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Organometallic Chemistry-I

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Module No. 5

Lecture No. 19

CARBONYLATION REACTIONS

1. **MONSANTO ACETIC ACID PROCESS**
2. **HYDROFORMYLATION**
3. **HYDROCARBOXYLATION**

Hello everyone welcome back so today we will discuss on carbonylation reactions. The last class we were discussing the hydrogenation reactions right. Today we will basically try to introduce carbon monoxide into the organic molecule how can one introduce these molecule this carbon monoxide into the molecule and therefore the carbon count can go up by one. So there are traditionally as you can see carbonylation method can be of few different type one is Monsanto acetic acid another could be hydroformylation and of course hydrocarboxylation and so on.

So first we would like to discuss the Monsanto acetic acid process and that involves incorporation of carbon monoxide into the molecule as you may know. So Monsanto acetic acid process.

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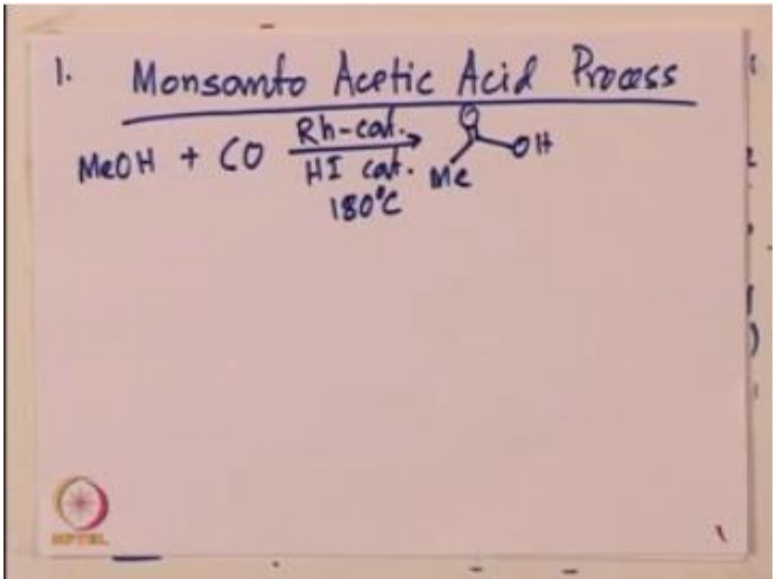

1. Monsanto Acetic Acid Process

Monsanto acetic acid process is the conversion of methanol plus carbon monoxide into corresponding acetic acid right. Now traditionally or historically rhodium catalyst has been used but industrially nowadays iridium catalyst is used you need also HI catalytic amount and that reaction temperature is 180°C. Now this reaction is quite interesting and it is done in industrial scale as you can see this is the industrial synthesis of acetic acid that we get.

Now the starting material is methanol and carbon monoxide how one can convert these two molecule into the acetic acid molecule also one thing to be noted that rhodium or iridium catalyst can be used for this mechanism for both of these catalyst are exactly same and most importantly you need catalytic amount of hydraulic acid that is HI. Let us try to look at the mechanism of these this reaction as you will see whatever fundamental type of reaction we have discussed it will come into play and it will demonstrate that these organometallic reactions are nothing but governed or dominated by the fundamental reaction that we have mainly discussed for this course okay.

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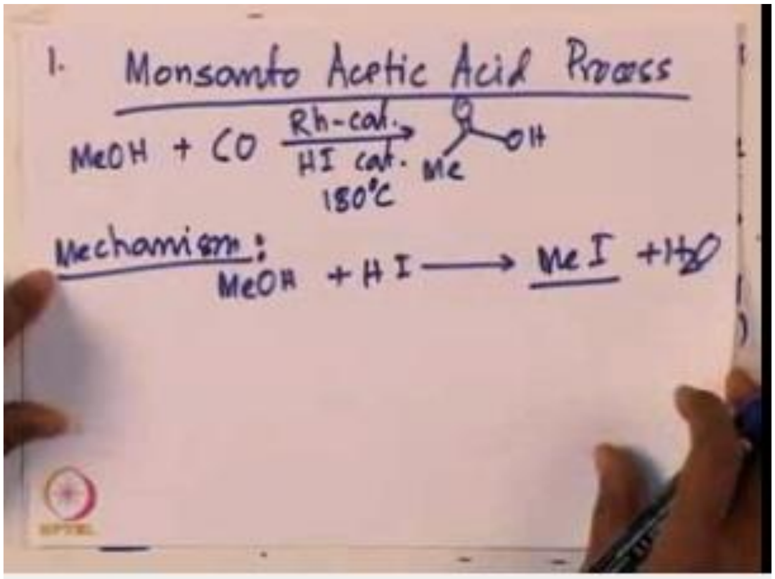

1. Monsanto Acetic Acid Process

$MeOH + CO \xrightarrow[\substack{HI\ cat.\\ 180^{\circ}C}]{Rh-cat.}$

Mechanism:

$MeOH + HI \longrightarrow \underline{MeI} + H_2O$

Let us look at the mechanism of course the first step of the mechanism is a conversion of methanol to cause to methyl iodide with the help of HI show you convert methyl iodide plus water methanol is converted to methyl iodide and water this is you know something you must remember without that the catalytic cycle cannot start so methyl iodide formation is absolutely crucial now from their own of course our a catalytic cycle will start off where rhodium will come into the picture.

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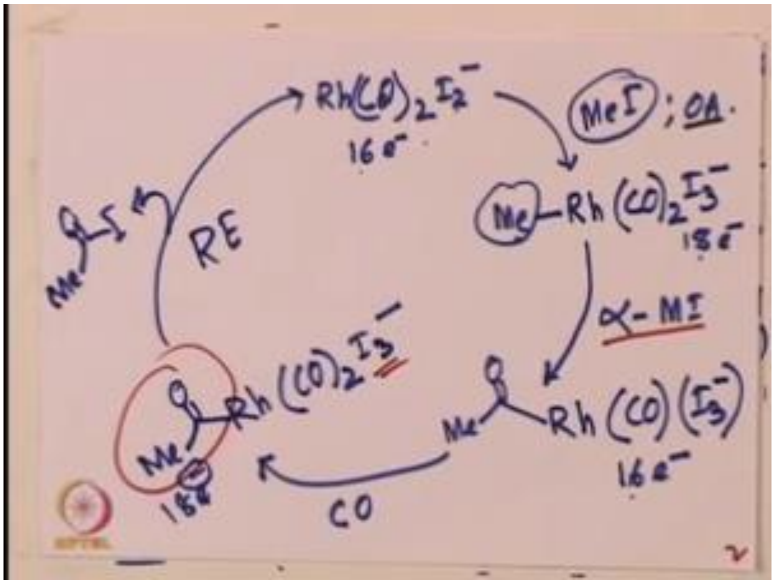

So that is rhodium Co dicarbonyl species that is the catalyst let us say is use it is a 16 electron species and the methyl iodide that we have just converted will participate in to the reaction and undergo oxidative addition right so methyl iodide oxidative addition will give you the carbon metal bond carbon rhodium born in this case carbon monoxide and I_3^- you started with two iodide and then you have one more iodide so that makes it I_3^- this is an eighteen electron species from their own you can undergo α migratory insertion that is what we have studied.

We have studied this oxidative addition we have studied oxidative addition we have studied also these α migratory insertion that means that where you will see that alkyl group will migrate into co that we have discussed again previously so you will get aisle equivalent formation with a metal component being there so one carbon monoxides less now so that carbon monoxide has been incorporated into this aisle component and you have I_3^- right now this is the α migratory insertion.

So alkyl group has migrated to one of the carbon monoxide to form the aisle group now from there on we have this species 16 electron right if you count so α migrated to oxidative addition gives you 16 to 18 electron 18 electron to 16 electron for α migratory insertion further you have now the carbon monoxide is interacting with the metal complex and therefore so these reactions are done under the carbon monoxide and most fear as we have discussed in the very first instant now we will have this two of the carbon monoxide as you can imagine one more carbon monoxide gets in gives you the 18 electron species.

So 16 to 18, 18 to 16, 16 to back to 18 electron species and you have of course I_3^- from their own reductive elimination will give you the CH3COI so that is coming from so this aisle unit and one of these unit I do will reductively eliminate and therefore you will get to get the aisle iodine so what we have seen in this particular species it is basically dancing between16, 18, 16 electron species and 18 electron species starting with a 16 electron species we have seen the oxidative addition that gives you the 18 electron species now that 18 electron species can give you again the 16 electron species where alpha migratory insertion is going on.

After that you 16 electron species again comes back to 18 electron species when carbon monoxide is interacting or coordinating with the rhodium center therefore you get again back, back to the di-carbonyl species next what is left to do is the reductive elimination as we have seen that one of the iodide and the sign units is this your note reductively eliminate to give you CH_3CoI.

So essentially we have seen oxidative addition, alpha migratory insertion, ligand coordination that ligand is here carbon monoxide coordination and reductive elimination all these fundamental Steps we have discussed earlier during the during this course, okay. So as you see all the organometallic reactions the mechanism becomes very, very simple and it is like the simplest you can perhaps imagine as you have some understanding of the fundamental steps.

Without the fundamental steps these understanding can be problematic therefore you know the major activity of major focus of this course as you as you have seen has been the discussion of the fundamentals of organometallic chemistry or the steps and therefore in organometallic chemistry almost any mechanism you can explain by these fundamental steps okay, moving on from desire CH_3COI of course you have this.

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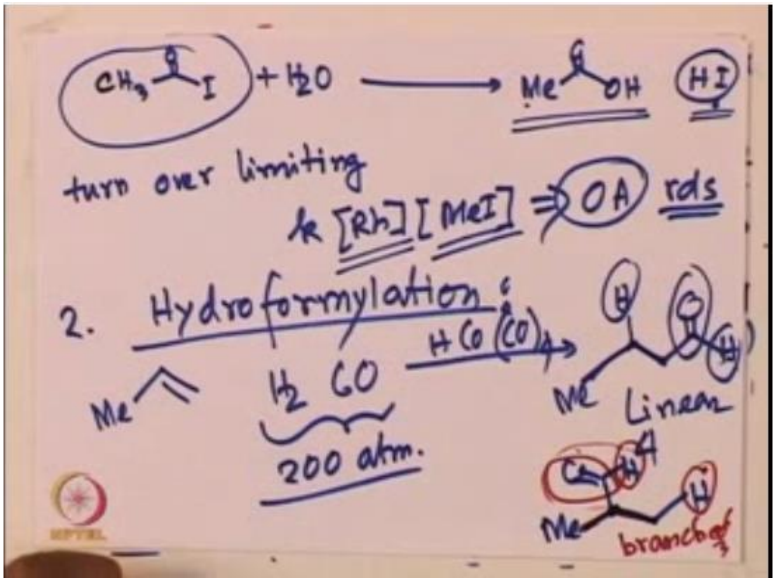

This iodide CH_3COI from there on you we will see that the hydrolysis okay CH_3COI hydrolysis that is the last step of the reaction and give you the acetic acid, right. So CH_3H and acetic acid anhydride red acid back, so hydrolysis of this unit gives you acetic acid and HI back, since it is a producing HI as you have seen in the very first instant that HI is used at the catalytic amount, okay.

So your catalytic cycle will carry forward with little bit or tiny amount of hydriodic acid, so the turn of a limiting step for the reaction would be turnover limiting step would be the one where your rhodium and methyl iodide is both involved so that means the oxidative Addition is the rate-determining step and therefore you have the first order dependence with methyl iodide first order dependence with the rhodium catalyst.

So the first very first step is the rate determining step thus the slowest step if you do the reaction either with rhodium or iridium both of them gives you the exactly same reaction mechanism that means the first step is the determining step where oxidative addition into the methyl iodide is going on at the beginning you have seen them ethanol conversion into methyl iodide and they were there you do not have involvement of too much of involvement of an organometallic intermediate but once you from the methyl iodide then.

You can take in to take that one into the catalytic cycle where it interacts with the metal centre to give you the oxidative addition and that is done out to be the rate determining step okay now we will move on to the next topic that is a hydroformylation it is of course the basic understanding will be similar to that of the just discussed reaction of the acetic acid process but we need to briefly look at that and appreciate the steps of this transformation okay so we are going to discuss the hydroformylation reaction hydroformylation okay.

As the name says it all what we have in our hand is the conversion of olefin in presence of mixture of hydrogen in CO and this is like 200 atmosphere pressure usual industrially used and you have a cobalt catalyst tetra carbonyl species hydrido cobalt her devoted to a carbonyl species and you have the possibility of forming two products okay where the famous are most common the linear product again one of the carbonyl and this hydride hydrogen two of the hydrogen as you can hydride you can see or the hydrogen atom equivalent you can see.

Carbonyl and hydrogen is getting into the only field okay starting from olefin you are going to get this product so this is the olefin backbone and hydride, and CEO is getting into it so this is the linear product it usually for this reaction for this particular reaction it is for equivalent and the other brand product so instead this aldehyde fragment can incorporate over here so that means you will have this you know COH and this H here of course you have again to hide hydrogen atom and one carbonyl equivalent.

So this is again you are the propane equivalent from over there you have seen that aldehyde is getting into the into the branch position or giving rise to the branch product so this is so called the branch product starting from alkene you have the possibility of forming two products that means linear and the brand product okay so it is a hydrogen NCO mixture known as also syn gas now this is the mixture reacting with the olefin to give you either terminal aldehyde or the branched aldehyde what all you have introduced into the olefin is carbon monoxide.

And hydrogen or h2 equivalent like two hydrogen atom or you can say the two hydrolytic you have and you have introduced that total unit that aldehyde unit that is getting generated if it is on a linear fashion that is the linear product and if that aldehyde is on the branch person or on the side that is the brand product and usually we see a four-to-one ratio which is equivalent to roughly one k/cal per mole energy difference for this linear is to brand Florida.

So getting selectively one of the products completely selectively one of these products is going to be challenging we will discuss more but instead of the propane let's say if you have studied then the scenario can be completely different because the metal alkyl species that is getting generated can be stabilized or the negative charge the benzylic position will be stabilized and therefore you may have the possibility of getting the brand as the major product but on the long chain olefin or aliphatic olefin will usually get the linear product as the major product, okay. Let us look into the mechanism of these reactions hydroformylation, so mechanism of the hydroformylation reactions, okay.

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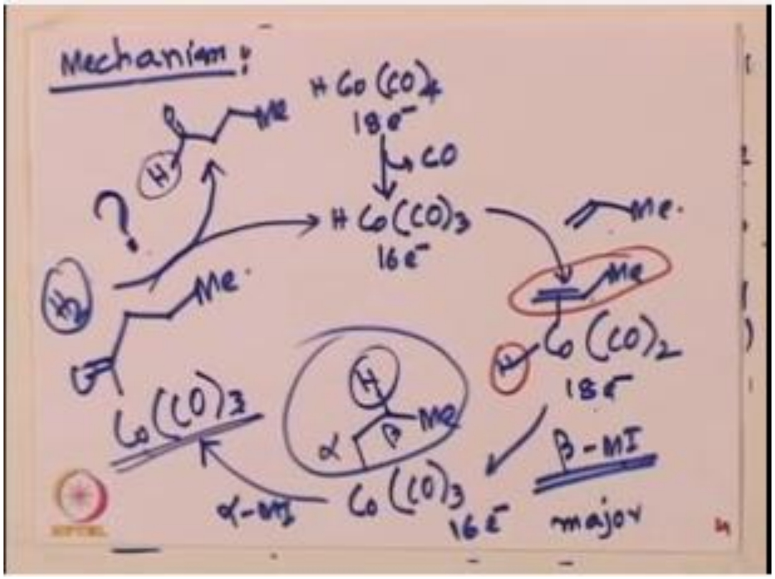

So what you start with is tetra carbonyl hydride cobalt species okay HCO (CO)4 you do that quick electron count it should be18 electron count and from there on you have one of the carbon monoxide is getting out of course you need a 16electrons so called little bit unsaturation is required and you get to HCO(CO)3 this is a 16 electron species from there on you have the interaction of this alkene to give you HCO(CO)3 and chord alkene coordinated intermediate of course this is going to be the 18electron species.

So 18 electron goes to16 electron goes to 18 electron this is the olefin coordination or so called ligand coordination you can say. Now from there on as you can imagine you have the hydride equivalent and you have the olefin show β migratory insertion can takes place should be very, very good at these things and understanding that this is the ensuing step that is going to go into predominate or will take over.

So from 18 to of course you are going to get a 16 electron intermediate with the hydride at the α β position that is why it is β migratory insertion into the olefin and this is of course it is going to be the major product of course this is the one which is going to give you the linear aldehyde right, of course there is a formation of the other one which is the branch product but that is going to be the minor one so 18 goes to16, 16 goes to 18, 18 goes to 16 so ligand dissociation, ligand association or olefin interacts and olefin coordination β migratory insertion that is the major state sorry, major product and from there on you can see the α migratory insertion so the whole alkyl group now will migrate into the carbon monoxide, so α migratory insertion will give you the cobalt speech stress carbonyl as I will intermediate, okay.

Alkyl intermediate so one this whole alkyl group has transferred to one of the carbon monoxide of course the 16 electron species you do have that and then from there on this process is occurring from there on what you will see is the interaction of hydrogen I am not going to write down the steps here we will discuss this in detail little bit and overall you will get the hydroformylation that is the linear product formation, okay.

So this is very, very important to understand that this is a completely electron withdrawing in or you know electron deficient intermediate you have three of the carbonyl and one of the SI unit so all the co-ligands are electron withdrawing in or you know electron deficient intermediate you have three of the carbonyl and one of the sayle unit so all the ligand are electron withdrawing and so oxidative addition will be difficult right into the hydrogen.

So what you have seen here is the carbonyl complex gives rise to an intermediate which is completely electron deficient as you know for oxidative addition you need to have a very electron-rich metal centre in this case it is very, very electron for therefore we have given this ? What is happening in there what will be the mechanism of incorporation of this hydride equivalent into these is into this molecule to give you the long-chain earlier.

Okay now if you again look back at this mechanism very carefully and simply you would appreciate that the all the steps involved in this process are very, very simple you start with an 18 electron species of course have to loosen up a little bit loosen up a little bit from18 electron species you gives right give raise to the 16 electron species and then olefin coordination occurs to give you the 18 electron species back and then you have the opportunity to do the β migratory insertion to form the Kyle intermediate metal alkyl intermediate from there on α migratory insertion can go on.

And finally you get an intermediate which is highly electron deficient but you have not introduced the hydro hydride equivalent yet or the hydrogen gas did not interact yet so therefore you know from this highly electron deficient intermediate if you have to incorporate hydrogen what would be the mechanism that is now one thing we need to look at it carefully but nonetheless as you have seen from olefin we get the aldehyde it could be either terminal or an internal one so called linear and the and the branch one and four aliphatic case.

Linear product predominate as you may see later on that for a benzene ring containing on or the subscribing or vinyl napthine cases we will see the branch product will predominate because that intermediate metal alkyl or metal intermediate alkyl intermediate or that will be stabilized by the electron withdrawing effect of the engineering in the case of alkyl group you have an electron rich alkyl group therefore the other product predominates okay.

Let us look back at that step where hydrogen were reacting hydrogen was reacting with the, with your alkyl inters an intermediate okay, so the last step we are going to discuss the last step.

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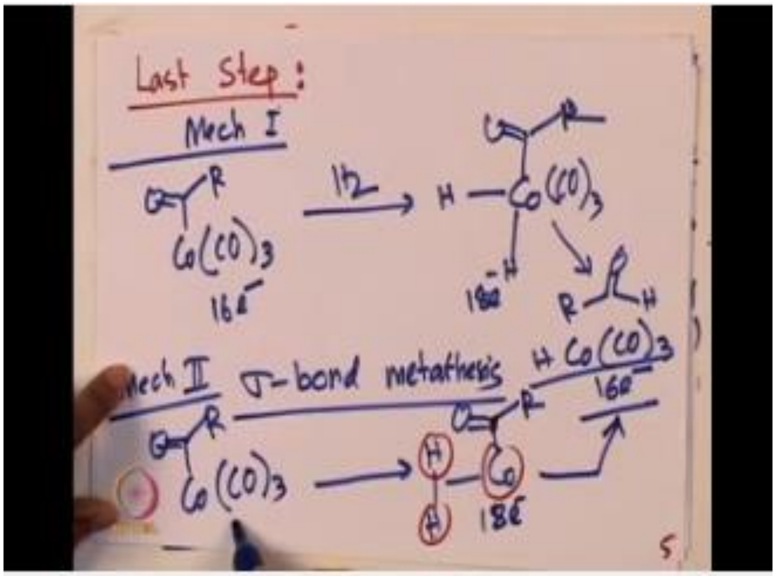

So mechanisms I the first type of mechanism would be the one where we have the oxidative addition of course that is one of the usual suspect we think that there would be an oxidative addition right and that will give raise from 16 electron to 18 electron species and $co\text{-}co_3$ c o r from here of course you can get r sorry this is r we are not drawing the r, RC H 0 and H co (co) $_3$that is your catalytic component right.

16 electron species you may get now the finally another mechanism is mechanism II that is the σ bond metathesis right so as we are saying that this mechanism will be will be unfavorable because of the fact that this is highly electron deficient intermediate further if you do the computation of chemistryor DFT studies, you will find that this is very high energy demand name, so therefore this one by virtue of its electron deficient character and also supported by the DFT studies or computation studies, that this is going to be highly energy demanding.

Sigma bond metathesis is I guess the as you have deep as we have seen previously, when oxidative addition is not going to be a preferred pathway, Sigma bond metathesis might will be and in this case it will be the case most likely although direct evidence is lacking, you will have this ordinance and we coordination it is a 4centered mechanism, it will pre door will occur, show that means this one this one, two three and four this for entered mechanism, will give rise to the product formation the same product formation, you will get.

16 electron species, goes to 18 electron back to 16 electron okay, so to sum up we have seen the incorporation of carbon monoxide into the olefin, two different processes we have seen today one is them Monsanto acetic acid process, where from olefin or from popping we have we have we have seen the different product formation, and for specifically for from propane in this case carbonyl equivalent formation, we have seen the branch product formation and the linear product formation, for alkynes linear product is the major one and for these for the last reaction we were trying to debate between the oxidative addition and Sigma bond metathesis.

And we kind of concluded that Sigma bond metathesis, will be the one which will which will what has happened basically because of the fact that oxidative addition requires the electron richness of the metal centre, which is missing in this case of having highly electron, withdrawing equivalent and therefore the alternative one that is sigma bond metathesis, will predominate or we will pick up and give you the product okay.

With that will close today's session, and I like you to request to study these leads but more carefully and understand that these are nothing but the discussion of the fundamental steps, that we have seen I will in earlier cases okay with that see you in the next class.

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