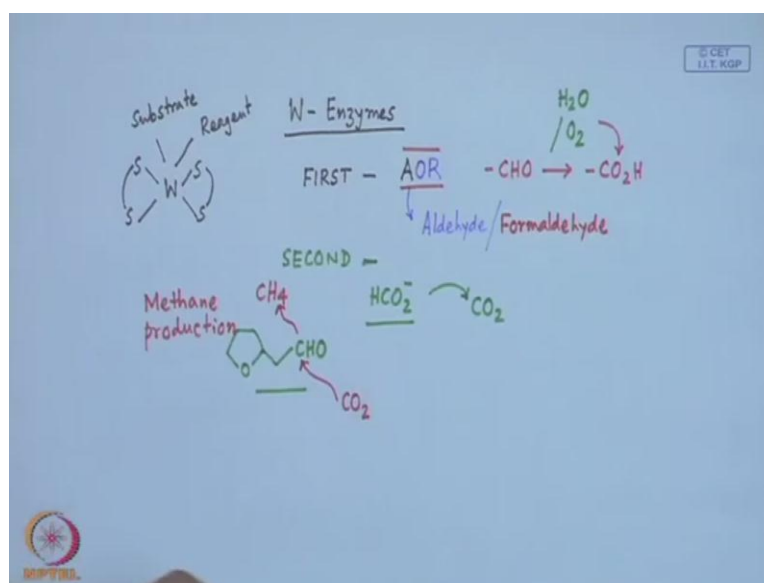
So, formate is HCO_2^- so, it will be working on the formate anion and just can examine for the elimination of CO_2 from the formate and some other thing is also there, that means if we have a furan substrate and if we get furan is attached to some methyl

group and some other aldehyde function on the furan ring. If those are handling because these are very useful biological fragment which can take part in different reactions so, that give rise to n formylmethanofuran. Which is utilized for their corresponding dehydrogenizes activity because these biological molecules are very important but, still again we are handling either the format or the formyle function this is nothing but, the formyle function attached to the furan ring and that furan ring is basically, utilized for this particular that means other groups are also attached to the molecule and that is utilized for several important bio chemical reactions.

So, these thing that means the format and the substituted furan derivative they are basically utilized by the tungsten containing enzyme because sometimes in physiological condition they go for fixation of CO_2 that means carbon dioxide fixation. So, carbon dioxide fixation is a very useful chemical technique where we can convert the carbon dioxide.

Which is basically polluting our environment and that carbon dioxide can be inserted to some important biologically important molecules and those molecules can be obtained through this format and n formylefuran derivative giving rise to tension formation of acetate and n formylmethanofuran respectively. So, n formylemethanofuran is the thing which this particular dehydrogenases is basically working on some substrate and the result of that thing is the n formylemethanofuran formation because these methanofuram derivatives are very useful reaction for the formation of methane also.

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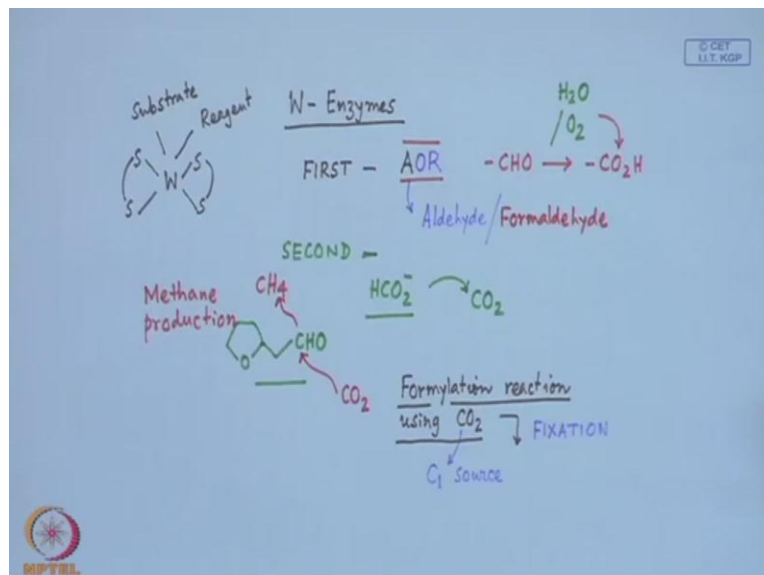


Because, once we get this particular thing and attach to some furan ring and if this is coming that means this formyle derivative if we can get it from carbon dioxide and ultimately if we can convert this formyle derivative to methane molecule, then this is a 1 carbon derivative this is another 1 carbon derivative but, attached to some bigger molecule and ultimately it is converted to the formation of the corresponding methane. So, the bacteria the methanogenic bacteria and all other groups of molecules are enzymes which are useful for production of methane can be known if we can little bit understand about the role of this tungsten enzyme for the tungsten center for handling this carbon dioxide formation of the formyl derivative and the generation of the methane molecule.

So, this methanofuran therefore, forms a family of chemical compound. So, these they group of useful chemical compounds we do not study all the time much about this methanofuran molecules. But, they are useful molecules and they are also found in methanogenic archaea. So, in methanogenic archaea is therefore, useful for handling the methanofuran derivative and that methanofuran derivative can be utilized for the production of methane. So, the methane production is therefore dependent on the tungsten center if the tungsten center is utilized for handling all these molecules. So, this methanofuran basically converts the formymethanofuran in an early stage of methanogenesis is a pretty complicated reaction and in some cases the formymethanofuran formation is taking place and the enzyme formylemethano dehydrogenase. What is we just discussed that it is there formylates the methanofuran

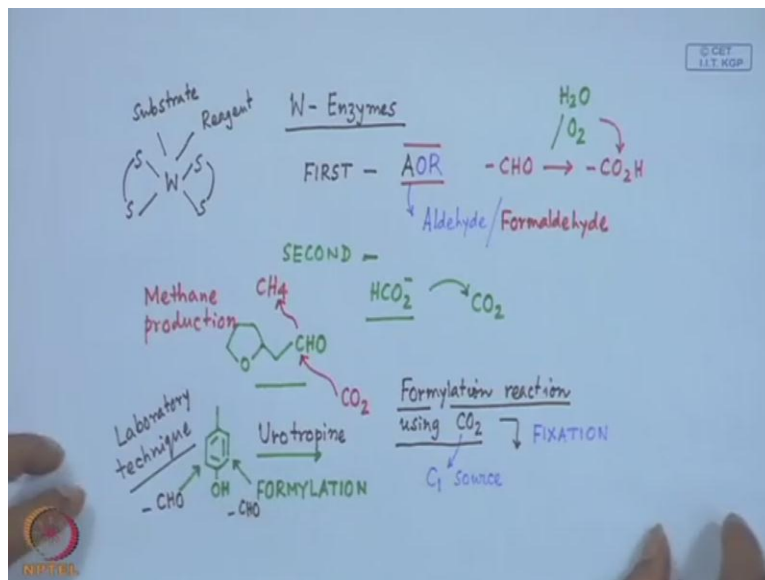
ring so, it is useful so for the formylation reaction also, the formylation reaction is taking place using CO_2 .

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So, any formylation reaction whether we can go for because formylation reaction is also a very good reaction for organic transformation so, formylation reaction if we can do using CO_2 as the sole carbon source. So, utilizing CO_2 so, nature is always overburdened with the CO_2 molecule that means the carbon dioxide gas and the environment pollution the global warming and all these things are dependent on the amount of carbon dioxide in the atmosphere. So, if we can fix that particular carbon dioxide in some useful organic transformation reaction. So, we call it as a fixation of CO_2 and this CO_2 is our very useful 1 carbon source for organic transformation. So, this 1 carbon source is basically utilized for the formylation reaction.

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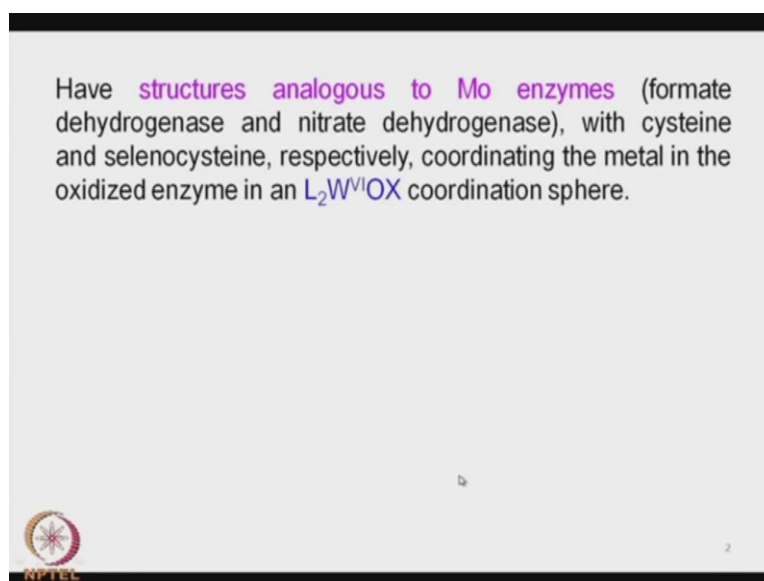


Which is a very useful reaction for the transformation of the different type of molecules because in laboratory what we can do in laboratory, if we have a phenol derivative and if it is 4 substituted 1 we cannot do any transformation that means the formylation reaction on this carbon or the formylation reaction on this carbon cannot be achieved using carbon dioxide. So, this biochemical path way is a therefore, very much useful to know whether we can also use those enzymes for the formylation of any useful molecule so, this formylation cannot take place using the source for that formyle group as carbon dioxide but can be done using urotropin. Which is nothing but, hexamethylenetetramine and that hexamethylenetetramine is utilized for the insertion of CHO group at position 2 and another CHO group at position 6.

So, when we have 4 substituted phenols and some laboratory technique is there this is a laboratory technique for formylation. We get the 2,6-dialdehyde molecule so, substituted dialdehyde molecule where by the insertion of 2 formyl groups on the benzene ring give us the product around this particular phenol OH function.

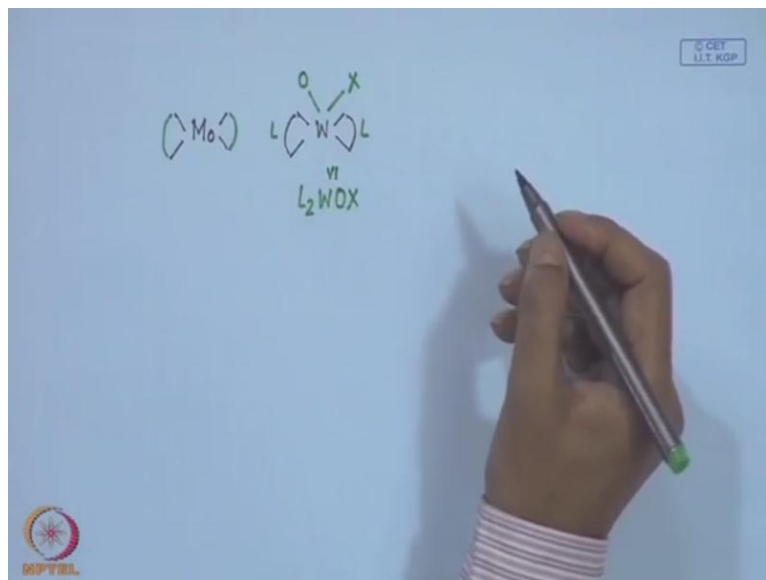
So, when the enzyme the formylmethanofuran so, basically we are talking all these cases the transfer of the formyl group from 1 molecule to the other and this particular formylation reaction is useful because this formylation is taking place using another enzyme. Which is formyle methanofuran dehydrogenase using CO_2 as source of carbon so, we basically fix the carbon dioxide molecule to some useful organic substrate.

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And all these molecules like this handling this methalofuran derivatives and all these they structurally they are analogous because, whenever we study this tungsten sites we all the time we side by side try to compare it with that of our molybdenum site. So, this is very much similar to that of well known and well established molybdenum site for format dehydrogenase and nitrate dehydrogenase. So, these groups of molecules how the molybdenum is attached to the oxygen and the sulfur donor atoms and how the redox behavior on the molybdenum center is taking part and whether the cystenie or celenocystenie residues also, can take part for these useful transformations related to the coordination. So, these are all related to the corresponding molybdenum enzymes and in the oxidized form when the metal center is in the plus 6 oxidation state.

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We get the species as the corresponding coordinated environment this tungsten. So, we have one over here and another one over here. So, directly we can just compare with the molybdenum site because the molybdenum also has a bidentate ligand here and bidentate. So, this is one and this is a second one so, 1 2 is there then tungsten is in your hand then we have o and the x so, this o is there it can be double bonded o or it can be OH function and some X group as chloride as some other group is also present and molybdenum is stabilized in the hexavalent.

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The second family of tungstoenzymes involves two types, both of which utilize CO_2 as the substrate. One is **formate dehydrogenase (FDH)**, which was the first W-containing enzyme to be purified. It uses NADP(H) as the physiological electron donor.

$$CO_2 + H^+ + 2e^- \rightarrow HCOO^-$$

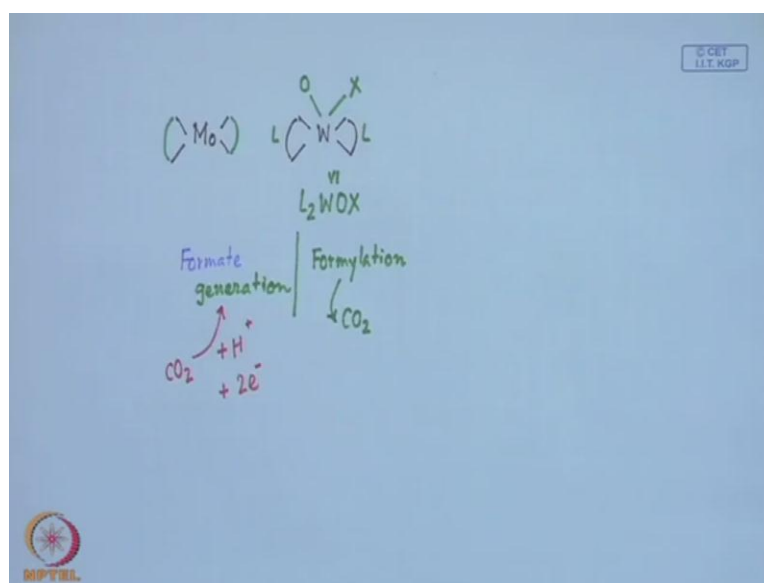
The chemical structure of NADP⁺ is shown. It consists of a nicotinamide ring (oxidized form) connected to a ribose sugar, which is further connected to another ribose sugar attached to an adenosine moiety. The adenosine moiety includes an adenine ring and a phosphate group. The structure is drawn in a detailed, skeletal format.

NPTEL

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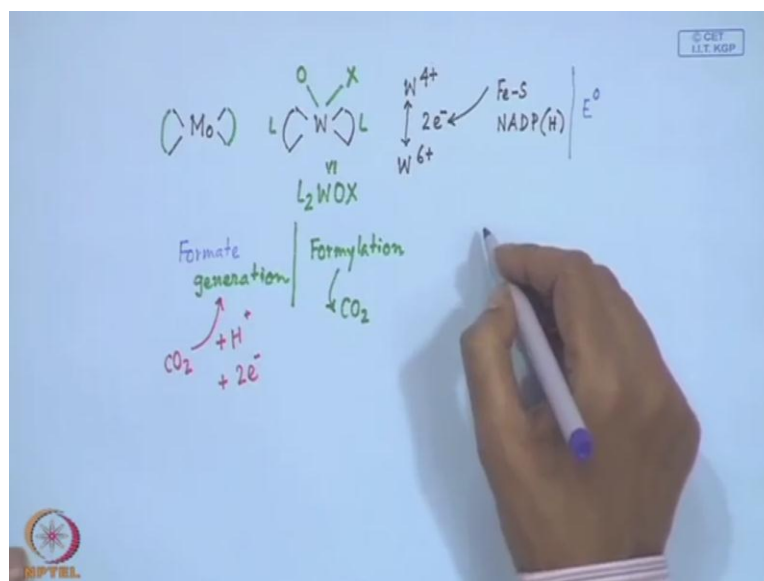
And this particular case when we see for this family of enzymes when we have the formate dehydrogenase C O_2 is our substrate and this C O_2 substrate is utilized for the transformation. So, when we have that formate dehydrogenase which is F D H and first time it was identified as this is one particular enzymes. Where instead of molybdenum we have the tungsten center and formate dehydrogenase is basically the corresponding transformation of this C O_2 molecule to the corresponding formate anion molecule and is the reductive pathway.

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So, how we can go for the corresponding format generation and this format generation is another pathway. Which we just now we have seen which is related to the formylation reaction and that formylatoion reaction is fully dependent on the species carbon dioxide and here also, the generation of the format is also dependent on the C O_2 source. So, interestingly in one particular case because this is a very important and the vital reaction which is related to the human respirations to all aerobic respiration, where we basically bond the system the carbon related fuel or the carbon related food stuff is oxidized to carbon dioxide. So, handling this C O_2 molecule in two different ways and is basically when we concert this C O_2 the format is basically, a reaction where we need both proton as well as electron which is a 2 electron reduction step and 1 proton is also utilized.

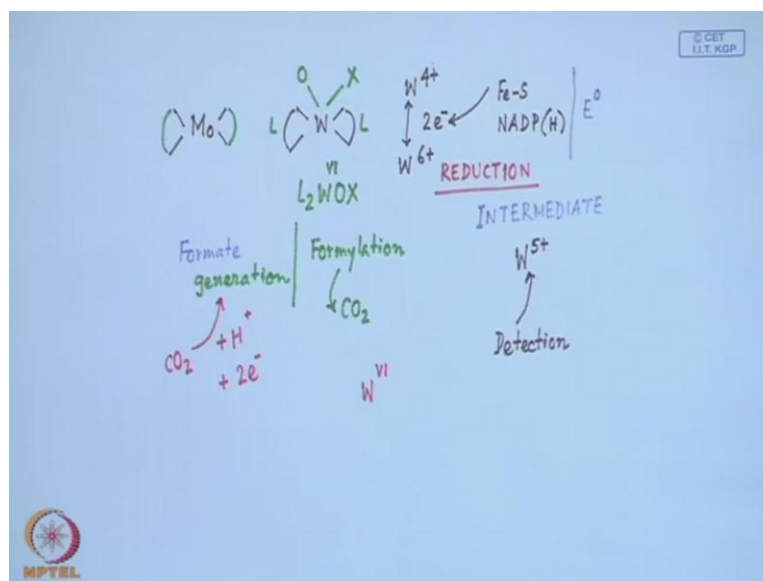
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So, that immediately gives us some important clue related to this particular tungsten center because this 2 electron process. We know that this 2 electron process can be achieved if we have tungsten in tetravalent state and tungsten in hexavalent state. So, basically this can settle between these 2 oxidation states. So, just simply change in oxidation state of the metal center can supply the electron and we can have some other source it can be our iron sulfur clusters pyridoxine clusters or it can be some other biological reductant like N A D P H etcetera.

So, when this pyridoxine molecules are present as well as some N A D P H molecules are also there which are well known biological reducing agents because we have to supply this particular electron this number of electrons to the system such that we go for the corresponding reduction of the CO_2 molecule. So, these things are available but, the choice dependent on the corresponding reduction potential the E^0 value the redox potential value or the half wave reduction potential value for N A D P H and iron sulfur cluster will tell us that which particular potential. We can reduced for the catalytic cycle at which particular potential we can deliver these 2 electrons to the hexavalent tungsten site such that these hexavalent tungsten can be reduced to the tungsten four site and if the particular one if the total reaction is a 2 electron transfer reaction but, if some catalytically active intermediate is formed there.

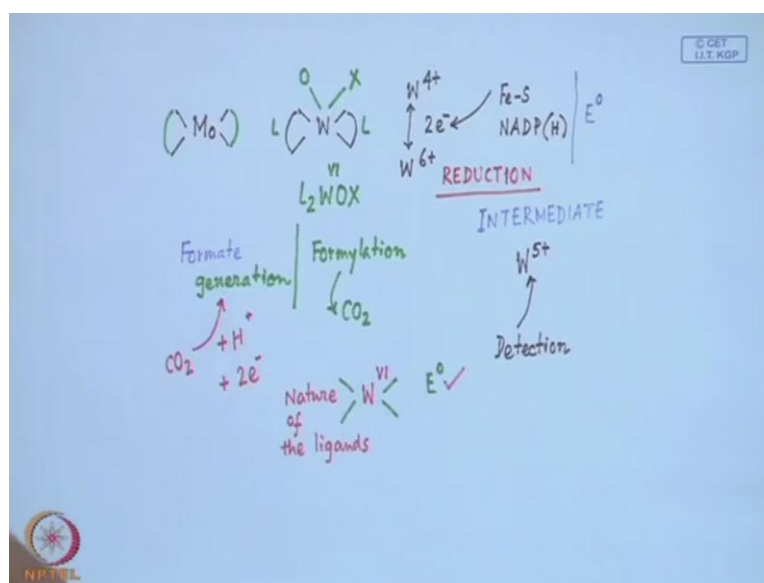
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So, if that intermediate is present which is a typical metal center metal ion center that means the tungsten center having intermediate oxidation state that means tungsten 5 plus. So, these 2 electrons cannot be delivered at a time that means the tungsten is not jumping is not moving directly in 1 single state that means is not a complete 2 electron transfer process such that it goes down to tetravalent state immediately, when it reacts with either pyridoxine molecule or the N A D P H molecule but, it can go through the intermediate oxidation state that means the pentavalent tungsten set so, this can be nicely detected soothe detection of this is possible and if this detection is possible.

We can immediately say that this tungsten 5 plus is involved for the catalytic cycling and it basically obtained from 1 electron reduction of the hexavalent state and finally, when 1 we get this corresponding format anion with the help of the 1 proton also, there is also, me side where the proton is also attaching to the substrate molecule and we get back this particular molecule to the corresponding hexavalent states. So, the reduction reaction that means the reduction for this particular reduction is very important.

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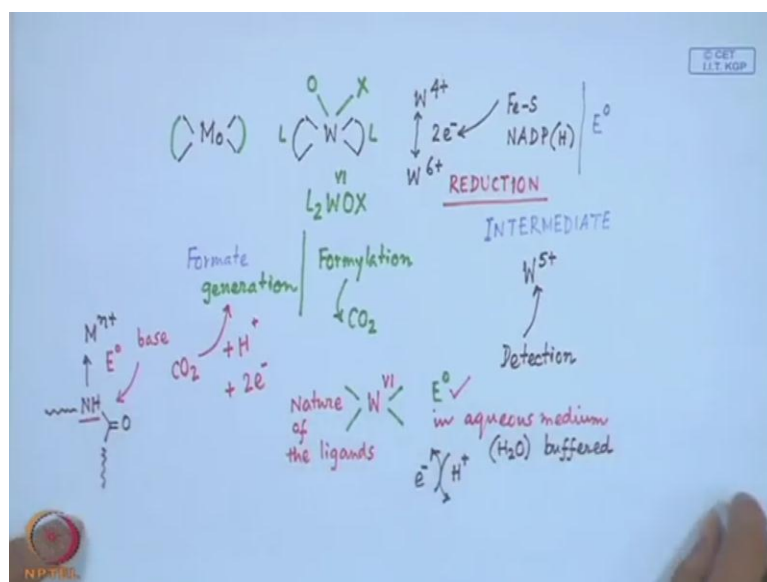


And what we have seen that if we have large number of this tungsten molecules in hexavalent state but, all these molecules cannot have the same E⁰ value so, that is why the importance of the primary ligand donor atoms are useful so, depending up on the nature of these legating groups so, the nature of this of the ligands do basically control the corresponding e⁰ values. So, if we have the corresponding e⁰ values for this particular site. Which is masked with that of our corresponding biologically available reducing agent then only we can settle between these oxidation states and tungsten is very useful center for delivering these 2 electrons required for the reduction of carbon dioxide to format anion?

So, when people discovered this things and they tired identify that when we are settling between the 2 oxidation states that means the tetravalent tungsten and the hexavalent tungsten. But, in this physiological condition in this physiological condition some reducing agents definitely are there and which is nothing but, our N A D P H so, N A D P H is the corresponding physiological electron donor for reducing the tungsten from the highest possible oxidation state. Which is plus 6 to the lowest 1 which is achievable in this particular medium which is the tetravalent 1 that means tungsten 4 plus. So, we have the bases we have the sugar unit and then we have the phosphate back bone for the nicotinamide adenine dinucleotide phosphate and this particular one is useful because it has a typical redox potential and it has also, some position because that is why we are writing as N A D P and N A D P H that means during electron transfer it can also supply

the required number of protons because sometimes we find that though we are doing a corresponding reduction reaction in water medium but, the required number of protons are not available because all these E^0 values what we are measuring say in aqueous medium.

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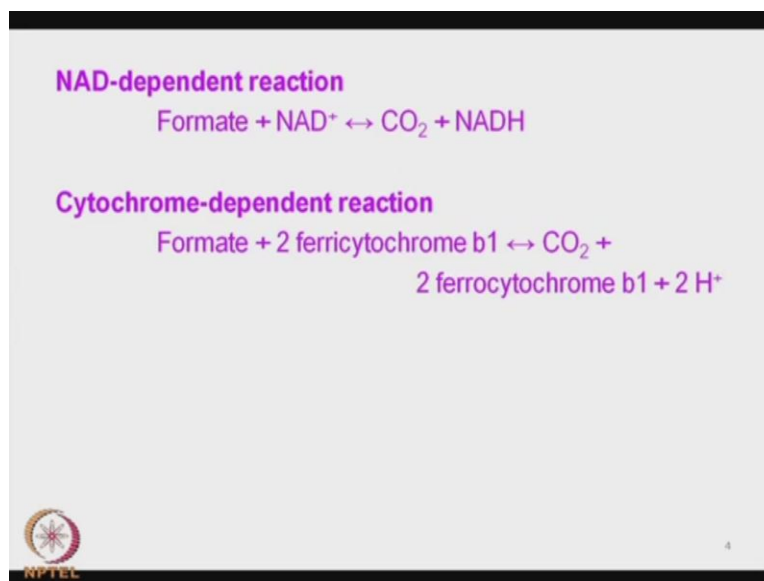
So, in aqueous medium when we are measuring by some electro chemical technique to determine the E half value. We expect that in aqueous medium they are plenty of water molecules and the medium is also buffered. So, at suitable pH value only it can either give rise to the corresponding number of protons so, it can accept the proton also, the transfer of electron. Whether the electrode is supplying the electron or the electrode is taking up the electron is also dependent on the availability of the proton transfer that is why we can have a corresponding electro protic equilibrium so, for that electron protic.

We also, think of that whether this particular thing is also going for deprotonation and when deprotonation is taking place our E^0 value is also getting lower is a typical example we all know that whenever we have a CONH back bone from a polypeptide chain. So, this CONH back bone for any polypeptide chain and we all know that this amide function or this oxygen donor atoms but, this is a quickly coordinating center this is a better corresponding donor center for coordination to any metal ion so, in this particular assembly that is the amide function is attached to the metal side. Whatever we get is that we can measure the corresponding E^0 value for this corresponding oxidation

reaction say so, if we are going to monitor the corresponding oxidation reaction we expect that some potential value is there where this hydrogen is attached to the amide nitrogen. But, if we can add some base and the base is taking up this as the proton so, H plus is removed by the base and our amide function is functioning as N minus so, charge density is more and more effective Charles transfer to the metal centre is there and we get basically, a lower oxidation potential for any kind of oxidation reaction. What we are studying for this particular metal centre so, if this potential is also matching for the corresponding E^0 values for the dioxygen molecule which is present in the air. So, that can immediately oxidize this particular metal centre to the higher level through the deprotonation of this particular amide function so, this is a very useful and a natural tendency for this transformation reactions.

So, this particular one therefore, is a very useful physiological electron donor because it can supply not only the electron but, also it can supply proton for the redox reaction.

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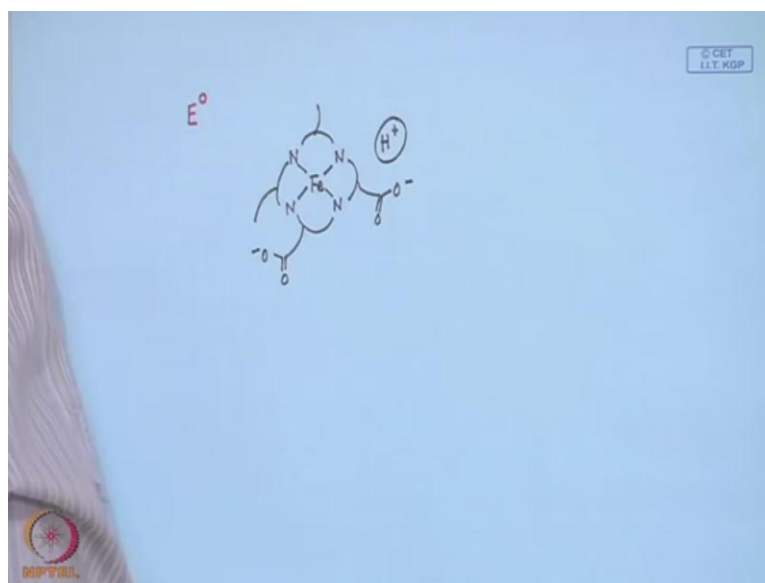
So, we can have 2 different types of reactions. What we call therefore, that if some reactions are there for the reversible transformation of carbon dioxide to format and format to carbon dioxide and that N A D P H is in formed so, if it is dependent on N A D P H this is our N A D P H phosphate N A D phosphate backbone is also there so, if it is dependent so, this is the oxidized form when we do not have the proton that means when oxidize this one proton is also lost the way. We have seen just now, that when amide

group is coordinating and if we are trying to oxidize the metal centre the amide function will have a natural tendency for deprotonation. So, similarly, the format is therefore, is getting oxidized by the oxidized form of nicotinamide adenine dinucleotide phosphate 2 carbon dioxide and NADH but, if we want to get the corresponding reverse reaction that means if we want to fix the C1 source 1 carbon source of organic matter that means the carbon dioxide it can be fixed as the format anion then the reaction should be with the reduced form of the NADPH.

So, reduced form of this will react with these in presence of the tungsten based enzyme for the conversion of continuous O₂ to format same thing also happens if there are some other group of enzymes available where the characterizing the characteristic E₀ value which all the time I am telling that this is important that E₀ value for the metal enzyme site depending upon the corresponding environment of the enzyme so, if E₀ value is not matched with that of our NADPH it can go for searching some other biological reductant or other biological reducing agent such as this ferricytochrome B₁. Which is nothing but, a porphyrin ring is B₁ type porphyrin attached to the iron centre and when this iron centre is in the ferric form that means the plus 3 oxidation state. We get ferricytochrome B₁ so, this ferricytochrome B₁ in its oxidized form which is like that of our oxidized form of NADP⁺.

So, this can oxidize our format function to carbon dioxide and 2 of these ferricytochrome B₁ is reduced to back to ferrocycytochrome B₁ so, this particular case is settling between the change in the oxidation state of the iron site or iron active site. Which is present with the cytochrome B₁ and with the elimination of the corresponding number of proton because, whatever proton is eliminating from this particular reaction because this is typically the corresponding oxidation reaction and this oxidation reaction is associated with the elimination of the proton which is coming from the format but, this ferrous cytochrome unit which is basically a cytochrome unit where we have the macro cyclic function.

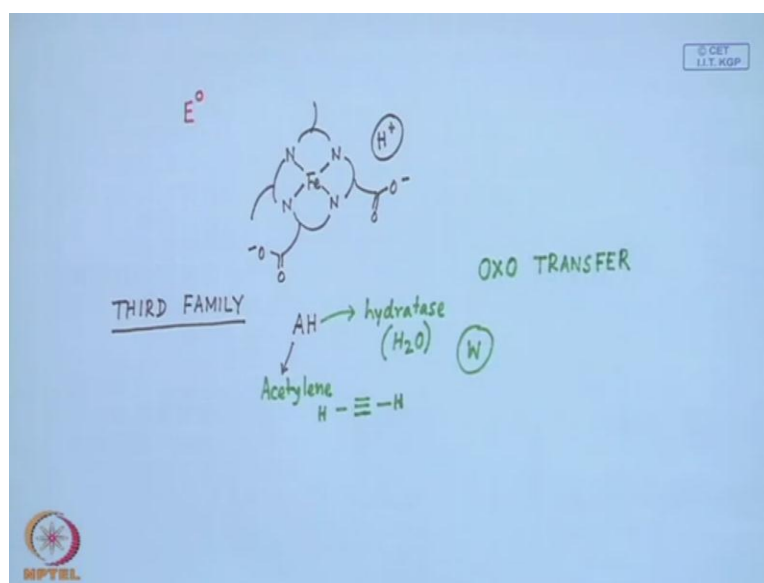
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And macro cyclic function can have several donor atoms present such as sometime the carboxylic acid groups are present but, these donor groups if they are not available for taking of the proton. Which is produced from the reaction so, these proton will be available in the reaction medium only so, this proton can remain in the reaction medium as a H^+ . Which is not directly attaching to the cytochrome site like that what happened with that of our N A D P H because in case of N A D P H it has also the corresponding proton demand for the corresponding electron transfer but, in this particular case if we have the corresponding in sometime we have the carboxylate groups attached to that but, if the corresponding P K V value that means the corrosion corresponding the basicity value for the corresponding anions is not matching with that of our corresponding proton abstraction tendency it will not go to attach this particular site chain carboxylate acid groups it will remain H^+ as H^+ in the medium.

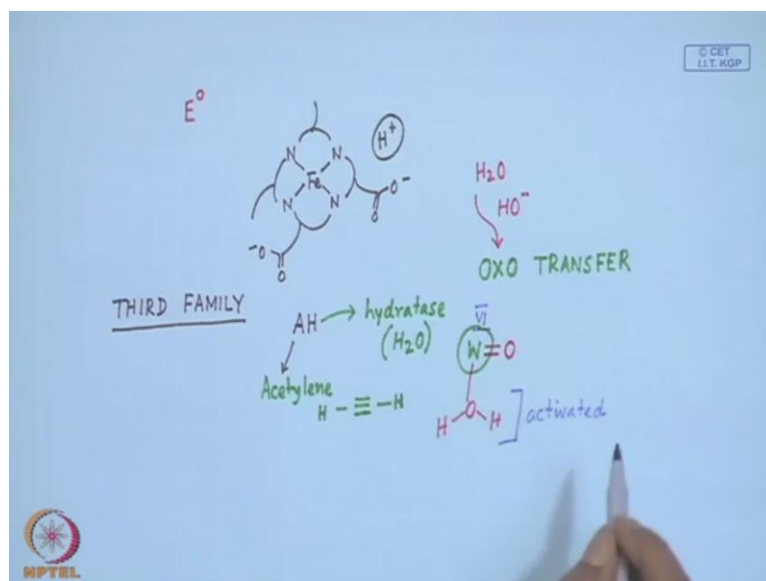
So, we have 2 different types of reactions which can be achieved through the involvement of the tungsten enzyme one is nicotine amide in dinucleotide phosphate dependent and another is typical cytochrome dependent. So, we see here that in 1 case it is it is dependent on N A D P H in another case in some of this reactions we have seen they are dependent on the iron sulfur proteins one more example here we have seen that it can also be dependent on cytochrome molecules also,

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So, after the second group of molecules we can now move for the third type so, third family of this tungsten bearing enzymes is a very interesting type of enzyme. Which is known as acetylene hydratase from *Pelobacter acetylenicus*? So, this particular enzyme is abbreviated as AH which is not to be confused with aldehyde so, A stands for the corresponding acetylene that means it is functioning on the acetylene unit acetylene and this is formed hydrates that means it can put 1 water molecule to the carbon triple bond of acetylene? Which is a very interesting reaction how we can put the water molecule on acetylene and which is catalyzed by our tungsten enzyme so, whatever oxo transfer reactions we have learned so far for the molybdenum group of enzyme and the tungsten group of enzymes where we have seen that the very important reaction for this are our oxo transfer reactions.

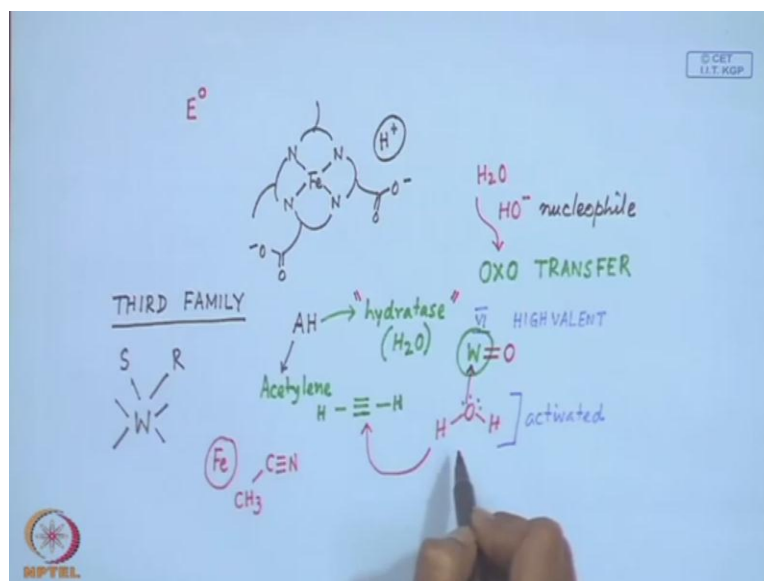
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So, these oxo transfer reactions can be very easily managed by the formation of the corresponding oxo group or tungsten double bond oxo function by the involvement of water molecule. Which is in the intermediation state go for deprotonation to hydroxide ion and ultimately to O^{2-} . Which is for the corresponding oxo formation oxo molecule formation because both molybdenum and tungsten have a natural tendency to form a very useful double bonded O single bonded O H or single bonded O H₂ function around the metal centre when they are also attached to some other legating groups like the terrain units so, the terrain sulfur groups are always there and finally, we have the two vacant positions two available sites for all these reactions.

So, therefore, once it is known that tungsten can handle this water molecule nicely. We can immediately see that this water which is attached to the tungsten site say 1 water molecule is attaching to the tungsten site. Which is not undergone any kind of deprotonation for hydroxide function or further deprotonation for the formation of the second oxido function on the tungsten molecule but, these water molecule once we have this we think that it has been in activated and this particular activation is much more. When we have this particular tungsten site in the high valent state?

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So, the high valent state is always very important on the metal centre for the relative activation of this so, we have two lone pair of electrons on this water molecule and these two lone pairs are donated. So, one of the lone pairs is getting donated to the tungsten site but, still the polarization is not that big that we expect that there should be some deprotonation of any of these hydrogens as H^+ but, it is getting activated so, when we are getting activation for this so, activated water molecule having some electronic charge on it then electrons are there it has not undergone any kind of deprotonation for extra charge development because this is there when charge is developed.

We have the hydroxide function which is a nucleophile well known nucleophile to all of us so, this nucleophile can go so, the reagent basically what we have just now, we have discussed also that on tungsten centre. We have the coordination sites and one is the substrate site that means S another is the reagent site. So, now this reagent is pretty simple reagent which is well known to us also that this acetylene is our substrate now and this water molecule is our reagent and which is getting activated that means its nucleophilic character has been increased and due to that change in the nucleophilic character of this water molecule it can simply go and attack this particular acetylene site. So, this hydration reactions are nothing but, the attack of the water molecule to that acetylene site because these reactions are well known for hundred years or more than 100 years this sort of reaction that means the hydration of acetylene molecule is well

known but, it can be synthetically made in the laboratory in presence of the mercuric ion and in presence of that mercuric tube plus your nucleophilic character on this water molecules is anions and this can go and attach to this particular acetylene molecule but, the condition for any kind of enzymatic reaction is little bit soft reaction and in this particular soft environment because the reaction temperature is very low.

Which is in the native condition that means in the water medium and atmospheric pressure so, everything is not very harsh condition and for the transformation but, the presence of the metal centered enzyme basically, play the important role for the corresponding hydratase reactions and these hydratase reactions are not only very much effective on the acetylene there are some are other group of molecule S are also known because this particular reaction that means the hydratase reaction is a very well known reaction. And when we have iron site also because some iron based enzyme has also been discovered and has been studied in detail also where the corresponding substrate is not acetylene but, it can be able to nitrial species such as aceto nitrial.

So, when we have aceto nitrial in our hand so, that can also go for the corresponding nitrial hydratase reaction but, the metal centre is different that means the same water molecule same activated water molecule can be dumped over the triple bond and this conversion for this is different compared to the conversion what we except for acetylene.


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The third family of W-containing enzymes comprises a single enzyme, **acetylene hydratase (AH)** from *Pelobacter acetylenicus* (Pa).

This enzyme catalyzes the hydration of acetylene to acetaldehyde. $\text{HC}\equiv\text{CH} + \text{H}_2\text{O} \leftrightarrow \text{CH}_3\text{CHO}$

It therefore catalyzes the hydration reaction, which is different from the oxidoreductase-type reaction catalyzed by all other tungstoenzymes.

In contrast to other tungstoenzymes, AH was isolated in air, although from an anaerobic bacterium, and was reported to be moderately stable under aerobic conditions.



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So, when we have the enzyme in our hand and this hydration reaction of acetylene is therefore operating so, addition of this water molecule on the triple bonded carbon C C triple bond of acetylene molecule C C triple bonded acetylene molecule. During the addition of the water molecule is immediately converted to acetaldehyde. So, this is the achievement that means the entire water molecule has got inserted within the acetylene system and this oxygen of the water molecule is now has been converted to the corresponding aldehyde function of the molecule and like that of the corresponding transformation that means, we immediately get another function that means this is acetylene and we get the corresponding acetaldehyde molecule and when it is catalyzed by this A H which is definitely a different reaction type.

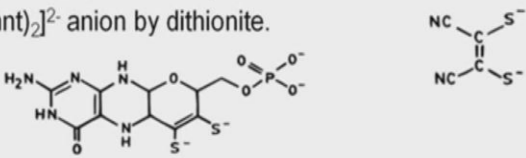
Which is different from the oxidoreductase type of reaction? Which is well known for all molybdenum bearing enzymes and all tungsten bearing enzymes that means the tungstoenzymes where the oxo group is formed and that oxo transfer reaction is very nicely is taken place but, here we have the activated water molecule instead and that activated water molecule is going to attach the corresponding triple bond date C C unit of the acetylene molecule.

So, this is the third type of this enzyme is little bit different from the other tungstoenzymes because this acetylene hydratase can be isolated in air although from an aerobic bacteria because this is not available for the aerobic bacteria but, this is available in an aerobic bacteria and is moderately stable in aerobic conditions. So, when you go for some aerobic condition when we have plenty of dioxygen molecule is available so, that plenty of dioxygen molecule is not interfering with any kind of this transformation reaction and is stabilized in some dioxygen environment and it shows the corresponding hydration reaction of acetylene.

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The likely participation of a reduced tungsten-pterin cofactor moiety for catalyzing the hydration of acetylene in AH is demonstrated by the model complex, $[\text{Et}_4\text{N}]_2[\text{W}^{\text{IV}}\text{O}(\text{mnt})_2]$ (1).

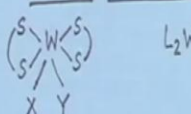
$[\text{W}^{\text{VI}}\text{O}_2(\text{mnt})_2]^{2-}$ formed by the interaction between Na_2WO_4 and Na_2mnt can be smoothly reduced in water to $[\text{W}^{\text{IV}}\text{O}(\text{mnt})_2]^{2-}$ anion by dithionite.



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MODEL COMPOUND



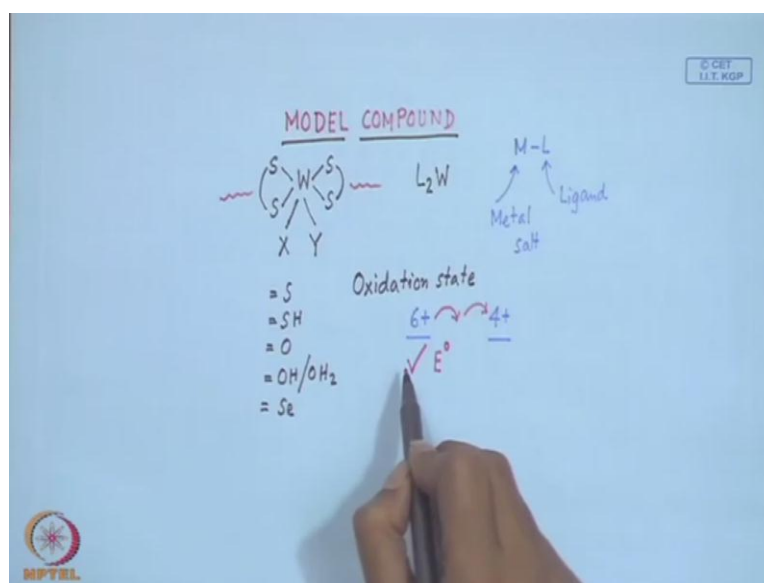
L_2W

- = S
- = SH
- = O
- = OH/OH₂
- = Se

And what we can understand little bit that, how this reaction is taking place we can go for the corresponding model studies. Which is useful technique for all that inorganic chemist the synthetic inorganic chemist you can handle this systems for the different model reactions so, the model compounds the model compound approach what we call it as model compound approach this model compound approach is very useful that we take a typical model compound in our hand and if it is a tungsten related enzymes. So, any kind of enzyme can be examined in that fashion that we have the tungsten centered 1 so, if we can have that means mimicking the corresponding active side what is available in

the nature or in the biological system that means what we have seen. So, for that the identification of the site that means the metal ligands trisometric this trisometric is when we have 1 metal centre we have 2 ligand discrete ligand system in the terrain unit. So, for the model compound also we try to preserve the same donor atoms if it is coming from tungsten terrain bearing 2 sulfur groups in the model compounds also try to put these 2 sulfur bearing units around the tungsten molecule. Such that we get a tetra coordinated form of the tungsten and then, how we use how we go for the different reactions for the generalization of this X and Y so, the availability of these X and Y they can vary from the different units like they can be sulfur they can be S H they can be oxygen they can be O H or O H 2 or can also be some selenium site.

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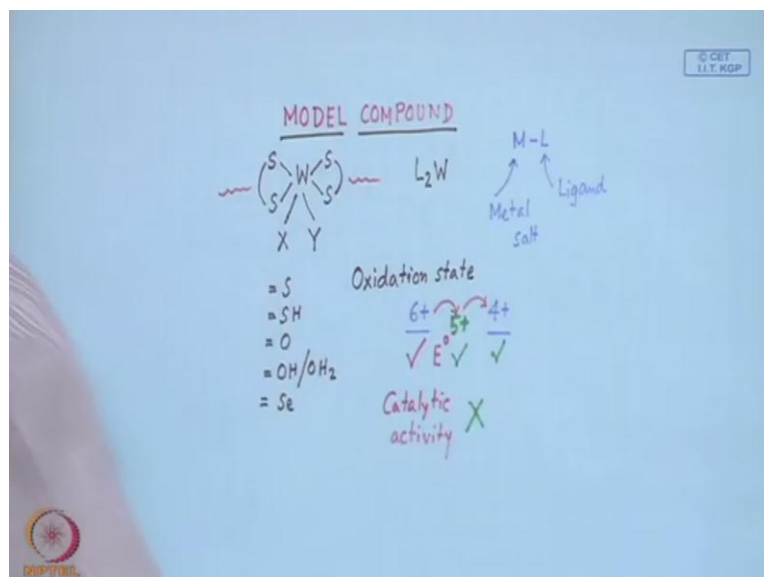


So, all these choices are there and depending upon the other part. Which is going to be attached on the tungsten as well as the corresponding oxidation state? Which is also important that which particular state is basically involved for the catalytic function so, when we talk about the tungsten site and when we do not know whether the hexavalent state or the tetravalent state is catalytically active to make this model compound that means the corresponding metal ligand assembly we have the metal centre as tungsten so, what type of metal salt we should use so, the choice of the metal salt is important and the choice of the ligand also and whether the same ligand system can stabilize this tungsten site either in the plus 6 or in the plus 4 oxidation state because, it is not possible to have any unique ligand system such that the same ligand can stabilize the tungsten

environment in both the two possible oxidation state that means the tetra valent and the hexavalent. So, depending upon it is corresponding stabilization and the electronic stabilization the 1 particular ligand if it diethyl type of ligand but, having a different backbone basically, all the backbones are different it can either stabilize the corresponding model compound in the plus 6 or plus 4 oxidation state. So, when we get the compound in plus 6 oxidation state that means the ligand can stabilize the corresponding model compound in the higher possible oxidation state that means the higher possible oxidation state.

So, ligand is well suited for the stabilization of the metal centre in the hexavalent state and the corresponding reduction potential that means the corresponding reduction potential for the transformation to plus 6 to plus 5 or plus 5 to plus 4 is low. So, synthetically when we make in the laboratory this particular species as a model compound we get the compound only in 1 particular oxidation state and that immediately gives us some useful information that whether that compound which has been prepared in hexavalent state is useful that means it can show the corresponding catalytic activity.

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So, that next can be tested for their catalytic activity. Activity so, catalytic activity for the hexavalent compound can be then scrutinized but, if we find that the compound which is prepared in the hexavalent state is not catalytically active. We should try to prepare the compound in the next step in the pentavalent step or in the tetravalent stage so, and then

if we are lucky enough because we have to change the corresponding ligands side to stabilize the tungsten center in the pentavalent state as well as the different ligands system for the tetravalent state. So, once we have these three oxidation states we can make in our system we then again test it for their catalytic activity and we can find that whether the corresponding catalytic site is active for the corresponding reaction if we just simply take the corresponding hydration reaction of the acetylene that the tetravalent state is active for the generation of acetyldehyde from acetylene or the hexavalent state is active for the generation of the acetylene hydration reaction to give you the corresponding acetaldehyde.

So, this will show we will just see for in our next class that we can have a bidentate ligands is $M N T$ what is that $M N T$ and how this can be formed so, 1 2 this fragment that means metal is to ligand ratio $N 1 2$ system is preserved that $M N 2$ is in our hand and is a sulfur bearing ligand and tungsten is in tetravalent corresponding tetravalent oxidation state is prepared and we get a corresponding tetraethyl ammonium salt and that is therefore, utilized for the corresponding transformation. So next day we will see how this model compounds can be utilized for the corresponding catalytic activity.

Thank you.