**Bioinorganic Chemistry**
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**Lecture - 24**
**Molybdenum Enzymes - III**

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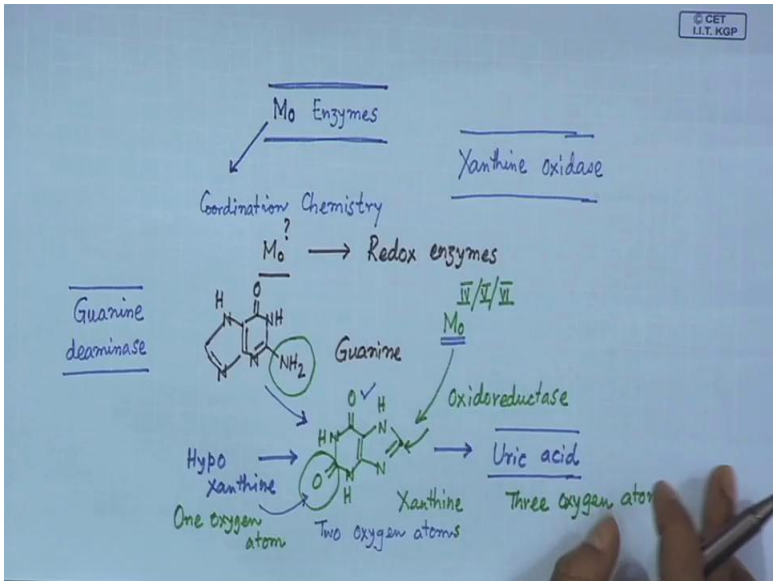


Hello, good morning everybody. So, we will still continue with our system which we are talking earlier about the molybdenum enzymes. And these enzymes are very useful in nature, because we are all using the corresponding coordination chemistry of the molybdenum center, and the central role which is been played by the metal ion is molybdenum in its several oxidation states. And during this change in the several oxidation states, it can go for a corresponding reactions and related to all these enzymes is the corresponding redox enzymatic catalysis.

So, we will see how the different molybdenum centers in all these biological systems are useful for all these redox catalysis in these redox enzymes. And this particular one is useful when we think of the very basic molecule like that we get from the different nucleosides is our the heterocyclic molecule guanine. So, we should know what is that particular molecule, and why we should know about this guanine which is the basic unit in all the different nucleosides and nucleotides; and this particular one is the guanine molecule.

So, this particular system whether this particular molecule can interact with that of our molybdenum center in different oxidation states starting from plus four, plus five and plus six. So, this particular guanine molecule can generate something what we see which is very much related to that molecule is that of our xanthine related molecule. So, we should know what is that xanthine. So, this xanthine molecule whether we can get that particular molecule from the basic ingredient, which is our guanine molecule, so if we write, so that is on the right hand side, because of five membered ring; here I have drawn it on the left and this is the five membered ring is drawn on the right. So, the basic change from this is that how if this is our xanthine molecule and we will be talking something related to how this centers; that means, the molybdenum centers the molybdenum enzymes which are functioning as the corresponding oxido reductase family of molecules.

So, these are therefore, the corresponding oxido reductase activity. So, this oxido reductase activity whether this molybdenum is the best choice for us for this kind of oxido reductase activity on the xanthine molecule and that will see that this particular xanthine molecule which can be derived from something; that means, if we get that particular molecule, some other molecule with some modification on the entire molecule which is hypo one; that means, it is the hypo xanthine, and it goes from hypoxanthine to xanthine, and then xanthine goes to uric acid.

So, if all these reactions are basically catalyzed by that particular molybdenum center and if we know the basic structure of these molecules, and what are the differences between these structures; that means, how xanthine is different from guanine, and if there is any biosynthetic approach is available in the living system that guanine molecules which is plenty and which is related to our purine and pyrimidine metabolism. So, how we get this particular xanthine molecule from the guanine molecule; that means, this particular pathway which is important and this is not our concern for this class that how this particular system is coming from guanine molecule, because there is one important group of molecules which are not belongs to this oxido reductase family of molecules, but they are guanine deaminize. So, as the name tells us that it is basically functioning some reaction or catalyzing some reaction where the amine function goes away; that means, in this particular molecule if the guanine has some NH2 function attached to the 6 membered heterocyclic ring containing this oxygen and two nitrogen’s on it. So, this N

H 2 function when goes out; that means, the guanine deaminize is working on guanine molecule and that guanine molecule is getting transformed to xanthine molecule.

So, this is one aspect which is not related to molybdenum, but you should know little bit of that how you can remove this N H 2 function from the entire basic structure of these and at the same time if we just turn around in the other side that this NH2 part to this NH2 part is now occupied by some Oxo function on the ring. So, we can think of that this molybdenum center what is present is basically doing some reaction where you can takeout or you can add some of the oxygen groups or the oxygen units on the heterocyclic ring. So, when already we have in the guanine molecule which is the parent molecule; already we have this oxygen function on it. Now, we are attaching another oxygen function by removing this NH2 group from the parent molecule. So, this is basically a molecule which has two oxygen atom on the ring. So, it is two oxygen; these two atoms are present on the ring.

So, if we go beyond this xanthine; that means, if we start from hypoxanthine to get xanthine, this hypoxanthine molecule is little bit different from that of our guanine molecule. So, if this oxygen is not there; that means, this will divide of this oxygen function on the entire molecule that is known as hypoxanthine. So, these oxido reductases based on molybdenum when they are working on hypoxanthine they basically insert or reduce one oxygen atom in the form of the ketone function on the six membered heterocyclic ring producing the xanthine molecule. So, this molybdenum enzymes are responsible for producing xanthine from hypoxanthine. So, not only that again it further, another group of molecules which will be active on the xanthine molecule itself; they are producing the uric acid which is also producing in our body.

So, this particular reaction when the xanthine is transforming from its own xanthine molecule to uric acid we call these molecules as xanthine oxidase, because the xanthine molecules are getting oxidation. So, this is basically a oxidase activity and for that particular oxidase activity, we get the substrate which is our xanthine substrate and the molybdenum based oxido reductase enzyme is working on it to insert further oxygen on the molecule that we will basically see in this particular class that how this oxygen is getting inserted on this carbon which is flanked by two nitrogen atoms; basically producing a system of uric acid where in the molecule like this of hypoxanthine and xanthine, we have three oxygen atoms now. So, we have three oxygen atoms; this is also

two atoms. So, therefore, it has one oxygen atom. So, in this form it is very easy to remember also and we can recall anytime that how the xanthine is different from hypoxanthine? How we get xanthine from the reaction of these guanine deaminize on guanine? Because we know the four basic nucleotides the adenine, guanine and two others which are responsible for the formation of DNA and RNA molecules, and these xanthine molecule further producing our uric acid in the system.

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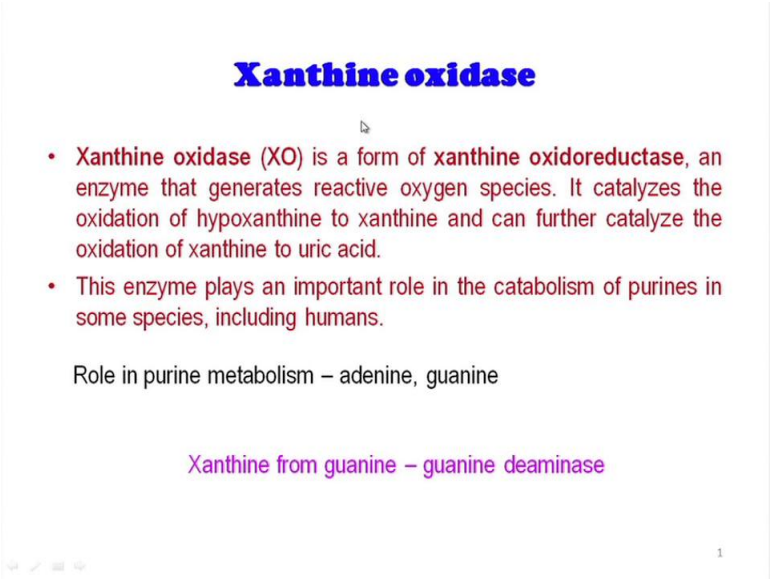


So, we get this Xanthine oxidase system and this xanthine oxidase therefore, basically a form of xanthine oxido reductase that we already told you that an enzyme therefore, how we can define that particular system generates reactive oxygen species. So, we call all these reactive oxygen species as ROS and these ROS groups are very important. So, we see that it catalyzes the oxidation of hypoxanthine to xanthine and can further catalyze the oxidation of xanthine to uric acid. So, the system; that means, the chain of reactions which is dependent on molybdenum and all these molecules or all these group of systems which we consider as xanthine oxidases, they are responsible for transferring these hypoxanthine to xanthine and xanthine to uric acid.

So, what we get the information which is the right one information for the production of uric acid in our body. So, the accumulation of large amount of uric acid in our body is basically dependent on the activity of these xanthine oxidase molecule, it also depends on the availability of this xanthine oxidase molecule, because we do not know how much

xanthine oxidase is available in the living system in our body also. So, it depends on the molybdenum availability also and what we have seen that this xanthine can be produced from the guanine molecule also. So, it can also control the corresponding balance of the guanine xanthine conversion as well as the conversion of xanthine to uric acid. So, basically it confirms us that we are going for some degradation reaction.

Where if you need large amount of guanine molecules to RO to stay there to form the DNA and RNA molecules, but at the same time if the guanine molecules are transforming to xanthine and then xanthine is transforming to uric acid, we are losing the most important molecules like guanine as well as xanthine from our system. Therefore, this class of enzyme or this enzyme plays an important role in the catabolism of purine in some species including humans. So, if we go for a catabolic reaction on purines and these purine molecules are not available, because these two purine molecules are very important; we all know the adenine and guanine. So, ATP molecules are also related to adenine.

So, adenine is related to ATP molecule then guanine is also the corresponding triphosphate molecules are there. So, if we go for any catabolic reaction on guanine that will immediately produce xanthine and that xanthine production will also be dependent on the corresponding production of uric acid. So, little bit we should know what I have told you that how we get the xanthine from the guanine; this is due to the guanine deaminase and then xanthine oxidase is coming into the picture, it is working on the on the corresponding xanthine molecule to produce the uric acid.

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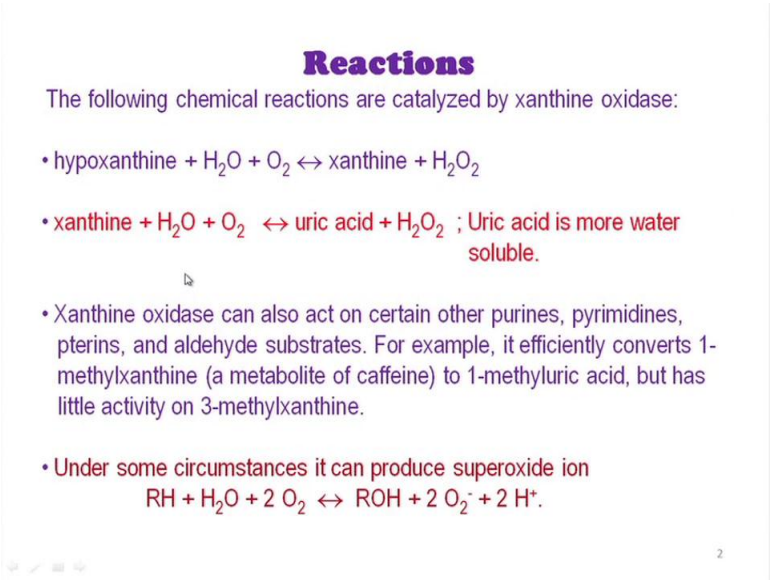


So, what are this basic reactions? So, structure wise we have seen that how the xanthine molecule is related to hypoxanthine molecule and xanthine is related to uric acid. So, we first know what those catalytic reactions are taking place. So, the catalytic reactions, all are catalyzed by xanthine oxidase is hypoxanthine in presence of water and oxygen is producing the xanthine molecule which is nothing but the corresponding oxygen insertion reaction on the parent molecule and at the same time it is producing hydrogen peroxide. So, when two such oxygen bearing molecules are involved in this reaction, because these are corresponding oxidase reaction; that means, we considering some reaction where the oxidation of the hypoxanthine is taking place. So, it is an oxidation reaction and if we find that the oxygen insertion is taking place.

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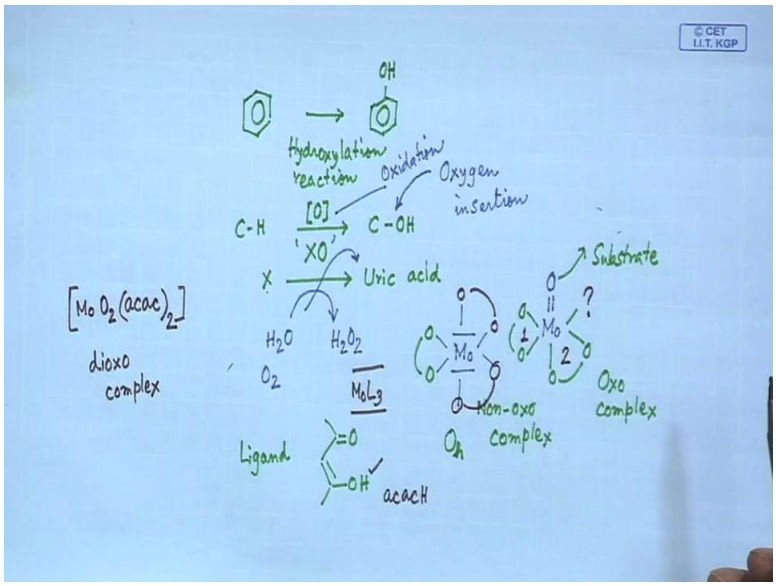


So, basic reaction is like that of our conversion of hypoxanthine to xanthine is nothing but is a corresponding type of hydroxylation reaction where we see that if we can have a benzene type of ring or molecule which can give us some phenyl type ring through that insertion of OH group on the CH function available on it, we consider it as a corresponding hydroxylation reaction. So, on the left we had a CH function and on the right we are getting a C OH function. So, this CH function is getting converted to C OH. So, this oxygen atom what is coming over there through that oxidase reaction or if you consider that of the conversion of the xanthine. So, xanthine oxidase is working on xanthine producing uric acid.

So, these two reactions are of same type and here on the xanthine also we have the CH function, and that CH function is getting converted to a corresponding C OH function on the heterocyclic ring not like a simple benzene ring type of thing where you have the entire skeleton is made up of carbon carbon bonds only, but there you have carbon nitrogen bond as well as carbon oxygen bond. So, the selectivity of that particular reaction is little bit different, but the typical reaction what is taking place there is nothing but oxygen insertion reaction. So, this is that particular oxygen insertion reaction and definitely, since this reaction is catalyzing by the reagent what we call as propending supplier of these oxygen; that means, those molecules which are behaving as a reagent over there can supply oxygen which is getting being inserted like that of your benzene ring or the xanthine ring is coming from two of these which is also very important one

which is available in nature also; that means, it is reacting on the left on H 2 O and O 2, and on the right hand side apart from uric acid we are also producing H 2 O two. So, during these particular reactions and all other reactions which are catalyzed by the available water and the dioxygen molecule; since, the basic reaction whatever we are writing over here is our oxidation reaction.

So, definitely the oxidation is taking place through oxygen insertion and due to this mixture of this; that means, the water and dioxygen you have one extra oxygen. So, that oxygen is going there to get uric acid from xanthine molecule. So, you have two reagents; one is water and another is dioxygen. So, it is very difficult to establish also and it is very difficult sometime to identify that whether this dioxygen is responsible for the oxygen insertion on the xanthine molecule or the water molecule is involved there for the insertion of the uric acid. So, to know that which is very important; that means, we have identified for all these system that the second group transition metal ion molybdenum in its all possible oxidation states which are definitely higher in nature which are plus four plus five and plus six and how this molybdenum center from starting from the very basic or very simple molybdenum complex; all we know.

So, this particular knowledge of coordination chemistry will help to unfold is also using for understanding how molybdenum center is responsible for this oxygen transfer reaction? So, if we have a non-oxo molybdenum center for the simplest possible arrangement, because the molybdenum center whether it is in plus four, plus five or plus six oxidation state, it can give us a corresponding hexa coordination arrangement which is octahedral in nature. So, these positions are all occupied by the corresponding ligand donor atoms whether they can be oxygen or nitrogen or sulfur, because the molybdenum will have high acidity for reacting with these species forming molybdenum oxygen bond, molybdenum nitrogen bond and sometime if the system permits or the available groups are there in all the living system or the non-living system what we have in the laboratory as the corresponding sulfur groups. So, we have a non-oxo coordination complex and that non-oxo coordination complex is converting to an Oxo complex.

So, formation of these two complexes immediately tells us that the molybdenum center has a very good affinity for reacting with oxygen center whether this can be supplied by large number of corresponding reagents; it can be simple water molecule; it can be the dioxygen molecule what is available there from there; it can be hydrogen peroxides or

any other peroxo reagents which can very easily supply the oxygen atom to the substrate converting it to the corresponding oxidized form. So, if we have a molybdenum based catalyst, immediately we will be tempted to think that molybdenum in its dioxo form or the non-oxo form. So, in the non-oxo form react with any of all these reagents, we do not know which particular reagent is therefore, giving immediately the corresponding molybdenum oxo species. So, that molybdenum oxo species is therefore, responsible for transferring this oxygen atom to the substrate which is very important.

So, whatever regent is getting activated, it can be your water molecule, it can be your dioxygen molecule or it can be your hydrogen peroxide, but will be activated by this transition metal ion the molybdenum from the second group transition element. So, this molybdenum center will be responsible for activating all these oxygen donors to immediately get a corresponding monoxo species or dioxo species. So, if this particular species in the catalytic form is not so stable, it can be our transient species also, but this oxygen is getting activated and then only these molybdenum oxo species can transfer these oxygen to the substrate molecule such that we get the corresponding conversion of the xanthine molecule to the uric acid. So, if we take a very simple ligand system, because like that of our protein we always think of some activation from the ligand system; that means, the coordinating groups.

So, the ligand system is there and this ligand system having two oxygen donor group. So, this is a bidentated very good ligand, which can immediately go and bind these molybdenum center in a bidentated fashion. So, this is nothing but acetyl acetone molecule and its tepodentated form, it is O O minus; that means, it is providing one single charge. So, this one acetyl acetone molecule can go and sit over this molybdenum center. So, if we think of that a particular non-biological system what we can get in the laboratory is based on molybdenum which is reacting; that means, utilizing the ligand which is acetyl acetone. So, if we have a molybdenum center and we take acetyl acetone AC AC, we sometime call it as ACAC ligand.

So, you have this ACAC ligand, you have this proton. So, this particular H goes away producing ACAC minus which has one single chart, because the charge neutralization on molybdenum center is also required. Because in most of the cases molybdenum is stabilized like chromium which is a group member of the chromium series in plus four, plus five and plus six oxidation state. So, if we have on the left one such acetyl acetone

at anion is coordinating to the molybdenum center and then on the right if we have another coordinating system; another acetyl acetone system. So, you have the molybdenum center. So, two acetyl acetone molecules are there and since they are all bidentated ligands; this is one bidentated ligands; that is another bidentated ligand. So, one two three four; so four positions around the molybdenum center are occupied, but we are considering here that it can form immediately as an octahedral complex; that means, all six positions are occupied.

So, we should have these two positions still available for binding either to some small groups like this water, dioxygen, hydrogen peroxide; any other ligand system or another group of acetyl acetone molecule. So, if another group of acetyl acetone molecule goes and bind to this molybdenum site we have the corresponding complex, because we should know how quickly we write the corresponding complex, we get a Mo ACAC whole three; that means, three such acetyl acetone ligands are fully covering the molybdenum center and we get a system which is nothing but Mo L 3 type of Gillette, but that particular Gillette when you have a non-oxo form.

So, that immediately gives us that if you have these two positions are still occupied by another acetyl acetone molecule, we get a corresponding non-oxo octahedral complex of molybdenum where you have three such acetyl acetone groups attach to this molybdenum center, but to get some oxo species the same methodology we can consider to get one of this. So, here the second acetyl acetone is this one. So, what happens to this one? So, you have two positions occupied by this one first acetyl acetone. So, this is the first acetyl acetone molecule; this is the second acetyl acetone molecule; then one position already, because we are talking about the activation of the dioxygen molecule. So, we are very serious very interested to know how the molybdenum is interacting with the dioxygen molecule and is sitting there nicely.

So, this particular position is also very much useful. So, if we have these two positions are occupied by oxygen itself, we get a corresponding compound which is Mo O 2 ACAC whole twice and we call it as not a simple dioxo complex, but it is also a dioxo complex.

So, this particular one how we are getting activated activation through water or dioxygen molecule producing hydrogen peroxide and the intermediate molybdenum, and

ultimately the substrate. So, if we have the hypoxanthine molecule, that hypoxanthine when reacting with water and dioxygen producing xanthine and H 2 O 2, and this xanthine further reacting with H 2 and O 2 giving uric acid and hydrogen peroxide. So, all these two steps we are basically producing something where our reagents are water and dioxygen, and producing the corresponding oxidized form as well as we are regenerating something which is hydrogen peroxides.

So, the production of this hydrogen peroxides are not very simple one and it is also not good for the living organisms, because we have the corresponding oxidation activity from this hydrogen peroxide, because these are also oxidizing agents. So, this particular accumulation or reaction is going. So, in one form; that means, which is why it is moving from the left to right. So, sometime we will find that in the biological system, it is the PH; that means, the corresponding level of acidity of the system that how many protons are available from one site to the other. The ph of the system as well as the solubility of the system either your reactant; that means the xanthine is more soluble or uric acid is more soluble in water that can drive the reaction from left to right. In this particular case, uric acid is more soluble in water of xanthine in water is less compared to uric acid.

So, this is another form of this driving force controlling on xanthine driving force or pushing the reaction from the left hand to right is that the uric acid what is producing is more soluble in water and that is why ultimately we get this particular uric acid in urine also. So, that is getting solubilized in that particular urine and this passing out from our body. So, when it is reacting with molecules like hypoxanthine and xanthine, we find that this sort of reactions; that means, involving molybdenum, involving water or involving dioxygen, it can also some other substrate. So, we can have large number of substrates.

So, like our purine derivatives, we can have also purine pyrimidine derivatives; we can have the terrine derivatives also. So, these are all different heterocyclic organic molecules which are useful as well as the aldehyde substrate. So, this particular part; that means, the molybdenum involving corresponding enzymatic reaction; that means, the molybdenum based enzymes which are acting on purine or pyrimidine molecules to oxidize them; they can at the same time can work on aldehydes to produce carboxylic acids. This is also another group of molecules; little bit will see about how this same molybdenum function or same molybdenum center can go for the corresponding

oxidation of aldehydes? So, it can function as xanthine oxidase as aldehyde oxidase. So, this particular conversion can have something where we get that this particular xanthine if it is substituted one say the position; that means, the position one on the particular ring is occupied by methyl xanthine. So, that is another source of that methyl xanthine which is a metabolite of caffeine what you consume.

So, in the caffeine system this is not only the bear xanthine molecule, but is a methyl xanthine molecule; but it can based on the same type of reaction as we get xanthine to uric acid, it can also convert immediately we can argue that that if one position is occupied by methyl; it has not much effect on the conversion of parent xanthine to uric acid, we can consider that it can also give you one methyl uric acid. But these particular molecules due to the presence of this methyl group will find, but has some little activity on methyl xanthine.

So, this is or these information's are very important that whether the substrate is only the pure xanthine or a methyl substituted xanthine and this corresponding molecule; that means, the xanthine oxidase which is working more which is active more on xanthine instead of three methyl xanthine. So, we will be lucky enough when we consume caffeine, we will not producing the equivalent amount of methyl uric acid in our system, because these xanthine oxidase which is much more active on xanthine will be less active on methyl xanthine and will get less amount of methyl uric acid in the system.

So, like that of our formation of aldehyde if we can have something; that means, if we have some methane or alkane type of hydrocarbons, any hydrocarbon based on this R function which is based on carbon and hydrogen, and another H where you have the CH bond. What we have just talking about that if we have a CH bond, it can be converted to a COH function. So, if you have methane on the left you are able to produce methanol on the right.

So, during that reaction same substrate; that means, is working on water and dioxygen, but if the reaction tritometry is different and the electron transfer pathway is different; that means, instead of reacting this substrate with one molecule of H 2 O and one molecule of O 2, we react it with one molecule of H2O and two molecules of dioxygen; we get the corresponding alcohol which is again the hydroxilated product; that means, hydroxylation reaction is taking place. But instead of producing hydrogen peroxide, in

this particular case that what we are producing here will also produce corresponding another important reactive species we all know that the super oxidase activity by some other biological system that at the same time producing super oxidase instead of peroxide. So, you will be producing superoxide and proton if we go in a different reaction.

So, under some condition where xanthine oxidase is not directly reacting on the xanthine molecule to straightway producing xanthine from hypoxanthine or uric acid from xanthine, but instead can produce the hydroxylation reaction is still on, but their substrate is different, but we can detect whether we are producing hydrogen peroxide or superoxide, because an alternate techniques are available where we can detect the production of hydrogen peroxide and the production of superoxide. So, identification pathways or identification techniques or the corresponding analytical techniques which can identify the presence of hydrogen peroxide and superoxide are different. So, immediately we can identify that whether our reaction is going through this way or is going by producing superoxide.

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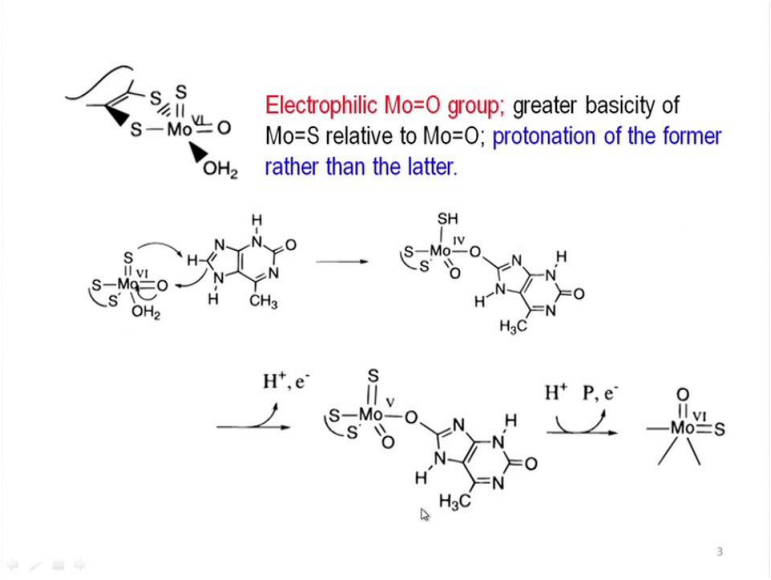


So, what we are looking at the corresponding molybdenum oxo function.

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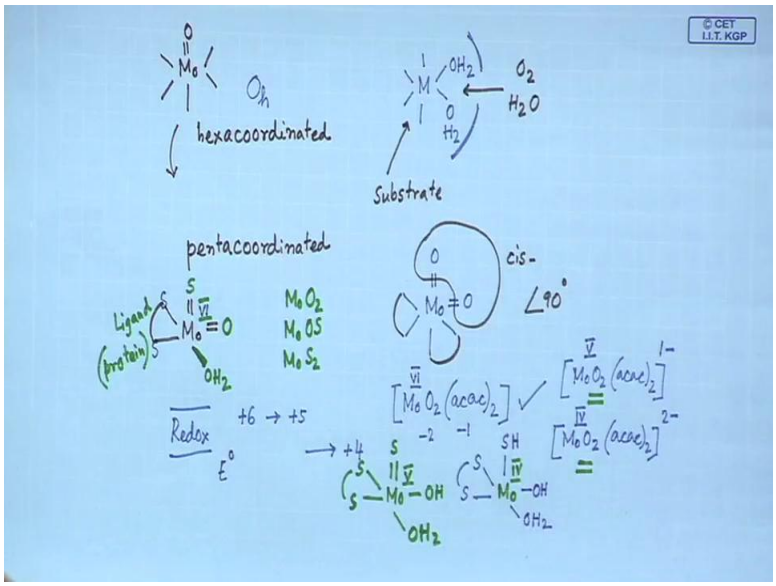


So, we have the system where we have the molybdenum oxo function what just we have seen in the laboratory prepared system where we are producing in the laboratory the Mo O 2 ACAC system where one of the group is occupied is corresponding molybdenum oxo group, but in the enzymatic functions what we will see that if we go down from a six coordinated species which we all know, we can call it as hexacoordinated one to a pent coordinated one. So, we are just basically what we are doing? We are exposing more of the molybdenum center to the substrate or to the reagent, because when you have this hexacoordinated system and if it is covered in octahedral fashion; that means, all the six positions in the regular coordinates of X, Y and J all the six positions are occupied nicely. So, you have little space to directly react with this molybdenum which is completely different if we all know like iron system or any other system that when we dissolve ferric chloride in water, we get a species like these also where you have the hexacoordinated species based on the metal center where all other position; that means, all six positions are occupied by a very small molecule which is water.

So, the getting water molecule coordinated to the metal center is important, because it is not occupying much space when you have the second water molecule is also is not occupying much space. So, we have some space available still where we can consider it as the vacancy. So, this vacancy is our approach site for the reagent, it can be our approach site for the dioxygen molecule or water molecule if we try to make this particular molybdenum center or any other metal center based on oxo or hydroxo or

simple water coordinated one and at the same time it can also some give some area where from our substrate can react with the metal center.

So, from going down from hexacoordinated to a penta coordinated species which we can have based on the molybdenum, if we have these two positions are occupied by double bonds here in this particular case or what we have seen just now that if we have molybdenum dioxo one based on acetyl acetone. So, you have two dioxo forms. So, this dioxo groups are nicely occupying this particular area on this side. So, this particular area from this is side is nicely occupied by this dioxo group which are coordinating to the molybdenum center from sys direction, because these two angles are ninety degree close to ninety degree angle.

So, this approach of the substrate will not take place from this side, but these two positions are occupied by the ligand groups. But if we go down from a six coordinated species, the octahedral coordinated species to a penta coordinated one, what will see that this particular two other positions which can be occupied by this sort of bidentated ligand. So, this is a bidentated ligand or acetyl acetone or anything from the ligand system also. So, we are creating more space at the bottom. So, this particular area is vacant. So, you have large amount of species available compared to nicely occupied positions of the six groups around this particular hexa coordinated one. So, in this particular case if we can have two both of them oxygen and also molybdenum has more affinity for sulfur groups also.

So, if we have two groups one is sulfur and another is oxygen, you can have both of them sulfur also and if we have this bidentated one is the ligand one, and this is simpler ligand system which is the corresponding water molecule. So, you get a penta coordinated species and only particular site is occupied by the ligand; this is also coming from the protein system if we are talking about some biological ligand like that of our available for the molybdenum center in xanthine oxidase. So, this can be from the protein origin. So, this protein origin is there. So, these two positions are occupied.

So, now, there should be some balance of formation of these two whether we are getting system which is Mo O 2 based or Mo O S based or Mo S 2 based. So, depending upon the groups which is attached to the molybdenum center and depending upon their electrophilicity on the oxygen and sulfur; that means, the electron density available on

the molybdenum center, we can control the corresponding reactivity pattern on this molybdenum center; suppose if we consider this in plus six oxidation state, because this particular center synthetically prepared molecule what we can have if it is the same example what we just discussed that if it is Mo O 2 ACAC. So, two of the negative charges are coming from these two acetyl acetone anion; two of the negative charges from oxygen O 2 system. So, two plus two minus four and plus two minus six.

So, this particular center is also in plus six oxidation state. So, it is a very special arrangement for molybdenum center is more stable arrangement, because we should also know which one is most stable one. Because for the catalytic activity some intermediate oxidation state which we can generate in transient fashion which is not so stable which life time is not very high. So, the stable one which is ultimately forming there is the corresponding dioxo species and if these ligand groups coming from these groups are coming from the sulfur origin. So, that can also control little bit the corresponding electronic nature on this molybdenum center.

So, not only these groups these terminal functions; the terminal pure inorganic donor groups like oxoanthio group as well as the ligand origin whether both of the these oxygen like acetyl acetone one sulfur, one oxygen or both of the sulfur that can also control the corresponding reactivity pattern on the molybdenum center. Then the corresponding reactions are taking place due to the corresponding electron transfer, because the redox is on and we should know how we can change the corresponding oxidation state based on the molybdenum. If it is the highest possible oxidation state available at this point whether we can reduce it from plus six to plus five or further reduction to plus four.

So, we can generate some species which can have some different reactivity pattern either catalytically more reactive or catalytically less reactive, but due to electron transfer we should able to produce that particular center based on the molybdenum in different oxidation state. So, if we know the corresponding redox pattern say this particular synthetically prepared molecule in the laboratory whether Mo ACAC whole two is electro chemically reactive or not; that means, we want to produce the corresponding species which is Mo O 2 ACAC whole two in minus one form. So, it has one minus charge; that means, this molybdenum is in plus five oxidation state; or further reduction

of it producing Mo O 2 ACAC whole two minus where this is in plus four oxidation state.

So, during these redox transformations, we are moving from plus six to plus five to plus four and what we are trying to push one electron to the molybdenum center. So, we are getting this particular center from plus six to plus five to plus four, but what we know all from our trivial knowledge from coordination chemistry that this oxo function which is very interesting function center attached to the molybdenum center and it is also true that whether you can have the corresponding system on chromium or tungsten will find that this particular center is stabilized mostly in the highest possible oxidation state when we have this dioxo form.

So, this plus six oxidation state will be stabilized by this group of ligands as well as this dioxo function is in the plus six. So, when we try to reduce it to the plus five or plus four, we do not need so much of this dioxo stabilization for the molybdenum center, because the molybdenum center we have produced from plus six to plus four. So, manipulation of these oxo groups can go from here; that means, we just simply go from these sulfur sulfur centers and these two where the corresponding oxo centers. So, we will keep all these positions intact; that means, OH two sulfur and sulfur. So, if we just simply move from a dioxo function to a OH function that would be the very important group change for the stabilization of the corresponding plus five oxidation state. So, if we consider that this is stabilized in plus six oxidation state, this group has been transformed to O H, but this particular one is still in double bound sulfur state.

So, you have the corresponding charge stabilization two negative from here to from where four and this is five. So, you have the corresponding stabilization in the plus five oxidation state. So, this is the most preferred arrangement for the groups around a center which is molybdenum in plus five and this was the corresponding arrangement in the plus six oxidation state. So, we should remember the corresponding differences in these two thing that means when we try to reduce the molybdenum center from plus six to plus five, we immediately not stabilizing corresponding oxo form, because we do not require that much of oxo stabilization for the plus five oxidation state, we can go from this oxo form to a hydroxo form.

So, at the same time what we are doing? We are just simply attaching one proton to this particular oxo function to the hydroxo function and then on the other side; that means, if we go down to a plus four oxidation state what happens then? So, if we go for plus four oxidation state, this already is in OH form; this two are the corresponding sulfur and sulfur; this is already what was present in the starting molecule which is OH two, but this will now go for a corresponding preference of binding S H function is stead of sulfur double bound to the molybdenum center.

So, if we go for reduction to molybdenum six to molybdenum five and molybdenum five to molybdenum four, you are getting the corresponding modification on these oxo function and thion function; that means, these two will also be converted to OH function and S H function. So, this particular environment is available what will see that you have the sulfur double bond with the molybdenum six, and the oxygen double bond to the molybdenum center, and the electrophilic nature on the molybdenum oxygen group which can control the reactivity pattern for the center, and the greater basicity of molybdenum double bound S related to the molybdenum double bound oxygen is important.

So, which particular function will have the greater basicity? So, depending upon of this basicity and the electro transfer potential; that means, at which particular potential molybdenum is stabilized in its reduced form; that means, the plus five form or the plus four from. So, basicity of that particular center will control that this particular function will go for the corresponding conversion to S H instead of O H. So, the protonation of the format; that means, the protonation on the molybdenum sulfur bond which was double bound will be converted to molybdenum single bond S H rather than the latter; that means, we are not getting the corresponding Mo A H function, but we will be getting Mo SH function instead during that particular reaction.

So, this particular site is our catalytic site and that catalytic site in plus six oxidation state is reacting with our system; that means, this is our xanthine system, and which we can have also a corresponding substitution like methyl xanthine system; that means, you have the methyl function still there, and we are trying to have the corresponding hydroxylation reaction on this CH bond. So, this particular C H bond is therefore, important and substrate will be approaching as I told you that this particular site where we do not have the burden of the ligand coordination, because this S S function which is the biogenic

ligand from the living system which is the terrine ligand. So, this particular part is little bit crowded and we have the water molecule at this particular site.

So, the approach for this; that means, you have the little bit of complex reaction; that means, we are trying to convert this CH function to C OH function; say it is better if we can takeout this H in the form of proton transfer or hydride transfer whatever it is. So, some group should be available which can interact with this proton or this hydrogen atom better than the other one. So, this particular point we have seen that since Mo S has higher basicity.

So, this will have more affinity on this particular hydrogen and this particular hydrogen is getting attached to this sulfur forming S H, and at the same time this oxygen is getting attracted by this corresponding carbon center which is nucleophilic in nature, and that nucleophilic carbon center will be attaching on this particular oxygen. So, what in essence we are getting? Instead of getting this particular function also as OH, because this proton is moving from here to here. So, you are getting SH function at the top, but this particular organic substrate is getting bonded to the molybdenum center as if oxygen is getting inserted between these carbon and hydrogen.

So, you can have now instead of this molybdenum oxygen bond now, you have M O C bond which is very much similar to that of the corresponding coordination of the phenolate group when you have the phenol after DE protonation. We have the phenolate group where you have the oxygen in the negative charged bearing species and that negative charged bearing species coordinating to the molybdenum center. So, if we think of it as the conversion of both the two groups of bearing sulfur and oxygen which were in double bonded form on the molybdenum is getting converted to SH and O something; that means, OPH if it is phenol and OS if it is the entire substrate based on some OH function of the alcohol origin.

So, this is also basically that of the conversion related to that of our OH function. So, this immediately getting converted from plus six to plus four and then again this particular one will push back then again this molybdenum center will be corresponding oxidizing center; that means, it can go up again from the oxidation state of plus four to plus five. So, during that oxidation process this was a two-step reduction process followed by an oxidation process for that molybdenum five.

So, this sulfur function in SH form again going back to molybdenum sulfur double bond and your oxidation state is changing from plus four to plus five, and now the system is ready. So, we are removing one electron as well as one proto from the SH function and one electron from the molybdenum center, and we are at molybdenum in the plus five oxidation state.

So, we will see in our next class that this particular center will also can able to characterize it if some spectroscopic technique is available such that we are able to characterize this particular center as the plus five oxidation state. We are happy that at the catalytic active intermediate is formed where molybdenum is formed in plus five oxidation state and at the last stage where your substrate is attached to this molybdenum center is removed; that means, V is our product from the substrate which is the hydroxylated form of the substrate molecule.

So, the hydroxylated substrate is now removed from molybdenum coordination and product we are getting there, and one proton is there is consumed over here; that means, this will be converted to O to OH, and we are getting back one electron also from the system, because the molybdenum will be stabilized from plus five again back to the plus six; that means, we are regenerating the catalytic species which we have started over here. But you see that when we write this in the firm form; that means, these coordination environment it is in the five oxidation coordinated form and here it is again we are generating the five coordinated form. So, this will see that again we are generating it. So, next day we will continue from here to how this particular one is responsible for in the R R systems.

Thank you.