Bioinorganic Chemistry
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Lecture - 27
Molybdenum Enzymes-VI

Hello and good morning everybody, so we are still continuing and an almost we have reached towards the end of the those Molybdenum bearing Enzymes.

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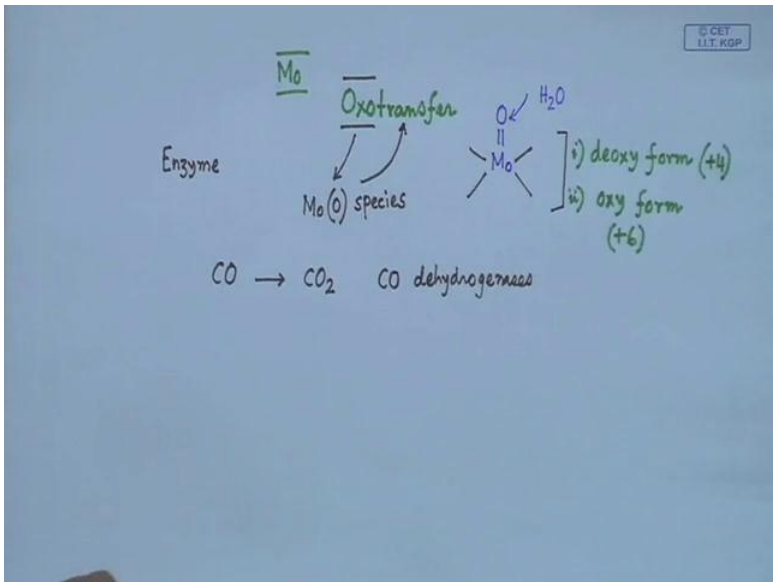

And they are basically what they are catalyzing we see that the most important thing that they are oxotransfer behavior. So, we are mainly concentrating our attention on this oxotransfer behavior based on the system where you have the molybdenum site which is monolingual in nature and we exploit the corresponding consequent behavior of molybdenum in three different oxidation states such that when molybdenum is present in our possible oxidation states like theatrics.

We gave the corresponding oxomolybdenum species and that is why it is most interesting that how you gave that his the activation of oxygen present in the water molecule by some molybdenum system. And when we gave the corresponding reagent, so oxomolybdenum thing is our reagent. So, we have that Mo species which is the oxomolybdenum species and that species we are utilizing for, so many biochemical reactions, so that is why they are functioning as enzymes.

So, to be a good enzyme containing molybdenum, so molybdenum has some other bound coordinating sides and those coordinating sides will help molybdenum to be active from some other sides, if we can have these sides already blocked by the proteinins. So, we can have this oxoside and some other side, which is related for binding to the substance. So, when we get this oxomolybdenum species as a reagent, so this is air reagent we can talk about the corresponding transfer of this oxygen to some other group.

So, this molybdenum species therefore very important to have it, so if we consider the very simple reaction that is the carbon monoxide oxidization. And already we have seen that several other complicated systems hearing nickel centers when we were discussing about the nickel containing carbon monoxide dehydronising. So, whether the same thing can be obtained from some other biological systems where the oxygen from the molybdenumoxo species can be transferred to carbon monoxide such that, we can take carbon dioxide for it is corresponding behavior of those enzymes molybdenum bearing enzymes as carbon monoxide dehydrogenizing.

So, these carbon monoxide dehydrogenizing will function nicely when we have the molybdenum oxocenter. So, these sides this oxomolybdenum sides has several interesting thing that when it is in the deoxing form. So, it can present in deoxy form, so when present in deoxy form it will have tremendous affinity for oxygen. So, immediately it can react to it water molecule without taking part in any other oxygen transfer reaction with the dioxygen molecule. Because the dioxygen molecule oxygen available from the air also can that reaction. So, once we get the deoxy form immediately it will have the corresponding tendency for the formation of the oxy form in some other oxidation States.

So, when we get these oxy form, we get this particular molybdenum side in the highest possible oxidation state that means, in the plus 6 form and when the deoxy form is available we think that this is present in plus 4 oxidation state. So, the redox reaction that means, the electron transfer reactions mediating between these two state that means, between the plus 4 state and the plus 5 state is always coupled with oxygen transfer. So, that is why these molybdenum sides that means, the monolenial molybdenum sides are very interesting to show the corresponding behavior for oxotransfer reagent.

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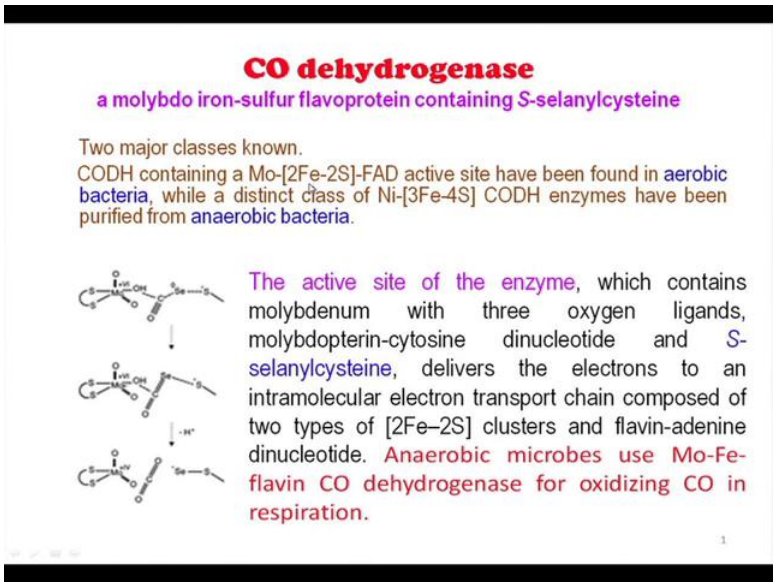

So, if we just see that what is their fond for the corresponding carbon monoxide dehydronizing which is nothing but, a molybdo iron sulfur flavoprotein containing s selanylcysteine. So, it has some important accepts to know that definitely it is a molybdenum bearing enzyme system. And this molybdenum bearing enzyme system what we have seen just now, that you need all the time for transferring electron to the molybdenum side or you can take out the electron from the molybdenum side and that is taken care of by the corresponding iron sulfur system or the flavor protein part.

Because this iron sulfur system, in the oxidized form can take up an electron and in it is reduced form it can give an electron to the molybdenum side. So, biologically this iron sulfur side or flavoprotein side can function as an oxidizing agent as well as an reducing agent, if the molybdenum is present in the lower oxidation state or higher oxidation state. So, this molybdo iron sulfur flavoprotein, so containing s selanylcysteine. So, so far we have seen in other cases like zenten oxidized or sulphide oxidized or nitric oxidized.

The molybdenum side is bound to sulfur group, but here some equiliar reactivity can be absorbed if the sulfur group on the cysteine is substituted by the silinium group that is why it is known as s selanylcysteine. So, this sulfur is there on the cysteine and apart from that we have the corresponding silinium group attached to that. And for that purpose we have two major classes of carbon monoxide dehydrogenase known and most of this cases during last 5 to 10 years structurally characterized.

So, one such species in the corresponding carbon monoxide dehydrazing containing this molybdo. The molybdo (( )) iron sulfur system which is 2 iron and 2 sulfur system which is not a 4 iron 4 sulfur system.

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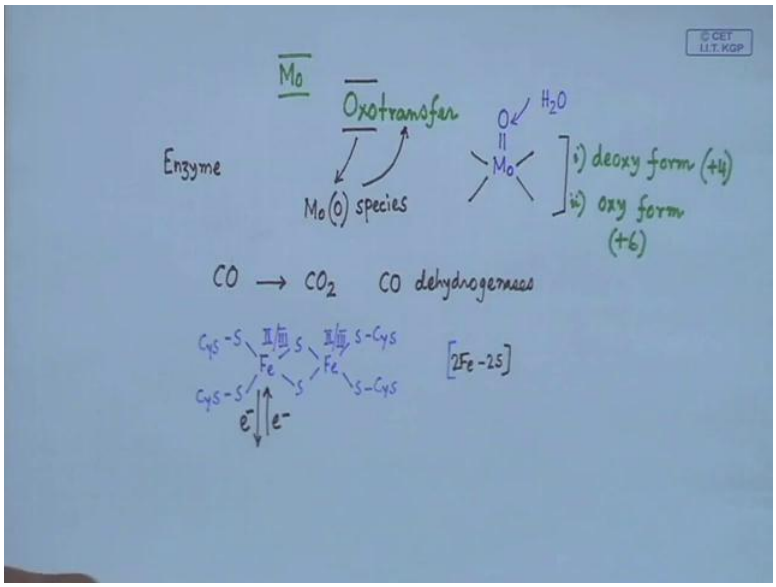

So, basically what derive we have we have this we consider as a corresponding 2 iron 2 sulfur system. And these two oxidation states of iron can settle between class two and class three and are responsible for giving rise to corresponding electron transfer to the molybdenum side. So, this is basically our Fe 2 Fe 2 S system and by changing the oxidation state on iron it can give of electron or take of electron.

So, one such spices like this that means 2 iron 2 sulfur system and one attached flavoprotein the flavid adinine dyniclotyle. The dyniclotyle system based on flavin, which is present in the active site and are obtained from aerobic bacteria. So, those bacteria which are dependent aero which are present in aero basically are written by this sort of molybdenum containing monoxide dehydranizing which is completely different that is why we say that it has a distinct class.

It is distinct class compared to that of which already discussed when we are talking about chemical bearing carbon monoxide dehdranizing. We have seen that this nickel cental is present along with 3 iron and 4 sulfur center which is basically when we put this nickel there. We see that this is also 4 metal 4 iron system which is cubin system. So, which is typically different for this carbon mono oxide dehydranization enzyme and it is obtain

when we purify anaerobic bacteria. So that means, these clusters are not dependent on the availability of the oxygen and we see that the two presence of these two clusters in one case it is the 3 iron 4 sulfur cluster in another case it is 2 iron 2 sulfur cluster is present. And depending upon the origin of the that means, origin of corresponding organic part.

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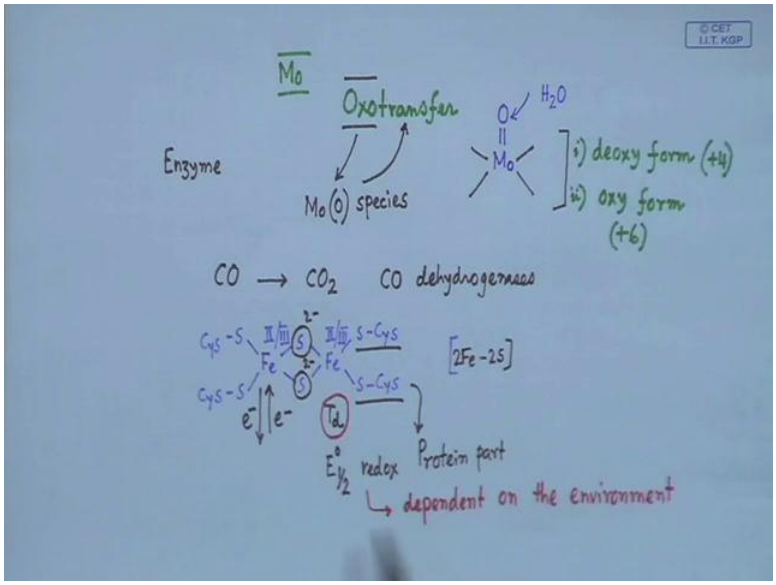

That means, this is our systine in sulfur this is our systine in sulfur and these are present from the protein chain or the protein part. So, this is basically coming from the protein part and these are the corresponding inorganic sulphid is 2 minus. So, this is an inorganic sulphide, this is an inorganic sulphide. And when we have a typical empartment, because this iron is a typical (( )) adjacent one is also (( )). But the corresponding protein in empartment and the sides basically, to control the corresponding half way potential electron transfer potential.

So, the half way potential, if we measure it by cyclic potenmentry, we will find that the corresponding reduction potential as well as the oxidation potential and we call it as a E half for it is corresponding redox reaction between the settling of the iron side from plus 2 to plus 3 or plus 3 to plus 2 is dependent on the environment. So, this E 0 for the redox copper is dependent on the environment what we have. So, if we have a tetrahedral environment surrounded by 2 systine in sulfur distribution two in organic sulfur, we get

one particular potential for the electron transfer, which is completely different from that potential what we get from the nickel system.

Because, nickel redox potential if it goes from nickel 2 to nickel 3 or nickel 2 to nickel 1 is completely different compared to the molybdenum red ox potential. So, we see that the depending upon these corresponding E zero values and electro chemical measurement basically first disturbed is that this particular aerobic bacteria having this CODH function. That means, this carbon monoxide dehydrating functioning is completely different from that of the other one which bearing is bearing the corresponding nickel site.

So, this particular one why we get the molybdenum site because we know for what is their nickel site. In this particular case you have the active site which is molybdenum centered part. And it has three oxygen ligands and the corresponding molybdopterin cytosine dinucleotide. So, sulfur sulfur ligands you know already the molybdopterin incase of zanthine oxidation in other cases we have the aces environment that is why the model compound to establish the corresponding catalytic behaviour of molybdenum always synthesize for molybdenum complexes in sulfur environment.

So, this sulfur environment are typically important apart from that when we have a pentan cooridinated form, that means two of these are sulfur bearing ligands and three of this are oxygen, one oxo this is the second oxo and third is the corresponding OH fuction.

So, that is why it has three oxygen ligands and we can also have sulfur selanylcysteine recudes. The sulfur selanylcysteine recudes when it is there and slowly interacting with the carbon monoxide. So, these carbon monoxide in which is there so, you have cysteine sulfur recude, which is attaching to the silinium. And the silinium is reacting with the carbon monoxide which is available they are called showing it is catalytic reactivity for conversion to carbon dioxide.

So, in this particular case this carbon monoxide is not directly attaching to the molybdenum site, instead it is slowly interacting with the OH function available on the molybdenum.

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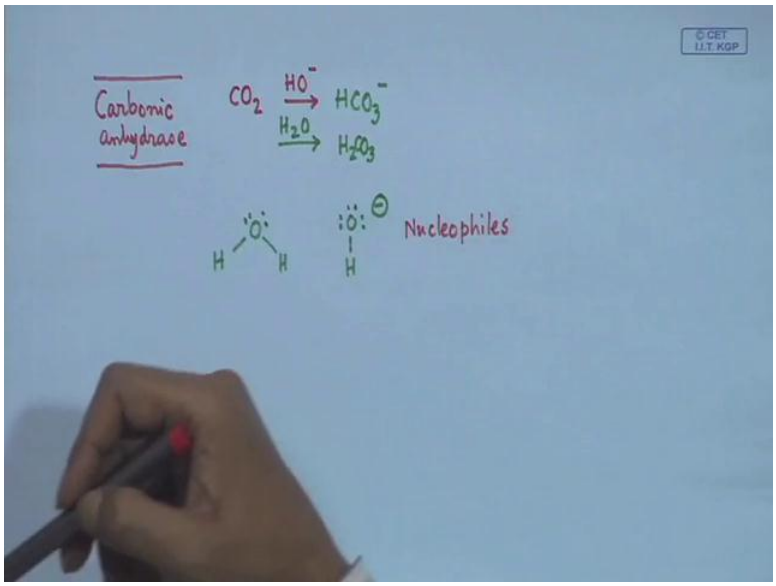

So, this is some kind of reactivity if at all what we know that for the corresponding hydration reaction of carbon dioxide. So, if we get the corresponding hydration reaction for carbon dioxide we call it has a corresponding reactivity for carbonic anhydrate. So, in case of carbonic anhydrate that means, this the corresponding conversions for carbonic acids and it is corresponding anhydrous form that is the carbon dioxide. So, if this is there then HCO 3 minus bicarbonate an iron is forming.

So, when it is reacting with HO minus responding carbonate iron and if it reacts with water molecule it is giving rise to the corresponding carbonic acid. So, this sort of things that means, whether we can have a reaction where we get a corresponding lone pair of electron. That means we have the water molecule and the corresponding lone pair of electrons available on these oxygen can attack to certain site that means, the carbon site which is corresponding electromotive in nature.

So, this particular water or these OH function have this lone pair of electrons on this and they have the charge. So, these are basically very good nucleophile. So, this nucleophiles when attack on the carbon dioxide water molecule it shows the corresponding reactivity pattern for carbonic anhydrate. And similar thing is also happening over here is the reagent which we get that means, the molybdenum hydroxide species. So, the molybdenum OH function the molybdenum OH function is basically available.

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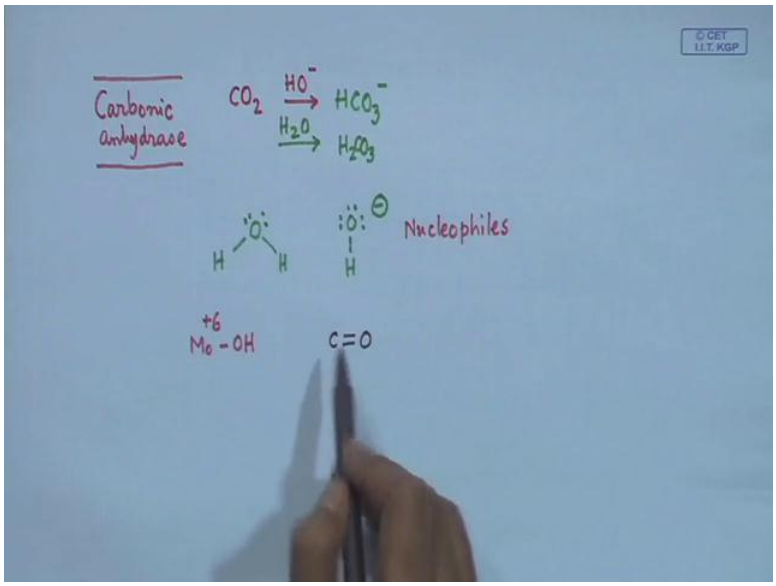

So, it is the same thing that these we talk about here that is the hydroxide function or water molecule there are very good nucleophiles. Also the molybdenum saying that has the higher oxidation state of class six something if it is there in the class six oxidation state. The nucleophilic corrector on these OH function which is attached to the molybdenum site is typically enhanced. So, it is much more stronger nucleophile compared to the isolated hydroxide an iron.

So, these molybdenum bound OH function can very easily attack the corresponding carbon monoxide molecule transfer this oxygen or OH group to this one. So, when this is there that means, the hydroxide nucleophile is further activated by molydbenum coordination and it is attacking to the attacking to the carbon monoxide molecule.

When this carbon monoxide molecule is suitably placed close to this part of the enzyme that means, this part if the molybdenum hydroxide function. And when it is there that means, the suitable functioning of the entire selanylcysteine is also taking part there and the weak interaction between the carbon silinium is getting lost.

So, in that particular position it delivers the electron to the intermolecular electron transport chain composed of two types of 2Fe and 2S clusters and flavin adenine dinecleolide.

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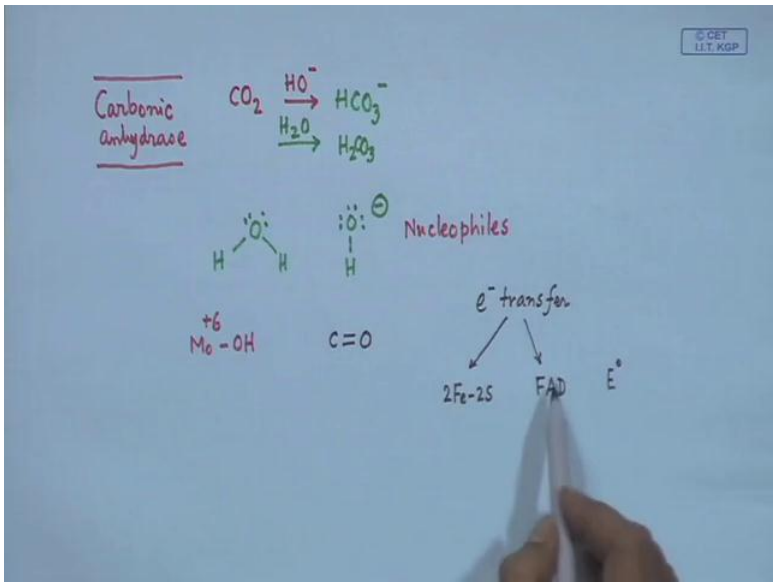

So, the electron transfer. So, two types of electron transfer. So, if we see that electron transfer is prepared for the oxidation reduction of the molybdenum site and electron transfer for some other part of the ligand system for the conversation of these hydroxide to water or the oxofunction. We need 2Fe two sulfur part as well as FAD part. And they are having two different E 0 hallows. So, depending upon the requirement or the corresponding reduction potential or the matching reduction potential for this molybdenum site or the other part we require the two iron two sulfur site or FAD site for the reduction.

So, in that particular way the anaerobic microbes so that is why, what we have seen that both these things both aerobic bacteria and anaerobic bacteria. There this anaerobic microbes can also have molybdenum iron flavin carbon monoxide dehydrogenase for oxidizing carbon monoxide during their respiration also. So, they are dependent on the carbon source for energy. So, the particular carbon zone when it is in the anaerobic condition that means, oxygen is not available there for the corresponding oxidation carbon monoxide to carbon dioxide.

But these OH function is basically originating from the water molecule. So, these OH function, which is attached to the molybdenum site can deliver these oxygen to the carbon monoxide carbon to convert it to carbon dioxide. So, during that sort of desperation where this microbes are surviving on carbon particles or the carbon source as

well as converting these carbon source to carbon monoxide. And finally, that carbon monoxide is ultimately bound to have it to convert it to carbon dioxide.

So, molybdenum is basically assisting in supplying these oxygen atom to the carbon monoxide molecule. So, these monolenious side therefore functioning as a very good oxo transfer reagent to carbon monoxide itself. So, we see find here that another group of carbon monoxide dehydrogenize molecule. Where the molybdenum site is responsible for transferring the activated OH nucleophiles to the carbon monoxide to converting it to carbon dioxide and the result is you have with the corresponding oxidation of carbon monoxide to carbon dioxide.

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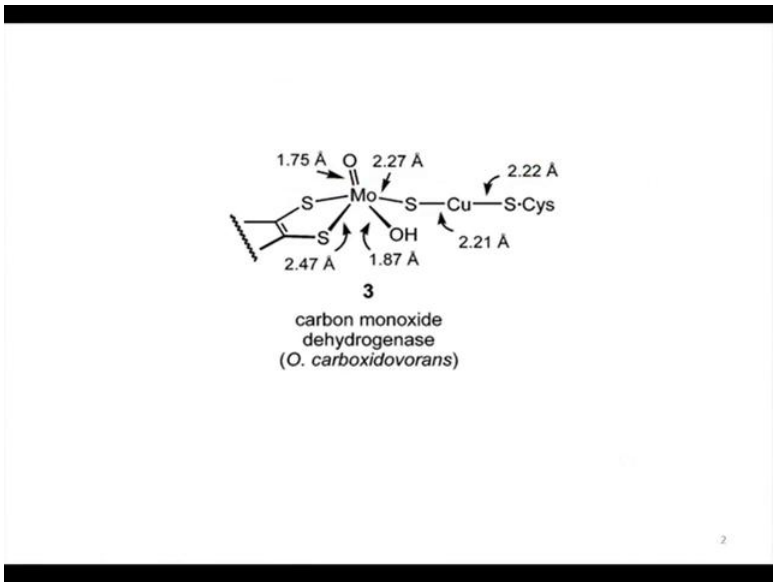

So, if we consider from another source, which is O carboxidovorans so, different bacterial source or the biological sources that they are for getting the carbon monoxide strength from their. Their corresponding changes are also observed that in one particular case this carbon monoxide dehydrogenase as CODH as different sort of things that this copper site is also available that means, it is dependent on another metal center for it is stability which is breezed by the corresponding sulphide function.

So, molybdenum if it has the terminal sulphide function so, that terminal sulphide function can behave with a very good ligand to any other system or copper system sulfur it should be basically initially what we have the we have the isolated copper system sulfur bearing species. And this molybdenum with the terminal sulfur group if it is their

terminal double bond sulfur which then start interacting with the copper site forming (based on this sulfur. So, what we need for this carbon monoxide dehydrogenase behavior that means, the transfer of these oxygen atoms from their, but now the environment is little bit different.

Compared to our previous environment where we have the typical dioxoform plus you have the corresponding hydroxide function attached to the molybdenum. So, here instead of that dioxoform you have the molobdum molybdenum site and this molobdum molybdenum site instead of having these second oxo function. We have a sulfur function it can it can be considered has this sulfur is there. As a dioxo function instead of another oxo and when it is interacting with the copper site it is converting to a sulfur beach.

So, the OH function available from their and it also shows the corresponding that the molybdenum oxygen bond is strengthened and these bond is strengthened basically can be distinguish that these molybdenum oxygen is a OH function or it is a molybdenum dioxide function. Because the molybdenum dioxide dioxide distance is sorted at a 1.75 Armstrong compared to molybdenum OH distance which is 1.87 Armstrong.

So, this particular one which having a longer bond distance already portanated, these OH function can attack the same carbon monoxide molecule and that carbon monoxide molecule can show it is corresponding behavior for oxidation by abstracting this OH function from the OH group attached to the molybdenum site or it is related conversing to carbon dioxide molecule. And the molybdenum site is showing it is corresponding site carbon monoxide dehydrogenase activity.

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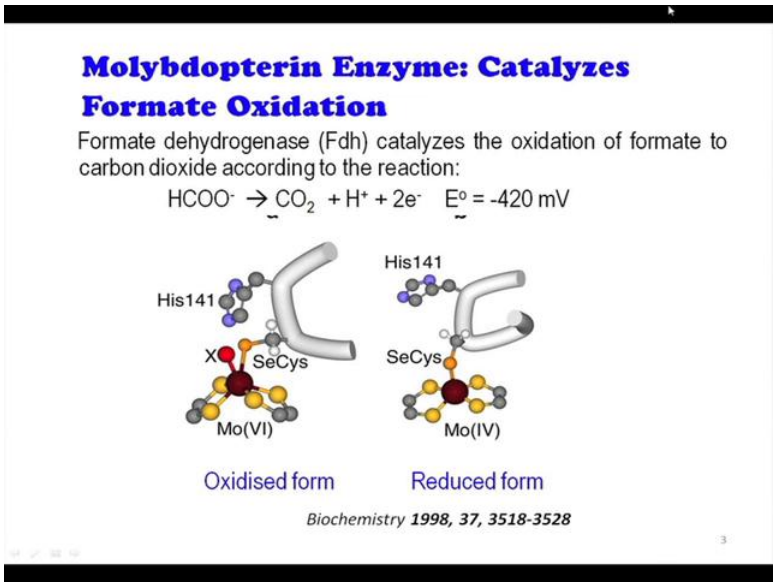

So, next is that another group of molecule related to the acculamation of this carbon bearing species because in biological system particularly the all aerobic and anaerobic bacteria the different microbes we are facing something were we can have this corresponding format type of groups are also available there.

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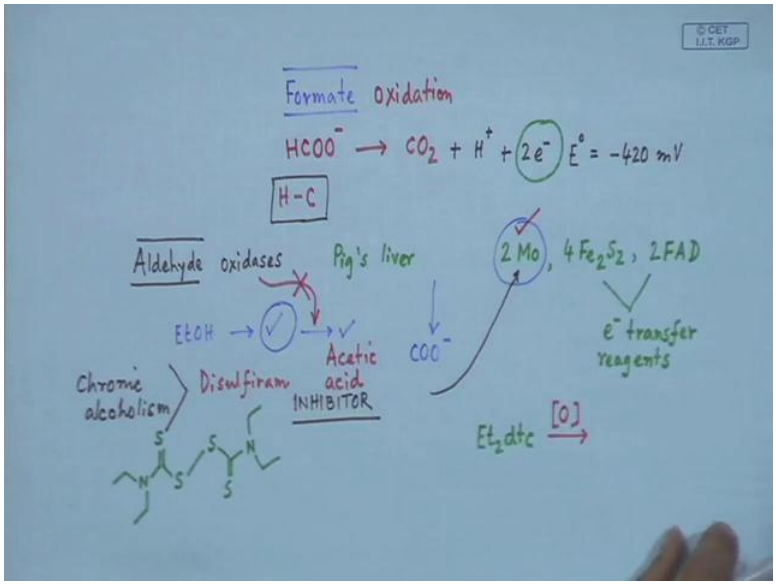

So, if we have any formate group so, this formate group another source of carbon bearing molecule, but here we have already this particular carbon is attaching to two oxygen. So unlike our carbon monoxide system, because in case of carbon monoxide system we

have the carbon attached to one oxygen end, there is plenty of scope for further oxidation of that side to carbon dioxide. But in this particular case, where the format is also oxidized to carbon dioxide. So, basically what we gave this view is also present over there and apart from that we have a carbon hydrogen bond.

So, basically for getting the corresponding format oxidation reaction we want to see something where we get this particular carbon hydrogen bond (( )). So, this carbon hydrogen bond (( )) important and this particular bond is the most important step for the format of oxidation reaction, and some other cases also related to these because this is format of oxidation and another oxo molybdenum bearing enzymes, which is responsible for the oxidation of aldehyde also. So, aldehyde oxidase are there and side by side you can discuss these two.

Because where we are talking to something where we have to to where we are talking something the most oxidized form of any carbon bearing species we know that is carboxy form goes if something is available in the alcohol or phenol form which can be oxidized aldehyde form. And that aldehyde form can be oxidized to corresponding acid form, an acid form is further responsible for elimination of carbon dioxide that means, is oxidation. Because this is when forming CO 2 it gives us the h plus from the this cleavage of this proton from the carbon and 2 electron.

These 2 electrons immediately (( )) that the typical oxidation reaction at certain (( )) value which is characteristic format of oxidation which is minus 420 mili volt. So, these particular values. Is important to seen that means, we have to supply this potential that means, we have to have some corresponding oxidizing agent which can take off these electrons these two number of electrons which is coming out. From this oxidation reaction so something should be there that be some oxidizing hint is their should be their. Having easy ray value of these which can be utilized for the corresponding availability of the electron form this format species.

So, in case of aldehyde oxidases we can have also with the common source of this is the pigs liver. Because all we know that the liver is responsible our mammalian liver is also responsible for the oxidation of alcohol to aldehyde and aldehyde to corresponding carboxy acids. And in this particular case, we need 2 molybdenum centers, 4 two iron two sulfur system that means, FE2 S2 we can write an in another form. So, also 2 of the

ferrine adinin dynuclirides are available there and those ferrin adinin dynuclirides are basically these two all we have seen that these are the the corresponding electron transfer reagents.

So, these electron transfer reagents can supply the corresponding electrons to the system for showing the corresponding aldehyde oxidation reaction. So, during this aldehyde oxidation reaction your molybdenum site is very important. And this molybdenum site is responsible for the production of the oxidation of the aldehyde to its COO minus that means, the corresponding carboxyl acid acid function. Which can be your formic acid also when we have the formaldehyde as a the source. But when we have the other acid like, when we have transferring we have converting the corresponding ethanol to acitaldehyde and then to acetic acid.

So, ethanol can be converted to their corresponding liver alcohol dehydrogen is there. So, liver alcohol dehydrogenies are available. And those liver alcohol dehydrogenies can oxidized alcoacete acitaldehyde. Then when it is forming the corresponding acetelaldehyde. This acete aldehyde molecule can be oxidized by the molybdenum site. To it is corresponding acetic acid form. So, this acetic acid form is again go for this production and if the intermediate is there that means, these aldehyde oxidase which is operating over here is not functioning and which is molybdenum dependent.

We also the human being also (( )) lots of problem related to the corresponding alcohol consumption. So, if we have alcohol and then alcohol is forming some amount of aldehyde in our body that means, the acetic aldehyde is form an immediately these aldehydy oxydases can be oxidized the corresponding acetic acid.

So, this is your acetic acid as our n product. So, if we go for something that means, if we can stop the action. So, again this is also molybdenum bearing thing that we are not discussed in here in detail because we have to discuss the format oxidation in detail. But one important reaction for these corresponding innovation of these aldehyde oxidases. So, if we care able to inhibit the corresponding aldehyde oxidatses. So, immediately due to the consumption of the ethanol.

So, the corresponding acetic acid is not form in our body. And liver is accumulating some amount of acetealdehyde. So, to stop the corresponding action of the aldehyde

oxidase. What we get that is inhibiter action. So, some inhibiter should be there. So, this inhibiter basically walking on this molybdenum side.

So, this is very simple and the classical knowledge of in activating the molybdenum side. Such that we are able to stop the corresponding function of the aldehyde oxidases. So, what people can do people can do that is as where the people are suffering from chronic alcoholism. Chronic alcoholism people are very much dependent on alcohol then. So, in chronic alcoholism one particular types of molecule which is known as dysulfuram. So, dysufuram is a very impotant type of molecule which is based on N N diethyl amen which is giving us when N N diethyl amen is reacting with carbon disulfide.

We get N N type ethyl corresponding di thio carbonate. So, this is N N di thio di thio carbonate. So, one unit of these and another unit of the same thing that means, it is the dimarized form. So, dimarized form of Et2 dtc. So, Et2 dtc di ethyl di thio carbomate. So, it is the dimarized form of that di ethyl di thio carbonate is in our hand. And interestingly that is the corresponding oxidized form that means, if we have the di ethyl di thio carbomamate and we oxidized it. So, oxidation gives rise to electron loss.

From S minus and S minus of the dio thermite carbomative unit giving a S S bond. So, this is the oxidized ligand and trade name of this is the corresponding disulfiram. This disulfiram can very easily function on these molybdenum site to so, the corresponding inhibition behavior on aldehyde oxidases. So, this aldehyde oxidases is not able to function then. So, the fluctuation with the corresponding molybdenum center by the aldehyde oxidase is lost. And the enzyme is becoming inactivate and the body is accumulating the person who is suffering from this chronic alcoholism. Will now have enhanced amount or enhanced concentration of acytil dehyde in the body. Seeing some unpleasant effect to the person. So, that particular one we when we have the corresponding accumulation of these aldehyde that means, what we are trying to show when the inivation is not there.

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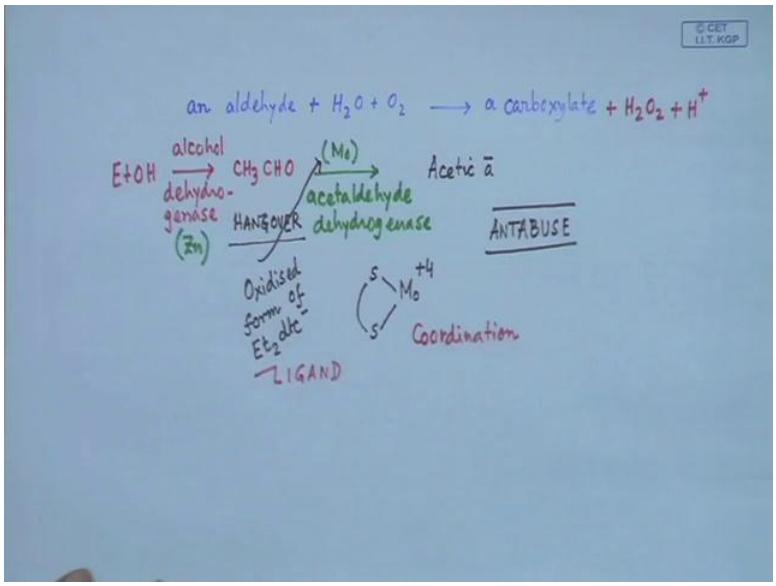

We have an aldehyde and that aldehyde is reacting with water and O2 giving a carboxylate verse for the corresponding aldehyde a carboxylate. Some amount of the corresponding h202 and the proton. So, we have ethonyl the person who is taking the ethonyl in this body forming acytil dehyde by the action of liver alcohol dehydrogenase. So, alcohol dehydrogenase we call dehydrogenase which is a zinc dependent enzyme. So, this alcohol dehydrogenase is a zinc bearing enzyme.

So, nicely it can convert the corresponding ethanol to acetaldehyde. Now you have the molybdenum bearing, now it is molybdenum dependent. Molybdenum dependent acetaldehyde dehydrogenase which is acetaldehyde dehydrogenase. So, this acetaldehyde dehydrogenase if it works nicely it can produce the corresponding amount of acetic acid of that alcohol consumed by the person. So, the di thio carbomate based corresponding di sulfurim. If it is added. So, di sulfurim is attaching there and this is the corresponding oxidized form of the dtc oxidized form of di ethyl di thio carbomate.

So, this oxidized form of di ethyl di thio carbomate. When it is given to the molybdenum site the form is then reduced that means, the molybdenum site will be in the lower oxidation state. that means, if these molybdenum is present in plus 4 or plus 5 oxidation state. It just happily accept that particular di dilfirom which is functioning as a good drug. So, it is antabused drug. Which is antabused alcohol abused antabused drug. So, if that antabused drug is available and that nicely binds to the molybdenum site. Since this

is the oxidized form. So, this is getting reduced and the molybdenum site is getting oxidized and the sulfur sulfur fluctuation is there.

So, the acetaldehyde dehydrogenase will not walk properly to act upon the acetyl dealdhyde formed in the body of the person. So, that is why we get accumulation of these acetaldehyde in our body. And that condition we call it has a very unpresent situation to the person who is consuming alcohol which is nothing, but the hang over condition. So, if we are able to control. So, if we know the step wise is the formation of these things. How alcohol dehydroganisation is working and how the acetaldehyde is functioning?

But knowing the very simple coardsan chemistry so, this part is nothing but the corresponding coordination chemistry on molybdenum site. So, what is our drug. So, these these coordination the drug is our corresponding ligand. So, these ligand is available and this ligand is going and attaching to the molybdenum site.

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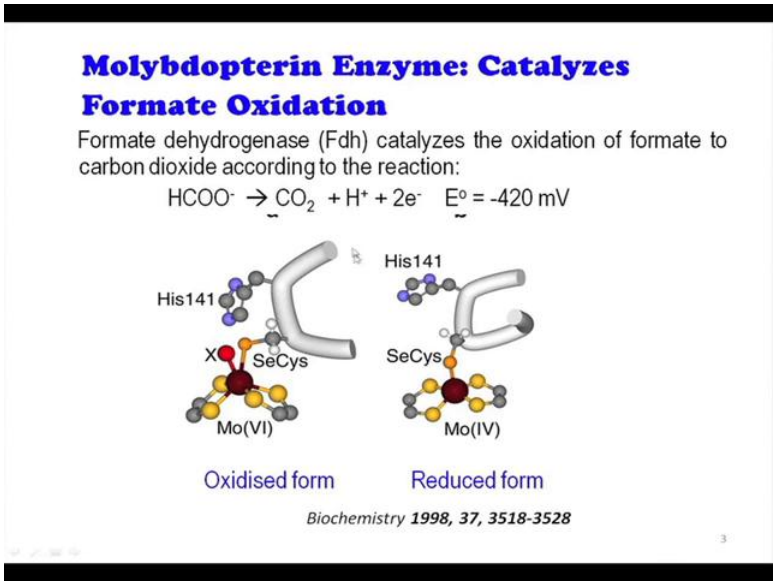

So, next if we see in that way that format the dehydrogenase now we have the ultimate form which is the oxidized form that means, the aldehyde has been oxidized and that aldehyde oxidized form is your formate. When we have the formate aldehyde in the system. So, formate dehydrogenase which is abrogated as Fdh which can catalyze the oxidation of format to carbon dioxide as for the following reaction. So, here we have already told you that the corresponding redox potential is important. And this redox

potential can give rise to the corresponding conversion from the format an iron to carbon dioxide. So, here also silinium bearing cystline recude is important. Thus we have seen just just now carb carbon monoxide dehydrogenase. And when this is attaching to the system. So, you have the long protein chain. And this protein arm his available and this arm is bearing one listineu recude which is listed in 141. And for the conversion from the oxidized form to the reduced form. We see something very interesting situation.

That this particular part though you are simply converting that these we are going for electron transfer. Because this particular enzyme where we can have still the iron sulfur molecules. The iron sulfur cluster molecules and fad molecules which they are available for the reduction of the molybdenum site. So, molybdeum site in plus six oxidation state can be reduced to molybdenum in plus five oxidation state and that plus five oxidation state can also be reduced to the plus four oxidation state.

So, we have these two forms which are most stabled. One is the oxidised form and another is the reduced form. And interestingly once we can have some modeling experiments people have done to propose the corresponding geometry around the molybdenum. As well as the corresponding change in the corresponding protein environment or the enzyme environment. So, in the oxidized form when molybdenum is in the highest possible oxidation state ,that means this size of the molybdenum site is small and this molybdenum site is always favored to bind.

It is maximum numbers of donor groups around it that means, it will prefer a corresponding coordination number of six. That means, a hexa coordination geometry should also be preferred for these molybdenum site. But since this particular one in within the enzyme pocket. We cannot get the most stable or the most regular corresponding coordination environment of six coordination number. That means, the octahedral geometry. We are not getting any octahedral geometry around these molybdenum site instead. We get some distorted octahedral geometry this is a highly distorted octahedral geometry.

Because ,it is not related to any square pyramidal geometry or it is not related to any kind of octahedral geometry. So, this highly distorted geometry has some coordination with the geometry which is available which is fevalent in the reduced form that means, when we have the molybdenum in plus four oxidation state. So, already this molybdenum site

has taken up two more extra electrons and those two electrons are attached to the molybdenum and the molybdenum site is now bigger.

So, these particular site will not attract all the six groups. So, it is happy it can stay in a five coordinated situation and instead of having some coordination from other extra group that means, the x group it is only bound to the cystiyne sulfur recudes. So, the cystine recudes that means, selenium selenium group. So, selenium atom is attached to the molybdenum site and it is again a little bit of distorted square pyramidal in geometry. That means, this four sulfur groups from the molybdopterin part these molybdopterin enzyme we are talking about the enzyme which is the corresponding molybdopterin enzyme. Because the molybdopterin part is our enzyme part.

So, this di sulfur group so, di thio group so, these two site di thio functions are there which is attaching to the molybdenum site and the fifth position is occupied by the selenium group. So, we get a highly distorted square pyramidal geometry and at the same time, this histelein 141 group as also moved little bit and these corresponding coiling of these particular backbone the protein backbone has changed. And this particular one is also telling us in that way that, the if the inter comparison is taking place from one part to the other. That means, molebdenum part to molebdenum enzyme.

We see that one in one hand if we can have the corresponding square kilometer geometric. and if we put the extra group this can be S that mean this can be allot. Which functional so, which is available for the carbon monazite dehydrogenase activites any other groups any unknown groups will evaluate oxide. So that unknown function is attaching to this particular side. At the side where the selenium group is also attach. It is not that it is going from bottom.

So this part length the is foots fare length on molybdenum. It is highly distorder and it is the going towards the corresponding silinium atom. And that's y the when the other group that means group X planitise coming . It is not going from the other side to make this particular geometric perfectly octra hectra in type. Estate it is attaching to the side where you have some available vacancy. These two groups have also most from these particular orientation and the get a highly distracted geometrics. So this, highly distract co ordination geometrics for any metal compiles is they are very much reactive.

So the reactivity pattern for those groups center and molybdenum is highly dependent on it is among the distortion and among the group ax which is attach the molybdenum That means if it is Oh which function it can remove from this particular side immediately when the sacristies available. So if the sacristies near by the molybdenum side. This S group can be donate to the sub site like wise what we a getting for the conversional the carbon monoxides to carbon dioxide by the donation of this OH group attaché to the molybdenum side.

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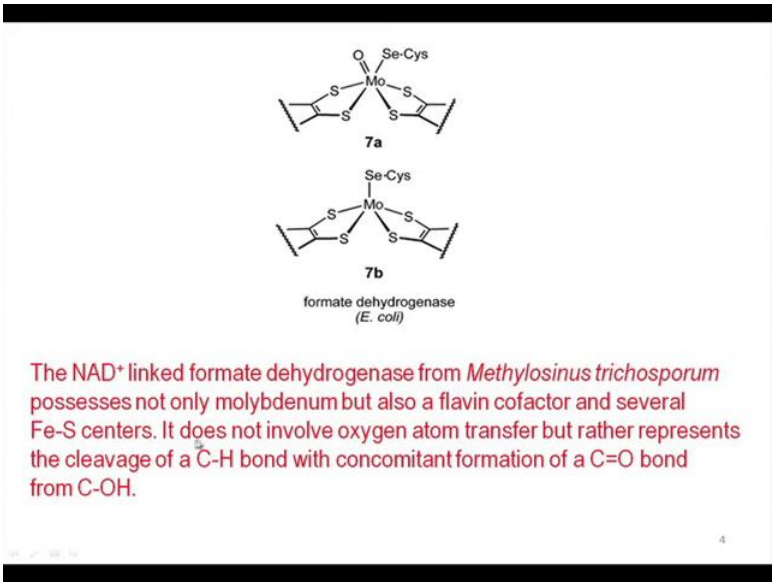

So if we have this is the situation where you have the pentad coordinate form. And this is a situation had we have the is that coordated form. So in inter co-ordinate form we have the selenium atom only attach the molybdenum side. And in the hexa coordinator form. We have the extra dioxide group attach to this selenium system. So that nicotinum my base not (( )) base. But the nicotinum my base some group so also available which can provide the electron to the system that means electron to the molybdenum. And obviously when we move from a group like fad to NAD.

We see that very is a change in the corresponding potential that each group allow is changing. That means in this particular case requirement for the reduction at some other potential which is different form fad. So NAD plus link format the hydrogenase. Which is getting form which your getting from another source so this is methylosinus trichosparm .If which has not only the molybdenum but the flavin cofactor also a flavin

cofactor is allot not flavin base but it is nicotonim my base. And some other iron sulphur centers. So it does not involve in other kind of oxygen atom transfer but represent the cleavage of the C-H bond.

What to a just discussing that the cleavage form the for made group. That means when you have the formic oxide a COO minus. A COO minus if we can break this bond Ch bond .We get the corresponding formational that carbon dioxide. So once we get discuses corresponding breakage of breaking of the corresponding CH bond. And at the same time we get the corresponding CO conversional C-OH group to C double bond which is very easy to have it. Because we already know that in the carbonze function. Two oxygen at terms a attach to this particular carbon side. And when this is forming the (( )) corresponding (( )) stay for this reaction is a corresponding bond cleavage is CH bond cleavage. And the formation of C double bond O form Co-H function

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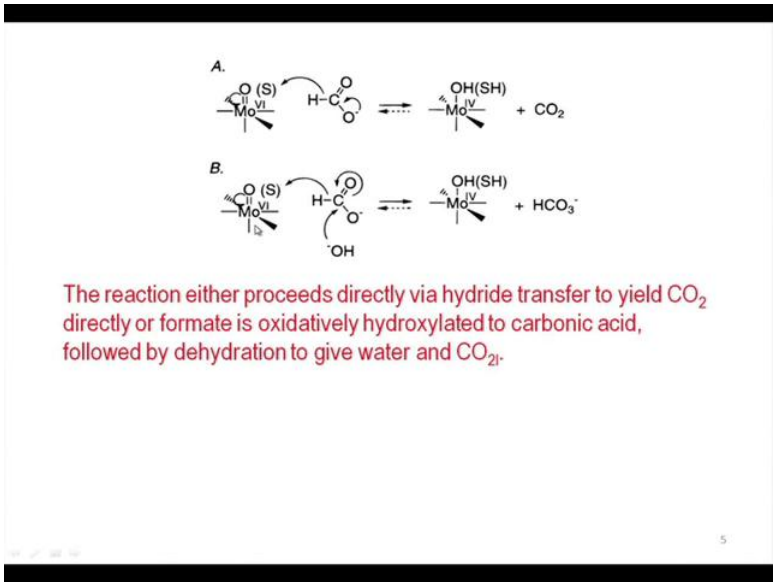

So to such possibilities we can have in our hand. Then molecular side is available and earlier proposal for that when the excess structure not known. If initially hard that is molybdenum side is attached to our assoc center. And this oxide center is in terms of its left on transfer these a electron density around this atom or around this molybdenum can give rise some important observation that how this format and none. This a format and none how this format and none is going to attack this molybdenum side. So the reaction can have two path. One is path a and another path b.

So these two path basically in one particular case it processed directly for the hydrate transfer. That's why what calling it corresponding CH bond cleavage. To hydrate transfer which is eliding Co2 so ones the hydrate transfer is taking part to a hydro oxide form a molybdenum in plus six oxidation state we get siddly the carbon dioxide and these O on the the molybdenum side is convert in to OH. Similarly sulpher is the very level little bit convert into is age. And another alternative path is the format is oxyidately hydro oxalate to carbonic oxide.

So these OH another nuclio file go nuclio file is coming now in to picture. And which is attacking TO these particular carbon. And when this hydrogen is transfer to your center on molybdenum oxfor as O is stage and OH. So, if it is sulphur it will be converted into stage, if it is oxygen will convert into OH .So during the conversion like the previous one that is the plam plus six to plus four. But now this oxygen is coming from hydroxide function not from the corresponding oxygen. What is available from their. so we know have the corresponding CO of oxygen on this carbon.

And which is their ford the corresponding the hydro oxalate form of the carbonic oxide what do have this discus just now. That carbonic and hydroger activity that means carbon dioxide can be alloy with a water molecule or OH minus to give the bicarbonate and an. That bicarbonate and nine for the golf for that dehydration to give as the water molecule and CO2. So we can have the two different choices because surrounding this enjoying. We have the hydroxide function length of hydroxide function and also we can have molybdenum on this oxygen atom.

So the leveling the experiment, if we go for complete leveling experiment on O eighteen. Using O eighteen and some of the leveling experiment and carbon protein also. So the leveling experiment based on O eighteen on the hydro oxide function are O eighteen attach to the molybdenum side. Will clearly till as the pitch particular path can be taken off. For the formation this particular carbon dioxide from this format and none. If the is the directly following from path a. We don't recollect any search level oxygen at at term on the produce carbon dioxide.

So gas geomatagraphy so GCMS discus chemotograph mass spectra meter. Which is length width the mass spectrometer the GCMS experiment. So GCMS experiment can identified the corresponding molecular with of the level and the under carbon dioxide.

And with the level has this two the produce carbon dioxide. We can identified that the park is other form that a path on form if path which is coming from the big path. So, this is the think that were we get the half format is skidding oxidized due to the presence for molybdenum into different oxidation state.

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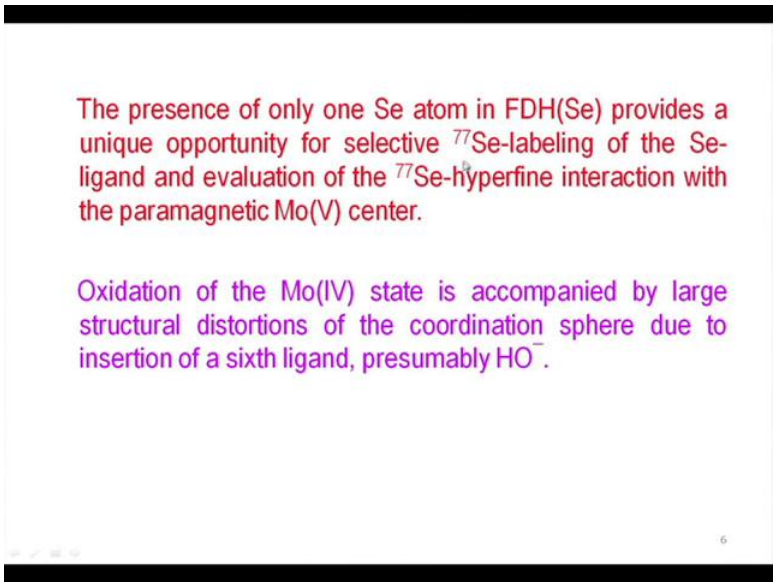

So this particular one so next will just consider that how the different leveling experiment on.

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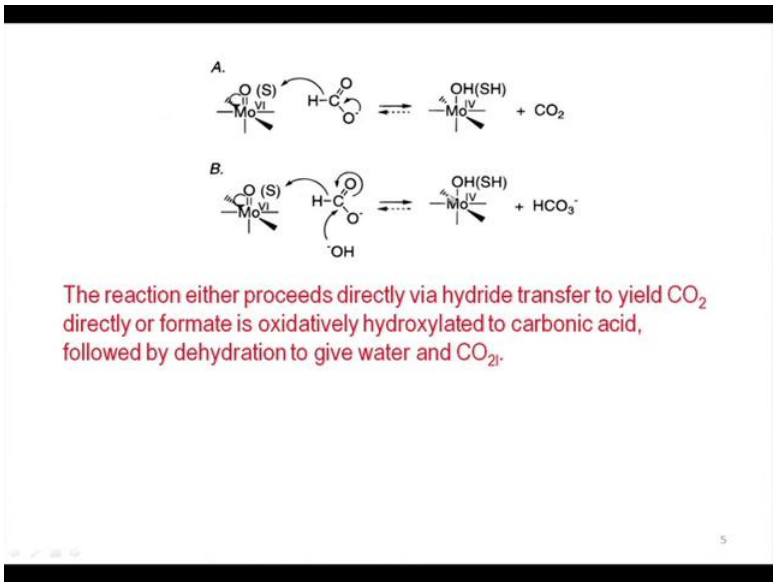

The selenium atom using if we a spectroscopy, ok.

Thank you.