Advanced Transition Metal Organometallic Chemistry
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Module - 12
Lecture - 59
Organometallic Catalysis Reactions: Hydroformylation

Welcome to the course on Advanced Transition Metal Organometallic Chemistry. Continuing with our discussion on organometallic catalysis reaction, today we are going to be talking about the largest scale industrial process under homogeneous catalysis. This way, application of organometallic chemistry is so huge, about 7 million tons per annum of the product is produced using this particular reaction.

And this reaction is none other than hydroformylation reaction discovered almost a century back by Otto Roelen. So, today we are going to be talking about this reaction which is the largest scale industrial process under homogeneous catalysis. We have, in this context let me note that we have also looked at the longest application of a industrial scale organometallic catalysis. And that was Wacker oxidation using ethylene to produce acetaldehyde.

So, that has been in place for more than a century now. And this reaction which is hydroformylation is the greatest application of organometallic catalysis, by which about 7 million tons of products are produced annually using this reaction in industry. This hydroformylation process is also known as oxo process. And there is, there are 2 similarities that exist between this, the largest scale industrial process which is hydroformylation and the longest known industrial process under homogeneous catalysis which is Wacker oxidation.

The similar, the first similarity being that both used ethylene or olefin as a substrates. So, both of this reaction, the longest known as the largest scale uses olefin as a substrate for conversion to the product which is an aldehyde. Now, in both the cases too, in Wacker oxidation, the longest known homogeneous catalysis process as well as this hydroformylation reaction the largest scale industrial process under homogeneous catalysis; the product so formed also is an aldehyde.

So, there is a lot of excitement about these 2 reactions. And we have covered in details the Wacker oxidation. And in today's lecture I am going to be talking about this largest scale industrial process under homogeneous catalysis reaction which is this hydroformylation reaction or the oxo synthesis.

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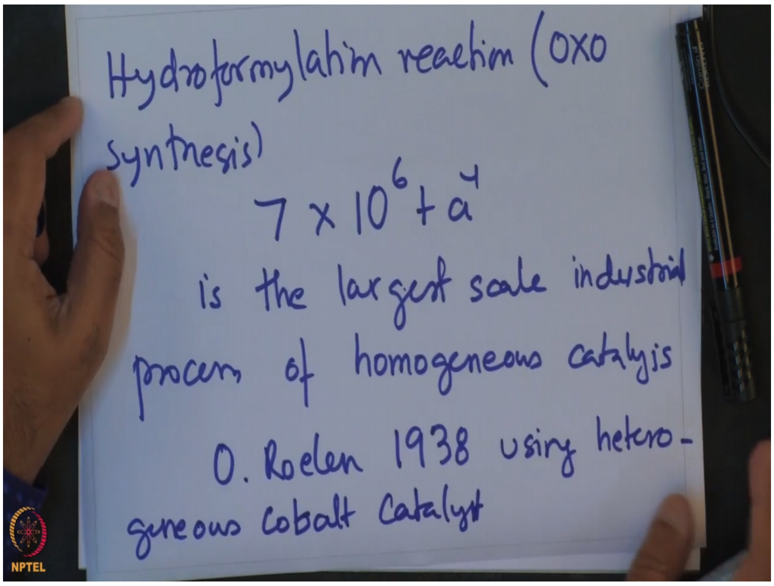

Hydroformylation reaction (oxo synthesis)

7×10^{6} t a^{-1}

is the largest scale industrial process of homogeneous catalysis

O. Roelen 1938 using heterogeneous cobalt catalyst

So, the amount of alcohol produced by this method is about 7 into 10 to the power 6 tons per annum, which is a large amount of chemical produced by this. And hydroformylation is the largest scale industrial process of homogeneous catalysis. The reaction was first observed and patented by Otto Roelen in 1938 using a heterogeneous cobalt catalyst. And the actual catalyst is a cobalt hydride complex which is formed from the carbonylation of cobalt oxide with hydrogen and CO.

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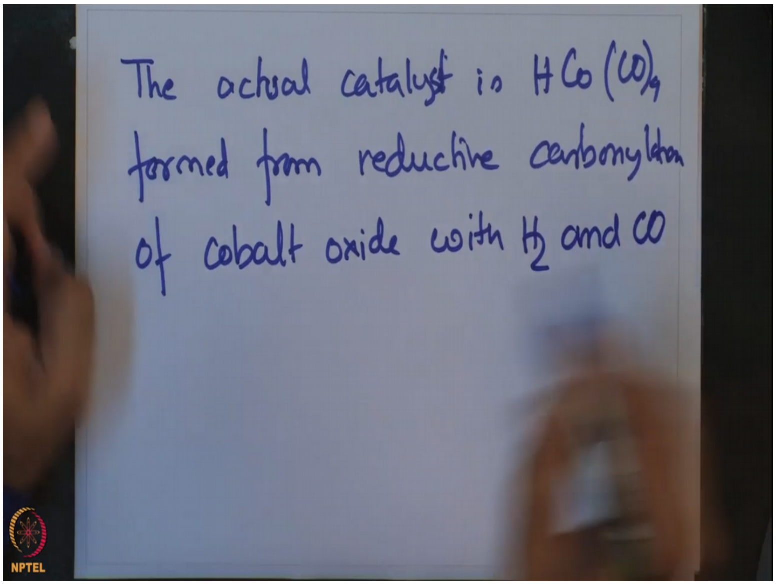

The actual catalyst is $HCo(CO)_4$ formed from reductive carbonylation of cobalt oxide with H_2 and CO

Is formed from reductive carbonylation of cobalt oxide with hydrogen and carbon monoxide. So, in fact, this hydroformylation is a addition of hydrogen and CO across a double bond and is actually given by this equation.

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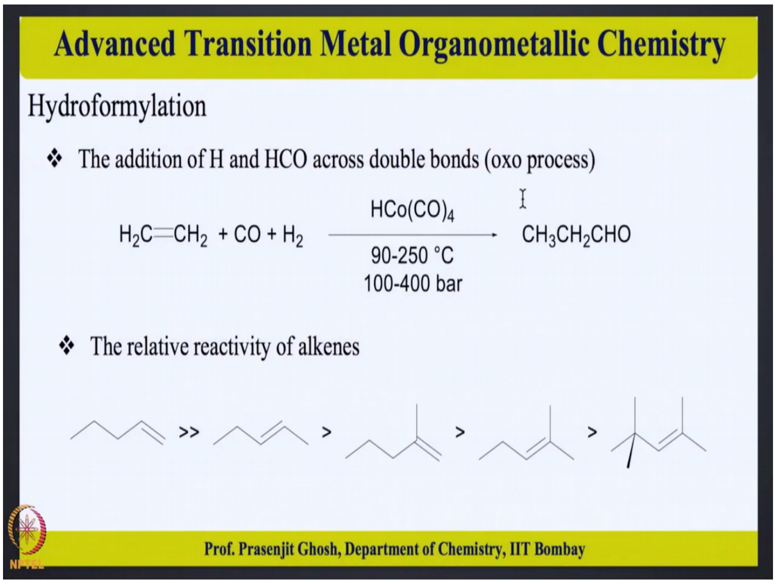

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Hydroformylation

- The addition of H and HCO across double bonds (oxo process)

$$H_2C{=}CH_2 + CO + H_2 \xrightarrow[\substack{90\text{-}250\ ^\circ C \\ 100\text{-}400\ bar}]{HCo(CO)_4} CH_3CH_2CHO$$

- The relative reactivity of alkenes

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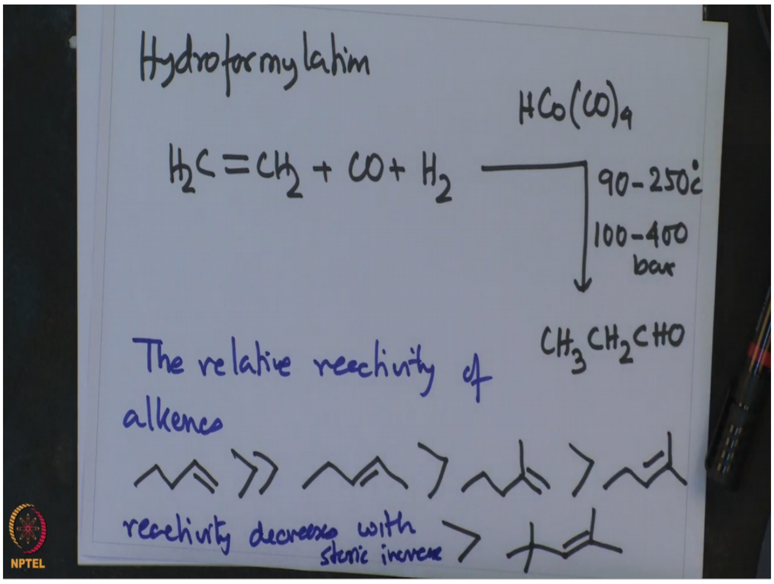

Hydroformylation

$$H_2C{=}CH_2 + CO + H_2 \xrightarrow[\substack{90\text{-}250^\circ c \\ 100\text{-}400\ bar}]{HCo(CO)_4} CH_3CH_2CHO$$

The relative reactivity of alkenes

reactivity decreases with steric increase

And the reaction is given by CH 2 CH 2 CO + H 2. The active catalyst is H CO 4, temperature range is about 90 to 250 degree centigrade, about 100 to 400 bar giving CH 3 CH 2 CHO. Now, the relative reactivity of alkenes in this transformation is given as follows. Is terminal alkenes to internal alkenes more reactive than sterically hindered terminal alkenes, more reactive than sterically hindered internal alkenes, more reactive than sterically further more sterically hindered internal alkenes.

So, reactivity decreases with increase in sterics. So, this is, reactivity decreases with sterics, steric increase. So, this is an important observation which shows that terminal alkenes are more reactive than the internal ones because of this reasons that this is more sterically remanding than this. And then, internal alkenes are more reactive than sterically hindered terminal alkenes and sterically hindered terminal alkynes are more reactive than sterically hindered internal alkanes, and this goes, goes on.

So, the reactivity decreases with sterics. Now, before I proceed to talk about the catalytic mechanism for this hydroformylation reaction, I must dwell a little bit on this coincidental correlation that I had just noted at the beginning of the class about the 2 industrial processes. 1 is this hydroformylation reaction which is by far the largest scale industrial process under homogeneous catalysis and also this Wacker oxidation reaction which is the longest known industrial process under homogeneous catalysis.

The similarity that I had drawn is the substrate and the product for these 2 industrial process. The longest known industrial process under homogeneous catalysis, Wacker oxidation. And the largest scale industrial process under homogeneous catalysis hydroformylation. For them, the reactants which is ethylene and the product which is aldehyde are the same.

So, one can see and the other point that I want to make is that the aldehyde as a product is very important starting intermediate to accessing many other functional, many other compounds because aldehydes are amenable to various transformation of various functionalities because they can be converted to different targets using organic manipulations.

So, these 2 process not only highlights the importance of aldehyde as a target material to be produced in industrial scale, but also this shows that there can be multiple ways of accessing aldehyde from ethylene through oxo process or through hydroformylation reaction. And each of them can be equally important and may be practiced in industry. So, this I believe is very important correlation that one should keep in mind while taking a look at hydroformylation reaction and Wacker reaction.

So, with this, let me just talk about the various products produced by hydroformylation reaction. Actually, it sets outs a set of reactions and C 3 to C 15 aldehydes are produced by respective olefins by oxo process. And they can be further converted to amines, carboxylic acids, alcohols. And that sort of once again highlights the important of aldehyde from industrial perspective for accessing other important compounds.

And hence, from that stand point, these 2 process gives direct access to producing aldehydes in large scale. And that is why they have been extremely successful and popular in the industrial world.

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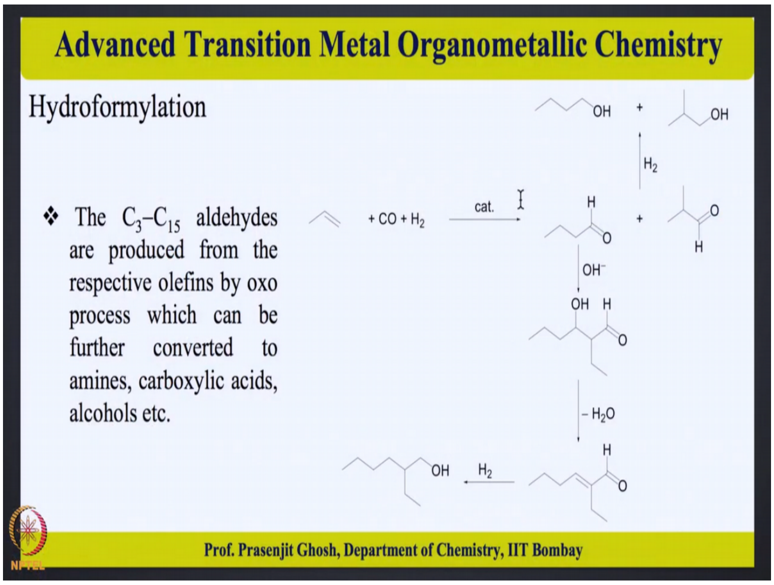

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Hydroformylation

- The C_3–C_{15} aldehydes are produced from the respective olefins by oxo process which can be further converted to amines, carboxylic acids, alcohols etc.

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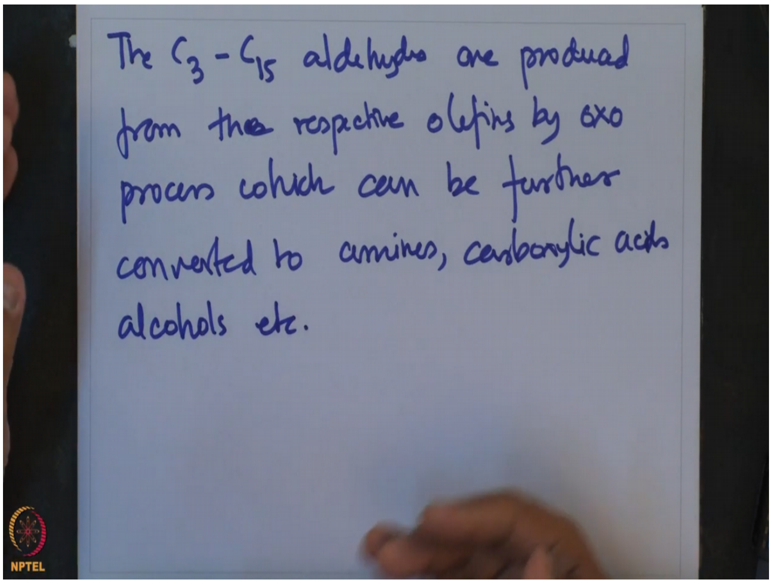

The $C_3 - C_{15}$ aldehydes are produced from the respective olefins by oxo process which can be further converted to amines, carboxylic acids alcohols etc.

So, C 3 and C 15 aldehydes are produced from the respective olefins by oxo process, which can be further converted to amines, carboxylic acid, alcohols and etcetera. So, from a industrial point of view as I said that aldehydes are extremely important, but they can be converted to whole range of other chemicals like amines, carboxylic acid, aldehydes. And this hydroformylation provides a useful method for synthesising this aldehydes from C 3 to C 15 fragments. And this is illustrated by this sequence of reaction.

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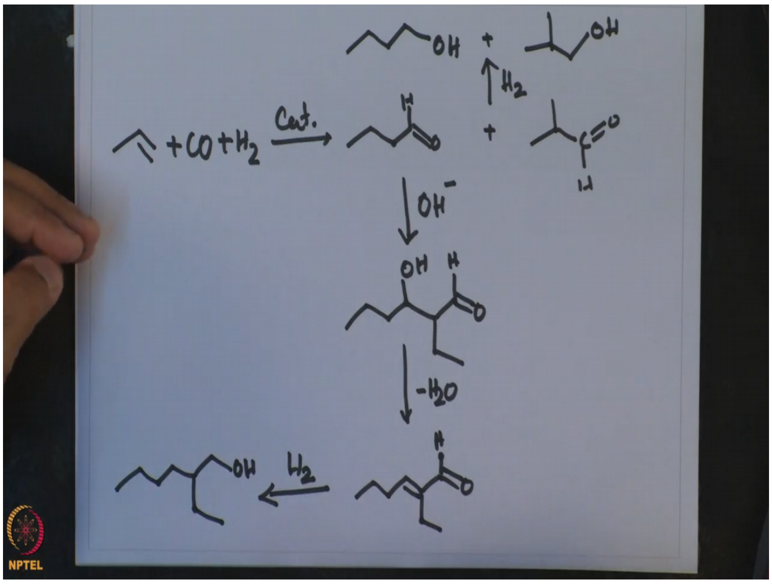

Propene + CO + H 2 in presence of a catalyst gives propenealdehyde that can be terminal or the aldehyde can form at the internal carbon giving a branched aldehyde. So, these 2 can be further reduced to corresponding alcohol in presence of hydrogen. And in that case, one would obtain these 2 alcohols. The, in presence of this, the aldehyde can undergo these 2 aldehyde can undergo condensation to give the following product that would eliminate water to give this.

And that in presence of hydrogen would produce the corresponding alcohol. So, what it sees that, these hydroformylation reaction sets out a several sequences of reactions that can eventually be used or leads to formation of different products. Now, hydroformylation of terminal alkenes are industrially important;

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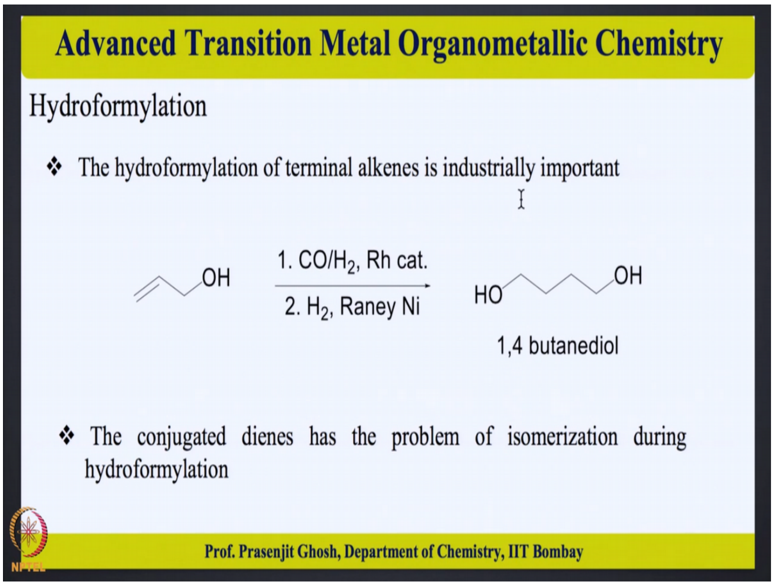

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Hydroformylation

- The hydroformylation of terminal alkenes is industrially important

- The conjugated dienes has the problem of isomerization during hydroformylation

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Because they, and 1 such usage is in production of 1 4 butanediol which is a very important intermediate in synthesis of THF the ethyl 2 ethylhexonol and a higher terminal alcohols.

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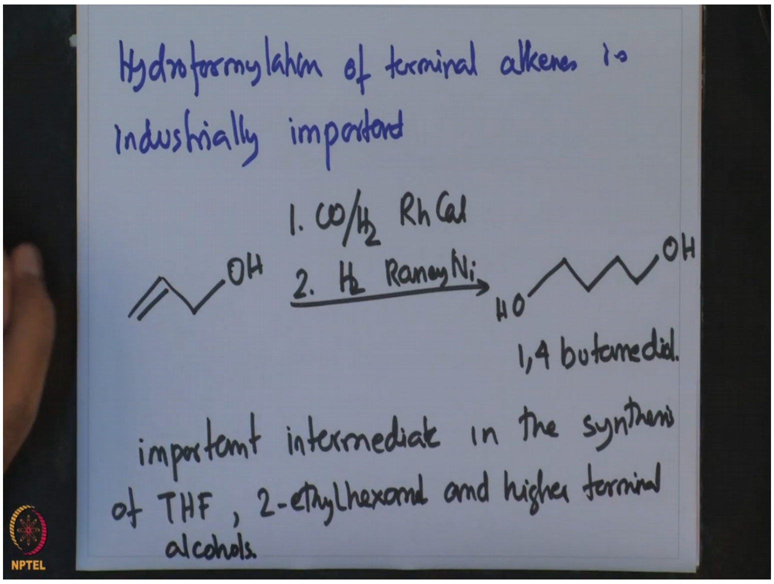

Hydroformylation of terminal alkenes is industrially important

important intermediate in the synthesis of THF, 2-ethylhexanol and higher terminal alcohols.

So, hydroformylation of terminal alkene is industrially important. And that is given by 1, CO H 2 and rhodium catalyst. And second is dihydrogen to give Raney nickel reduction to produce this 1 4 butanediol. And this butanediol is used in the important intermediate. Used in the synthesis of THF tetrahydrofuran, 2 ethylhexonol and higher terminal alcohols. So, one can see the impact of this hydroformylation reaction for producing intermediates which are industrially important and for several reasons.

And this can be done by taking terminal alkenes and then, converting them to aldehyde. And then, subsequently reducing with hydrogen and Raney nickel to give this butanediol.

Conjugated dienes has the problem of isomerization during hydroformylation reaction. And this is governed by energetics of the diene itself.

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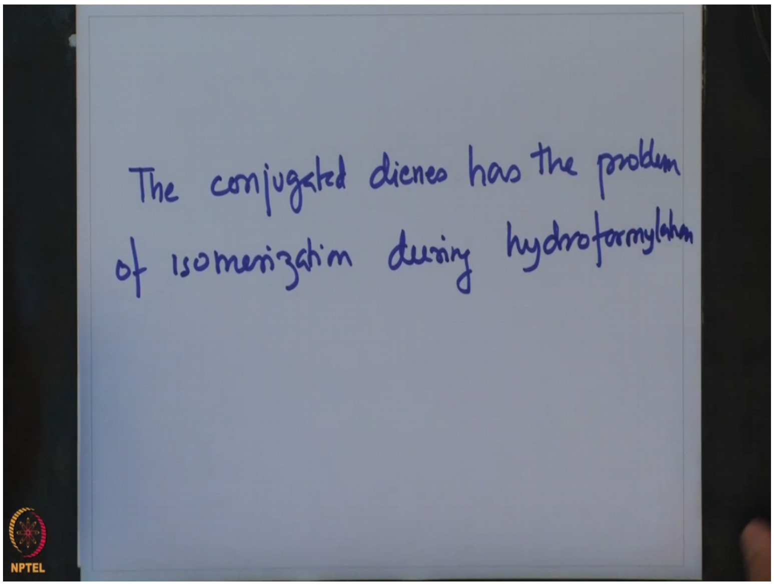

The conjugated dienes has the problem of isomerization during hydroformylation

The conjugated dienes has the problem of isomerization during hydroformylation. And this is primarily due to the very close energetics of the conjugated dienes and their isomers. And that is probably what governs this isomerization process during hydroformylation. Now, let us take a look at the mechanism of hydroformylation.

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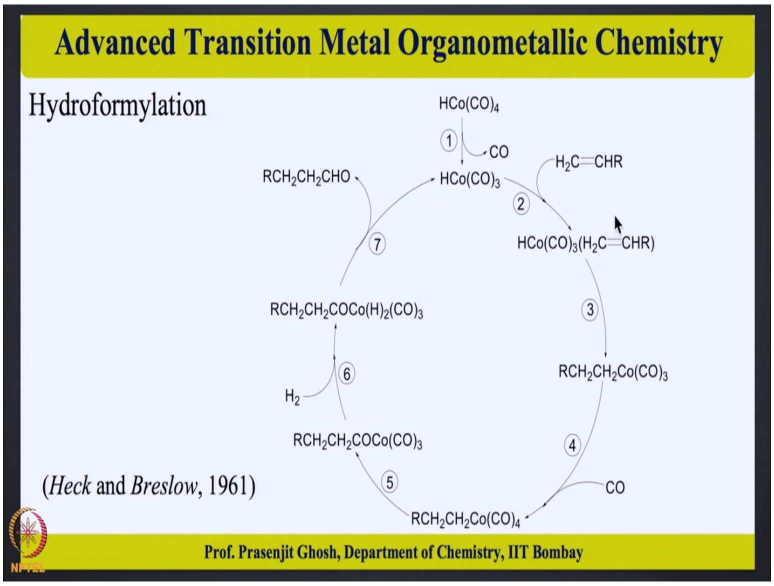

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Hydroformylation

$HCo(CO)_4$

① $-CO$

$HCo(CO)_3$

② $H_2C{=}CHR$

$HCo(CO)_3(H_2C{=}CHR)$

③

$RCH_2CH_2Co(CO)_3$

④ CO

$RCH_2CH_2Co(CO)_4$

⑤

$RCH_2CH_2COCo(CO)_3$

⑥ H_2

$RCH_2CH_2COCo(H)_2(CO)_3$

⑦

RCH_2CH_2CHO

(*Heck* and *Breslow*, 1961)

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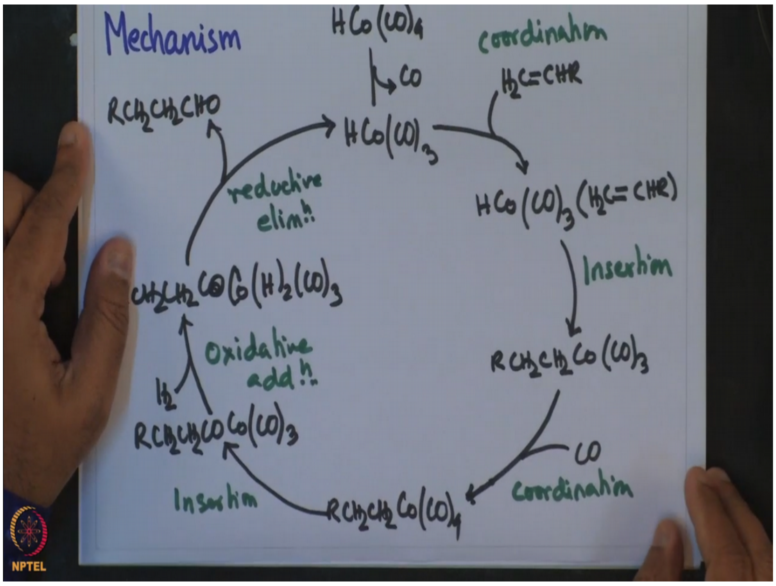

So, the active catalyst is a cobalt hydride tetracarbonyl which loses a carbon monoxide CO to give the active species H Co CO 3. So, then comes this olefin coordination step H 2 C CH R. This is the coordination step. So, that coordinates and forms H Co CO 3 H 2 C CHR. And then is the insertion, insertion of this olefin into the cobalt hydride bond to give the cobalt alkyl complex R CH 2 CH 2 Co CO 3. So, this step is the insertion step.

Then, as the compound due to this insertion of olefin into cobalt hydride bond, becomes coordinatively unsaturated. And that vacant site is occupied by the CO which was liberated over here, to give R CH 2 CH 2 Co CO 4. And this is the coordination step again. But this time around, this is coordination of CO. Subsequently to the CO coordination is migration of the coordinated CO into the metal alkyl bond R CH 2 CH 2 CO Co CO 3.

So, this is migration of the coordinated CO. So, this again, the coordination insertion into the alkyl bond. So, now, so far, if I look at this hydroformylation process, we had seen that there are 2 sequences of coordination insertion happening over here. The first coordination insertion happened with respect to the olefin. The olefin got coordinated. And then inserted into a cobalt hydride bond. And then, the subsequent coordination insertion occurred with respect to CO.

The CO got coordinated and then inserted into the cobalt alkyl bond. So, there are 2 steps of coordination insertion occurring over here. And then, one with carbon monoxide, the second one is with carbon monoxide. The first one is with alkene. And then, the reaction of hydrogen is the oxidative addition giving R CH 2 CH 2 CO CO cobalt dihydride, CO 3. So, this is a cobalt oxidative addition reaction occurring over here in which the hydrogen activation occurs.

And then, finally, the reductive elimination giving rise to the product R CH 2 CH 2 CHO. So, this is the reductive elimination step. So, with this, the cobalt hydride tricarbonyl is regenerated. So, this sort of closes the loop and finishes this catalytic cycle of this very important reaction which is the biggest largest scale industrial process known so far. So, this reaction, the catalytic with cobalt hydride consists of 6 elementary steps.

There are 2 sequences of coordination insertion occurring. The first one is occurring with the olefin and olefin coordination versus olefin insertion into a cobalt hydride bond to give the cobalt alkyl moiety. And after the cobalt alkyl moiety is formed, the second sequences of coordination insertion is seemed to occur. And this second insertion is occurring of with respect to carbon monoxide.

So, carbox coordinates and then inserts into cobalt alkyl to give the cobalt acyl bond R CH 2 CO CH 3. And after this, this oxidative addition of dihydrogen is seemed to occur to give a cobalt dihydride complex which eventually will reductively eliminate to give the required hydroformylated product along with the regeneration of the catalyst. So, and subsequent to this the cobalt catalyst there is an improvement on this.

And people have come up with; there is a rhodium catalyst which is right now be commercially used even though rhodium is very expensive. But the catalyst is so active that its high turnover number, extremely high turnover number in a mixed for its expensive metal. Okay. So, with that, let me just conclude today’s lecture on hydroformylation reaction and recapitulate what we had discussed in today's talk.

As we started off on hydroformylation reaction bearing and analogy with respect to the Wacker process which is the oxidation of ethylene to give acetaldehyde. And what we had noted that, both the process of hydroformylation forming olefins to aldehydes and the Wacker process converting ethylene to acetaldehyde. For both of the process the starting materials are same which are olefins.

And the product are also the same, which is aldehydes. We have also noted that these aldehydes are important intermediates which can further be converted to other targets. And that is why, there is a huge demand for large-scale synthesis of aldehyde. We had observed that these hydroformylation also known as oxo process was discovered around 1938 by Roelen and subsequently patented and then followed up.

The catalytic cycle of hydroformylation reaction involved a formation of cobalt hydride tetra carbonyl species which then underwent a sequence of coordination insertion with the reacting substrate which is an olefin to give a cobalt alkyl complex. And that complex then again underwent a sequence of coordination insertion to give a cobalt acyl complex using with carbon monoxide.

And finally, the addition of hydrogen to give oxidative addition followed by reductive elimination would close the loop and give the desired product aldehyde along with the formation of cobalt hydride species. So, with this, I conclude today's lecture on hydroformylation reaction. And formally all the topics that has been covered in this course is covered with this discussion on hydroformylation reaction.

I sincerely thank you for patiently be hearing me in this lecture and I look forward to the last lecture which is of the course which is in the next lecture which would be the next lecture in which I would give a summary of all the topics that has been discussed as a part of this course. So, with that, thank you and goodbye.