# Advanced Transition Metal Organometallic Chemistry
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## Module - 11
## Lecture - 55
## Organometallic Catalysis Reactions: Carbonylation of alcohols

Welcome to this course on Advanced Transition Metal Organometallic Chemistry. We have been discussing C1 chemistry in the last few lectures. And C1 chemistry usually refers to the chemistry related to carbon monoxide, particularly from their utility perspective. Now, 1 important feature of C1 chemistry is its industrial importance that this chemistry right now is the main focus of attention, as it is most likely going to take over the other industrial processes.

So, in this context we have looked at 2 important examples of carbon monoxide chemistry or though rather the C1 chemistry; the first one being water-gas-shift reaction which exploits the reducing power of carbon monoxide to convert water to hydrogen which is important as a fuel. And then, subsequently we have looked at the complementary feature of oxidising power of carbon monoxide which oxidises hydrogen to water and instead producing carbon hydrocarbons which can also be used as a fuel.

So, these 2 important industrial processes that we have discussed in the last 2 lecture. I must note that this is one of the finest demonstrations of C1 chemistry that we have been discussing in the last 2 lectures. Now, today, we are going to take another important example of C1 chemistry which is the carbonylation of alcohols.

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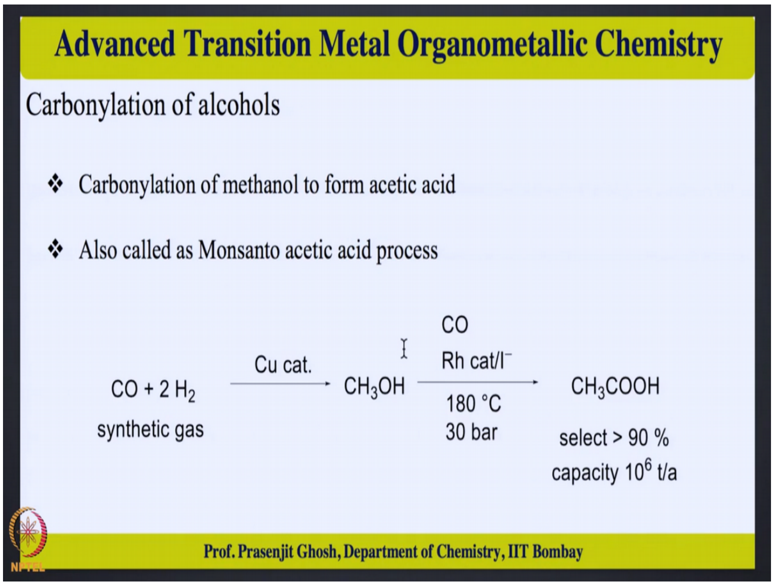

## Advanced Transition Metal Organometallic Chemistry

Carbonylation of alcohols

- Carbonylation of methanol to form acetic acid
- Also called as Monsanto acetic acid process

$$\underset{\text{synthetic gas}}{CO + 2\,H_2} \xrightarrow{\text{Cu cat.}} CH_3OH \xrightarrow[\substack{180\ ^\circ C \\ 30\ \text{bar}}]{\substack{CO \\ \text{Rh cat}/I^-}} \underset{\substack{\text{select} > 90\ \% \\ \text{capacity}\ 10^6\ \text{t/a}}}{CH_3COOH}$$

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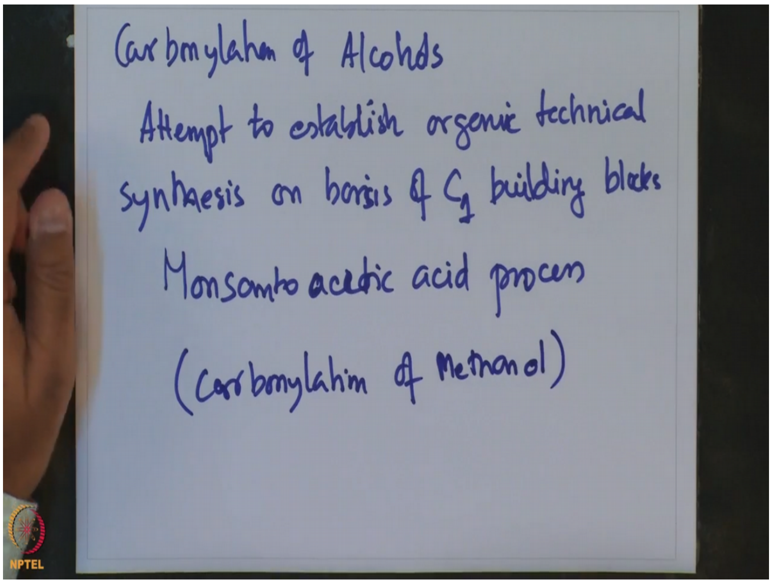

Carbonylation of Alcohols

Attempt to establish organic technical synthesis on basis of $C_1$ building blocks

Monsanto acetic acid process

(Carbonylation of Methanol)

And this is an attempt to establish or represents an attempt to establish organic technical synthesis on basis of C1 building blocks. And this is popularly known as Monsanto acetic acid process or carbonylation of methanol.

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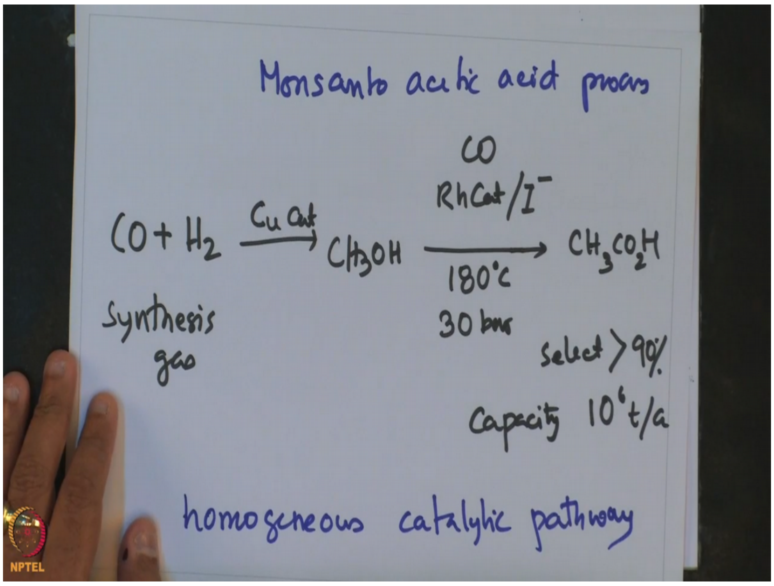

Monsanto acetic acid process

$$CO + H_2 \xrightarrow{Cu\ cat} CH_3OH \xrightarrow[180^\circ C,\ 30\ bar]{CO,\ Rh\ Cat/I^-} CH_3CO_2H$$

Synthesis gas

Select > 90%

Capacity $10^6$ t/a

homogeneous catalytic pathway

This reaction is beautifully given by this equation CO + H 2 which is nothing but synthesis gas, in presence of copper catalyst produces methanol. So, this is a example of Fischer-Tropsch synthesis that under copper catalyst CO is; and hydrogen produces methanol. And then, upon reaction with carbon monoxide rhodium catalyst and presence of iodide at 180 degree centigrade and 30 bar of pressure produces acetic acid; selectivity more than 99 % and capacity 1 million ton per annum.

So, this is a huge scale process and popularly this is known as Monsanto acetic acid process. And this is also an example of homogeneous catalysis at is best. And this is performed in a homogeneous catalytic pathway. Now, what is important over here is that this extension of C1 chemistry which is nothing but the carbon monoxide and hydrogen the synthesis gas is converted to methanol.

And subsequently using this Monsanto acetic acid process, one thus produces acetic acid. And this overall scheme of things can be seen as an attempt to establish or prepare higher technical organic technical compounds from C1 building blocks. So, this is a sort of producing more complex carbon architecture from simple C1 block. And Monsanto acetic acid is a part of that.

And this is indeed a effective catalyst, as one can see the selectivity is more than, product selectivity is more than 90 % and the annual capacity is about 10 to 1 million ton per annum. So, that is hugely a large scale process. Now, before we start discussing about the catalytic pathway for this Monsanto acetic acid process, I must mention that in the catalyst over here is a rhodium catalyst, but it also requires presence of I –.

So, this role of I – in this Monsanto acetic acid process is interesting. And this will be more prominent as we looked at the, look at the catalytic cycle of this Monsanto acetic acid process. And also this Monsanto acetic acid process can be named as carbonylation of methanol. So, that means this carbon CO inserts into methanol to give acetic acid. So, with that, let me just look at the mechanism for this Monsanto acetic acid process.

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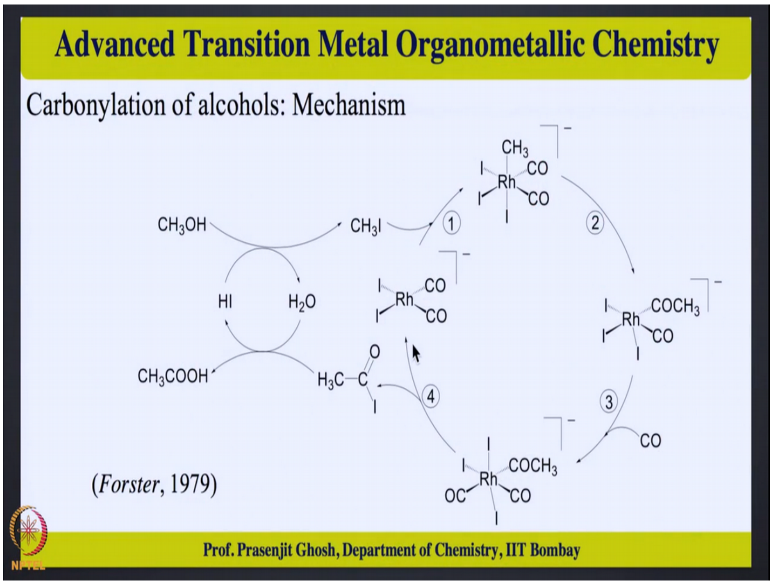

Advanced Transition Metal Organometallic Chemistry

Carbonylation of alcohols: Mechanism

(*Forster*, 1979)

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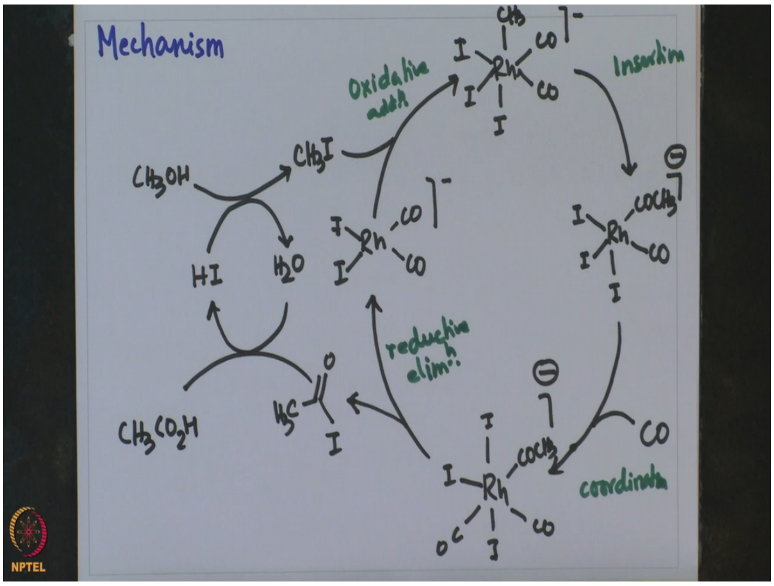

Methanol produced from synthesis gas reacts with hydrogen iodide producing water and methyl iodide. So, that is the role of iodine in the sense that it converts this methanol to methyl iodide. And methyl iodide then subsequently enters the catalytic cycle. So, the catalyst is this rhodium bis iodide dicarbonyl anion. And the methyl iodide enters it and undergoes oxidative addition to give rhodium triiodide anion.

So, this step is oxidative addition subsequently formation of this triiodide then undergoes carbonyl insertion to give rhodium CO CH 3 anion. So, this is insertion or migratory insertion; one can call it migratory insertion of carbonyl into the rhodium methyl bond. And the third step is CO coordination in the vacant site to give rhodium dicarbonyl triiodide methoxy compound.

So, this step is coordination carbon monoxide coordination followed by reductive elimination to give CH 3 CO I and regeneration of rhodium diiodide dicarbonyl anion. So, this is reductive elimination. And that reacting with water hydrolyses this CH 3 CO I to give acetic acid and HI. So, this is a very important reaction which produces acetic acid. And what one sees that there are 2 catalytic cycle.

Actually, the first one is the conversion of HI to water and subsequently back. And the other catalytic cycle involves the oxidative addition on a rhodium 1 species by methyl iodide followed by carbon insertion in the rhodium methyl bond followed by CO coordination to a metallic rhodium. And then subsequently reductive elimination to give CH 3 CO I which getting hydrolysed by water to produce acetic acid.

So, this is a beautiful example of 2 catalytic cycle working in tandem and produce on an industrial scale in synchronicity to produce acetic acid in very high turnover number. Now, there is another in this context, another important synthesis is worth mentioning.

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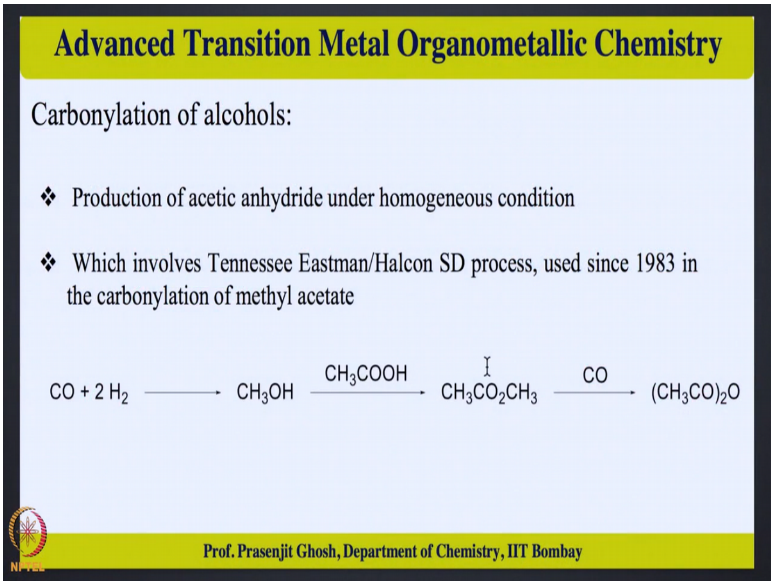

## Advanced Transition Metal Organometallic Chemistry

Carbonylation of alcohols:

- Production of acetic anhydride under homogeneous condition
- Which involves Tennessee Eastman/Halcon SD process, used since 1983 in the carbonylation of methyl acetate

$$CO + 2H_2 \longrightarrow CH_3OH \xrightarrow{CH_3COOH} CH_3CO_2CH_3 \xrightarrow{CO} (CH_3CO)_2O$$

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And which is this production of acetic anhydride. And this involves Tennessee Eastman/Halcon SD process. So, production of acetic anhydrides under homogeneous condition.

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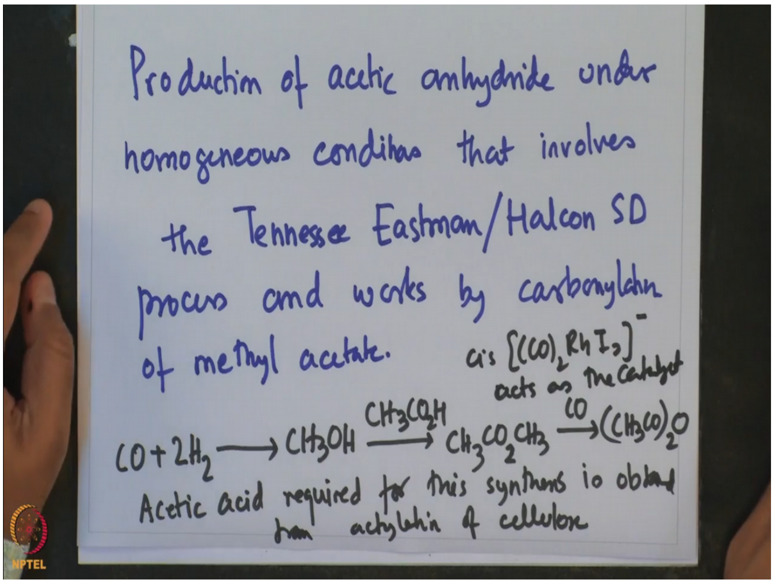

Production of acetic anhydride under homogeneous conditions that involves the Tennessee Eastman/Halcon SD process and works by carbonylation of methyl acetate.

cis $[(CO)_2RhI_2]^-$ acts as the catalyst

$$CO + 2H_2 \longrightarrow CH_3OH \xrightarrow{CH_3CO_2H} CH_3CO_2CH_3 \xrightarrow{CO} (CH_3CO)_2O$$

Acetic acid required for this synthesis is obtained from acetylation of cellulose

And this involves a reaction of industrial process which is called Tennessee Eastman/Halcon SD process. That involves the Tennessee Eastman/Halcon SD process and this works by carbonylation of methyl acetate. So, this is again beautifully given by this CO + H 2 which is nothing but a synthesis gas generating methanol which then reacting with acetic acid producing methyl acetate which reacting carbon monoxide to give acetic anhydride.

And these acetic acid required for this synthesis is obtained from acetylation of cellulose. So, with this, we come to the conclusion of our discussion on this important reaction which is carbonylation of alcohols. And what we see that this involves in important industrial process by the name of Monsanto acetic acid process. And these Monsanto acetic acid process involves a rhodium catalyst.

And it is, the process is achieved in presence of iodine. And we had looked into the catalytic cycle for this Monsanto acetic acid process. And what we had observed that this catalytic cycle proceeds, this proceeds by oxidative addition of methyl iodide. And this methyl iodide is obtained from methanol by a treatment with H HI to give water and methyl iodide. So, this methyl iodide so formed then reacts with the rhodium carbonyl 1 compound through via an oxidative addition process to give a rhodium 3 compound.

And then a CO insertion occurs on the rhodium 3 into the rhodium methyl group, followed by CO ordination and finally reductive elimination to give back the acetic acid so formed. Now, in this, we have also seen that the offshoot of this reaction is extended for producing acetic anhydride, which is nothing but carbonylation of methyl acetate. And this has also been performed under industrial scale in which carbon monoxide and hydrogen is converted to as methanol.

And then, subsequent reaction of the methanol to acetic acid produces methyl acetate. And finally, the carbonylation of methyl acetate produces carbon monoxide. And the acetic acid required for this reaction comes from acetylation of cellulose. So, with this we have made a full circle in terms of the C1 chemistry is concerned. And we had looked into the various catalytic processes that are currently in place in industrial scale using this organometallic complexes.

Now, another important attribute of this Monsanto process is that it is an attempt to convert C1 speed stock to higher technical higher order of organic compounds in terms of converting it to acetic acid. And then subsequently, acid be used converted to something using the C1 chemistry. So, the importance of C1 chemistry can be gauged by 4 industrial processes that we have been looking at so far.

The starting with it was this Fischer-Tropsch synthesis, followed by this Monsanto acetic acid synthesis and also Tennessee Eastman/Halcon SD process. And lastly, the process is related to water-gas-shift reactions. So, one can in overall see how the C1 chemistry is gaining prominence in the way of utilisation of carbon monoxide. So, let me just take back a bit and look at the broader picture of the few lectures that we have been discussing about.

In the beginning what we had seen that organometallic complexes are particularly useful in carrying out various kinds of C-C and C-heteroatom bond forming reactions, many of them done under catalytic fashion. Now, as far as the substrates are the concerned, one can see that olefin or primarily ethylene which is a source for converting it into fine or other chemicals using various industrial processes.

Now, even though ethylene can be used for conversion to higher order organic targets. However, the another useful approach, is to convert carbon monoxide to generate these compounds. And from this perspective alone, the C1 chemistry gains relevance. And with respect to C1 chemistry, we had looked at the reducing as well as the oxidising aspects of carbon monoxide in the form of water shift gas reaction, carbon monoxide was oxidised to carbon dioxide along with production of hydrogen by reaction with water.

Whereas in a Fischer-Tropsch synthesis, carbon monoxide was converted to hydrocarbons along with generation of water. Now, these, one of the, even though these are industrial processes, one of the main (()) (23:53) for this processes is the fact that they have poor selectivity and requires very harsh conditions. And from that perspective, their the homogeneous catalyst development were required.

And one of the strategies that involves are exploited for developing the homogeneous catalyst is being able to carry out this reaction involving the pathways that would include metal, the carbon monoxide activation by coordination to metal followed by the reaction with hydrogen. And that indeed worked successfully for developing the homogeneous catalyst counterpart for the water-gas-shift reaction as well as for the Fischer-Tropsch synthesis that we had encountered so far.

Now, as far as the Monsanto acetic acid process is concerned, this is a beautiful relay process which starts from synthesis gas, goes all the way to methanol and finally carbonylation of methanol to acetic acid; all done using a homogenous catalytic pathway in presence of iodide. And the reaction one of the main strength of the Monsanto acetic acid process is its selectivity where acetic acid is selectively formed with the product selectivity of > 90 %.

And also, the thy throughput or the capacity for this process is amazing as it produces about 1 million ton of acetic acid per annum. And we had seen the power of homogeneous catalysis, and in this context, I should also note that how in Fischer-Tropsch synthesis, in synthesis gas, carbon monoxide and hydrogen in presence of another rhodium carbonyl compound would produce ethylene glycol.

And the, that turnover was about 3 million tons a year. So, there are processes extremely powerful homogeneous catalytic processes that produces a large capacity of chemicals using this homogeneous catalytic pathway. Now, again with respect to Monsanto acetic acid process, one wants to note the importance of using, the importance of the presence of iodide, as it converts methanol to methyl iodide and which then enters the catalytic cycle as was discussed earlier.

Now, going even further, let me just once again recapitulate that Monsanto acetic acid process can be extended further beyond to produce acetic anhydrides. And this is by this Tennessee Eastman/Halcon SD process which is which employs the principle of exploitation of methyl acetate. So, what is done over here is synthesis gas is converted to methanol and then reacted with acetic acid to produce methyl acetate and subsequently carbonylation of the methyl acetate would result in the acetic anhydride.

Now, this acetic acid so required for this Tennessee Eastman/Halcon SD process is obtained by acetylation of cellulose and thus the reaction proceeds. As in the case of the Monsanto process, rhodium the catalyst used over here is the, catalyst used is this rhodium cis dicarbonyl rhodium I 2 – acts as the catalyst. And this is the same catalyst that was used for Monsanto acetic acid synthesis process.

So, with this, I would like to conclude today's discussion on carbonylation of alcohol. We have covered 2 important industrial reactions. One is this Monsanto carbonylation of Monsanto acetic acid synthesis. The other one is Tennessee Eastman/Halcon SD process. The first one makes acetic acid and the second one makes acetic anhydride. Both uses same catalyst which is rhodium dicarbonyl dihydride anion.

And both are used for large capacity throughput synthesis. So, with this, I once second thank you for being with me in this lecture. We are going to take up and other interesting topic of hydrogenations of alkanes in the next lecture when we meet next. Till then goodbye and thank you.