Advanced Transition Metal Organometallic Chemistry

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Module - 10
Lecture - 49
Organometallic Catalysis Reactions: Olefin Oxidation

Welcome to this course on Advanced Transition Metal Organometallic Chemistry. We had been discussing carbon-heteroatom bond forming reaction. And moving on from the carbon-heteroatom bond forming reaction, we are going to be discussing some more applications of organometallic catalysis. But before I do that, let me just recapitulate what we have been discussing in the last few lectures.

To begin with, we looked at a palladium catalysed C-C bond forming reactions. Then we went on to move to various types of carbon-heteroatom bond forming reaction. In another context we have looked into carbon-nitrogen bond forming reactions, carbon-boron, carbon-silicon bond forming reactions. Much of these reactions are addition type reactions and very few of them are sigma bond metathesis type like cross couplings type.

And in the silylation, hydrosilylation reactions, we had seen another interesting reaction which is dehydrogenative coupling in which the silicon-silicon bond is formed as a part of this silylation reaction. Now, we are going to focus on some more interesting catalytic applications of this organometallic complexes. In particular, various reactions that we would be looking at are:

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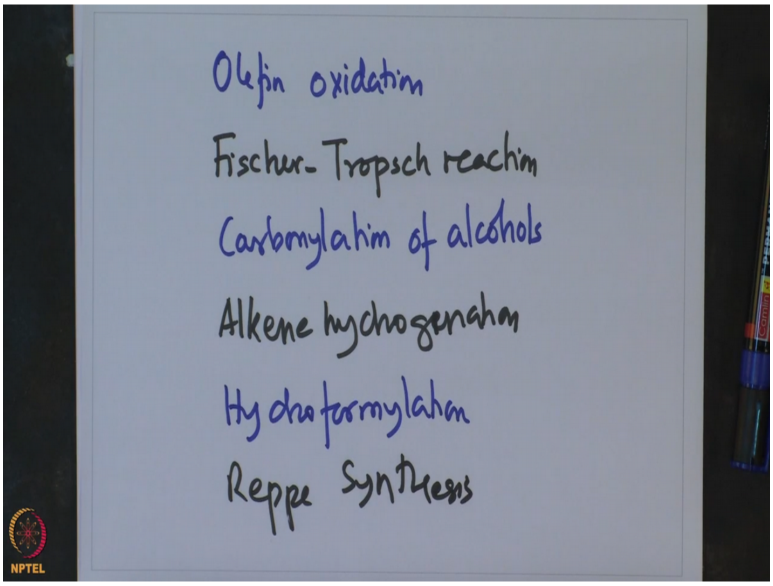

Olefin oxidation

Fischer-Tropsch reaction

Carbonylation of alcohols

Alkene hydrogenation

Hydroformylation

Reppe Synthesis

Olefin oxidation, Fischer-Tropsch reaction, carbonylation of alcohols, hydrogenation of alkene, alkene hydrogenation, hydroformylation reaction and this Reppe synthesis. So, these, the length and the breadth, the extent of the chemistry demonstrated by this variety of reaction sort of highlights the scope of organometallic complexes in homogenous catalysis.

It sort of again promotes or the utility of organometallic complexes or dominance of organometallic complexes in the world of homogenous catalysis can be understand by the scope of reaction, the diverse reaction that this organometallic complexes carry out. That currently are used in large scale industrial processes. So, with that we are going to be focusing on the first reaction which is olefin oxidation reaction.

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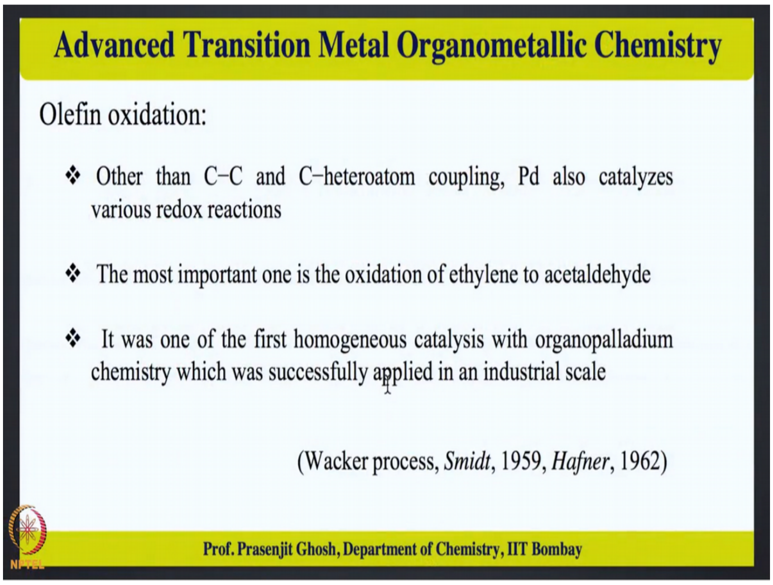

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Olefin oxidation:

- Other than C–C and C–heteroatom coupling, Pd also catalyzes various redox reactions
- The most important one is the oxidation of ethylene to acetaldehyde
- It was one of the first homogeneous catalysis with organopalladium chemistry which was successfully applied in an industrial scale

(Wacker process, *Smidt*, 1959, *Hafner*, 1962)

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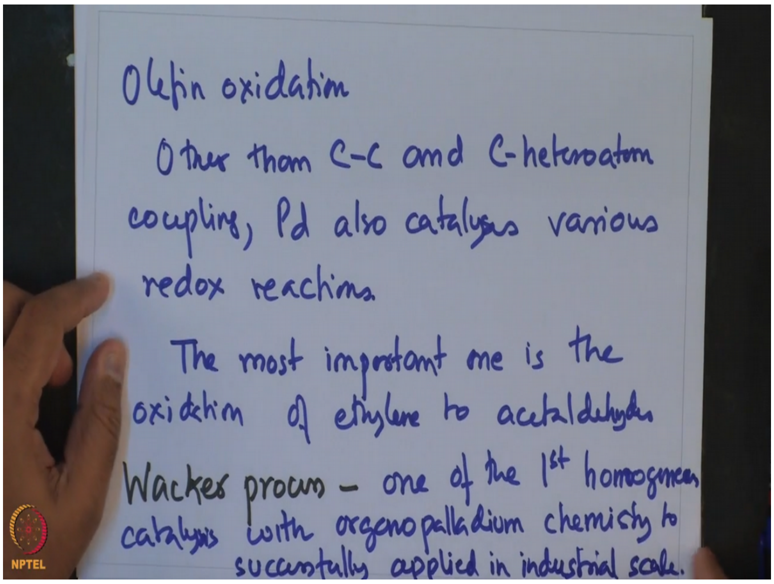

Olefin oxidation

Other than C-C and C-heteroatom coupling, Pd also catalyses various redox reactions.

The most important one is the oxidation of ethylene to acetaldehyde

Wacker process - one of the 1st homogeneous catalysis with organopalladium chemistry to successfully applied in industrial scale.

Now, other than, the palladium in organometallic chemistry is mainly known for their C-C carbon-carbon or carbon-heteroatom coupling reactions. But palladium also catalyses various other redox reactions. And olefin oxidation is one such thing. We are going to be looking at it in bit more detail. So, other than C-C and C-heteroatom coupling, palladium also catalyses various redox reactions.

The most important one is the oxidation of ethylene to acetaldehyde. This is a interesting reaction. Is the oxidation of ethylene to acetaldehyde. And this is popularly known as Wacker's process. And it was one of the first homogenous catalysis with organopalladium chemistry to be successfully applied in industrial scale. So, this is popularly known as Wacker process.

Wacker process, one of the first homogenous catalysis with organopalladium chemistry to successfully applied in industrial scale. So, this Wacker reaction is something that we are going to be looking at in much more detail. And this is a very interesting reaction. It, this Wacker process consists of multiple elementary steps, including a copper couple. And we are going to look in that in bit more detail.

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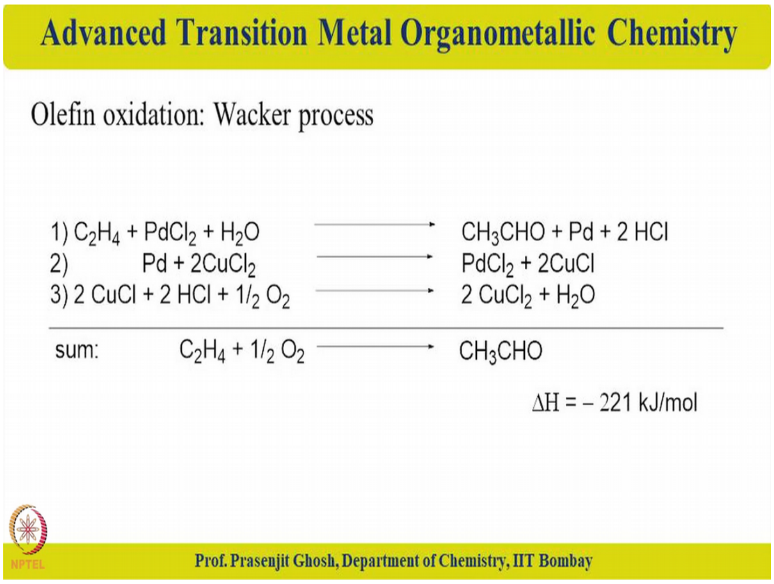

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Olefin oxidation: Wacker process

1) $C_2H_4 + PdCl_2 + H_2O \longrightarrow CH_3CHO + Pd + 2\,HCl$

2) $Pd + 2CuCl_2 \longrightarrow PdCl_2 + 2CuCl$

3) $2\,CuCl + 2\,HCl + 1/_2\,O_2 \longrightarrow 2\,CuCl_2 + H_2O$

sum: $C_2H_4 + 1/_2\,O_2 \longrightarrow CH_3CHO$

$\Delta H = -221$ kJ/mol

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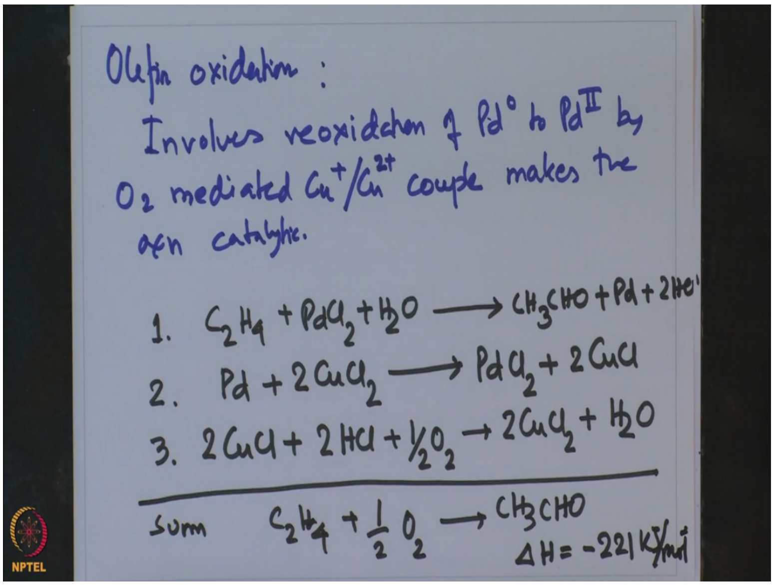

Olefin oxidation :

Involves reoxidation of Pd^0 to Pd^{II} by O_2 mediated Cu^+/Cu^{2+} couple makes the rxn catalytic.

1. $C_2H_4 + PdCl_2 + H_2O \longrightarrow CH_3CHO + Pd + 2HCl$

2. $Pd + 2\,CuCl_2 \longrightarrow PdCl_2 + 2\,CuCl$

3. $2\,CuCl + 2\,HCl + \frac{1}{2}O_2 \rightarrow 2\,CuCl_2 + H_2O$

sum $C_2H_4 + \frac{1}{2}O_2 \longrightarrow CH_3CHO$

$\Delta H = -221$ kJ/mol

This process is known for over 100 years. It is a pretty old process involves the oxidation palladium 2 palladium 0 couple and reoxidation of palladium 0 to palladium 2 by oxygen mediated copper 2 copper 1 copper 2 couple. Involves reoxidation of palladium 0 to palladium 2 by oxygen mediated copper + copper 2 + couple, makes the reaction catalytic. The elementary steps are given by this equation.

First, C 2 H 4 + Pd Cl 2 + H 2 O, CH 3 CHO + Pd + 2 HCl. Step 2 is Pd + 2 Cu Cl 2 Pd Cl 2 + 2 Cu Cl. Step 3, 2 Cu Cl + 2 Hcl + half O 2 giving 2 Cu Cl 2 + H 2 O. Now, first is acetylene with palladium chloride, keep acetaldehyde + palladium 0. Next come the oxidation of palladium 0 to palladium 2 with copper chloride becoming cuprous chloride. And cuprous chloride is first further oxidised to copper 2 chloride in presence of oxygen.

So, the net reaction is C 2 H 4 + half O 2 giving CH 3 CHO. And delta H for this reaction is – 221 kilojoule per mole. So, this is a interesting reaction in which acetylene is converted to acetaldehyde. This is one of the first homogeneous catalytic process that has been used in industrial scale was is known. And that this, the reaction involves the oxidation of acetylene to acetaldehyde and the process, the palladium 2 gets reduced to palladium 0 and the catalytic cycle is completed by reoxidising palladium 0 to palladium 2 by a copper 2 to copper 1 couple.

And then the copper 1 then further gets oxidised to copper 2 in presence of oxygen. So, let us, this is quite an interesting reaction. And we are going to be looking at the catalytic cycle to get an idea as how this reaction works.

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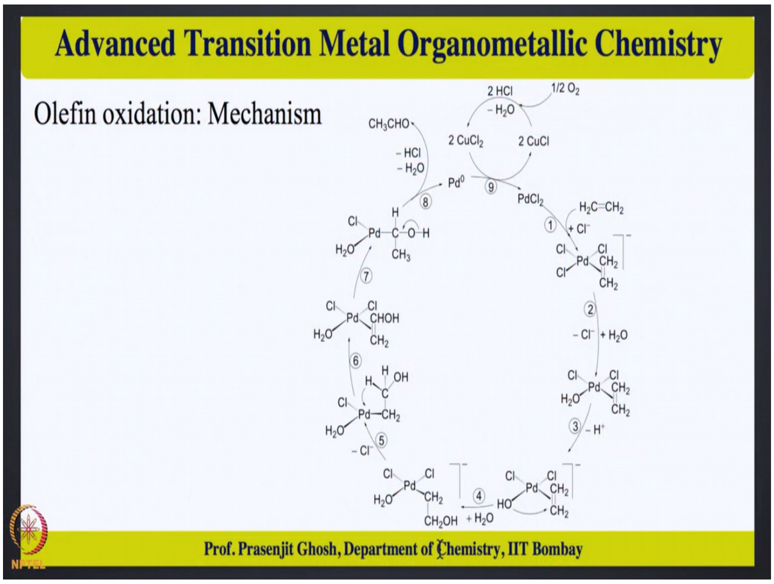

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Olefin oxidation: Mechanism

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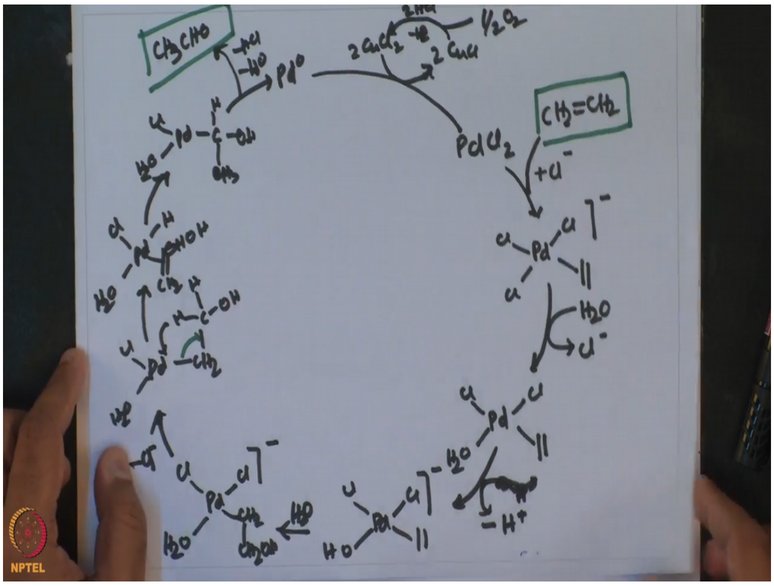

So, the first involves the reaction of a palladium Cl 2 is reacting with Ch 2 Ch 2 + Cl – to give this complex Pd Cl, Cl, Cl, olefin anionic. The next step is water getting added and Cl being eliminated to give this aqua coordinated complex, CL. This is a neutral complex which loses a proton to give a palladium hydroxo species Pd, Cl, olefin, Cl, OH. This palladium hydroxo species then reacts with water.

So, water goes and attacks and protonates this hydroxo 2 alco water. And this olefin becomes Ch 2 OH. So, this gives Pd, Cl, OH 2, CH 2, CH 2 OH, Cl, –. And then, this loses chlorine to give Pd, Cl, OH 2, CH 2, C, OH, H, H. The hydrogen then attacks palladium 2 give a palladium hydride. And then, olefin CH OH, CH 2, water, chlorine, that undergoes this hydride insertion to give Pd, O H 2, Cl, C, H, CH 3, OH.

That eliminates – HCl – water to gives CH 3 CHO and palladium 0. Now, this palladium 0 gets converted by 2 Cu Cl 2 to 2 Cu Cl and that goes back with half O 2 – H 2 O to give 2 HCl. So, this is a complex scheme in which the first, the Pd Cl palladium 0 becomes oxidised palladium 2, then coordination of the olefin. Then, replacement of the chloride with the water.

After the replacement of the chloride with the water, the water loses a proton H – to give anionic hydroxo species. Then water is added to this olefin. And this becomes CH 2 CH 2 OH. Chloride is lost. And to, so to give Cl, water, CH 2 neutral compound CH OH. Now, the hydride sort of attacks the palladium. And the olefin is created which is, this hydrogen goes. This bond breaks to give a olefin coordinated palladium hydride chloride aqua complex.

Now, this hydride chlora aqua complex then undergoes this hydride transfer to this olefinic bond to give palladium methyl. And then, that eliminates HCL, HCL as well as water to give this acetaldehyde and platinum 0 palladium 0. And then, once the palladium 0 is formed, then that using this copper 2, copper 3 cycle goes back. So, the interesting, there are 3 interesting aspects of this reaction.

The first is this formation of this olefinic double bond. The second is the attack of this double bond hydrogen on the methyl which is the formation of the acetaldehyde and the first one obviously was the attack of the water followed by deprotonation to form the palladium hydroxo species. So, this is a complex cycle and this catalytic cycle produces ethylene 2 acetaldehyde.

These are 2, this is the reactant and this is the final product of the reaction. And this has been catalysed by this organopalladium species. So, this is an interesting demonstration of how the palladium based complex can carry out oxidation of ethylene 2 acetalene. So, the there are steps involved; we are seeing the first one obviously the logan the chloride being replaced by water. Then there is isomerization.

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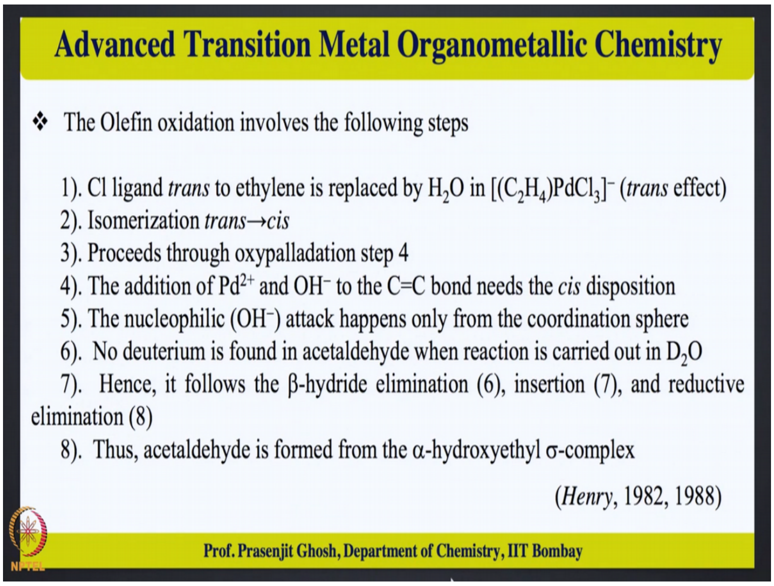

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❖ The Olefin oxidation involves the following steps

1). Cl ligand *trans* to ethylene is replaced by H_2O in $[(C_2H_4)PdCl_3]^-$ (*trans* effect)
2). Isomerization *trans*→*cis*
3). Proceeds through oxypalladation step 4
4). The addition of Pd^{2+} and OH^- to the C=C bond needs the *cis* disposition
5). The nucleophilic (OH^-) attack happens only from the coordination sphere
6). No deuterium is found in acetaldehyde when reaction is carried out in D_2O
7). Hence, it follows the β-hydride elimination (6), insertion (7), and reductive elimination (8)
8). Thus, acetaldehyde is formed from the α-hydroxyethyl σ-complex

(*Henry*, 1982, 1988)

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Then addition of hydroxide to the double bond in the cis disposition. Nucleophilic attacks only when the coordination sphere beta hydride elimination insertion, reductive elimination, so on and so forth. So, the regioselective, now the olefin oxidation can also be done in a regioselective fashion. And so, that speaks us about the breadth and the scope of this catalytic cycle Wacker process.

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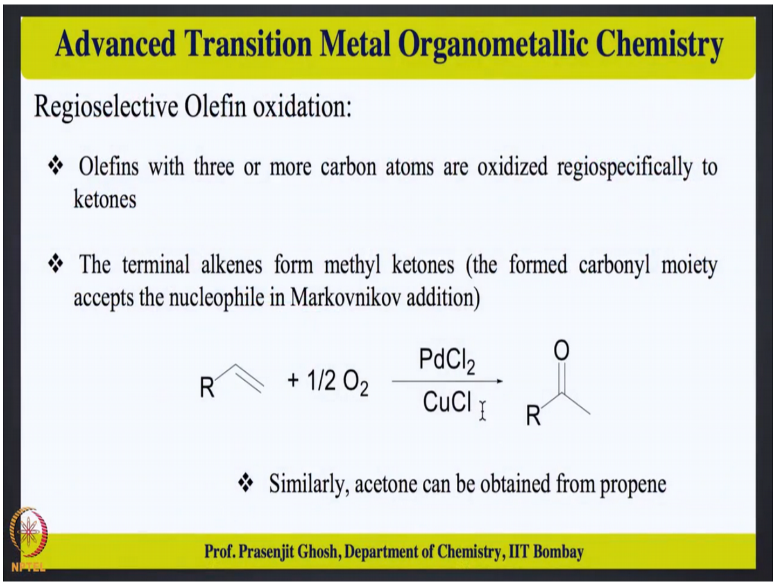

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Regioselective Olefin oxidation:

- ❖ Olefins with three or more carbon atoms are oxidized regiospecifically to ketones
- ❖ The terminal alkenes form methyl ketones (the formed carbonyl moiety accepts the nucleophile in Markovnikov addition)

- ❖ Similarly, acetone can be obtained from propene

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So, let us talk of now regioselective olefin oxidation reaction.

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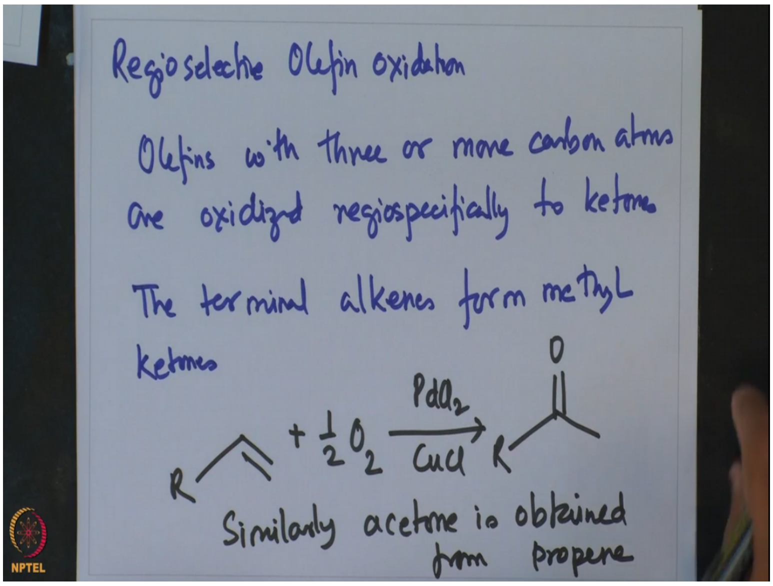

Regioselective Olefin oxidation

Olefins with three or more carbon atoms are oxidized regiospecifically to ketones

The terminal alkenes form methyl ketones

Similarly acetone is obtained from propene

So, olefins with 3 or more carbon atoms are oxidised regiospecifically to ketones. The, and as a result, terminal alkenes from methyl ketones are formed. So, terminal, the terminal alkenes form methyl ketones. And this is illustrated by this example, R + half oxygen with Pd Cl 2 Cu Cl giving this methyl ketone. Similarly, aceto propene gives acetone, similarly acetone is obtained from propene. Now, there is another chemoselective oxidation of olefin.

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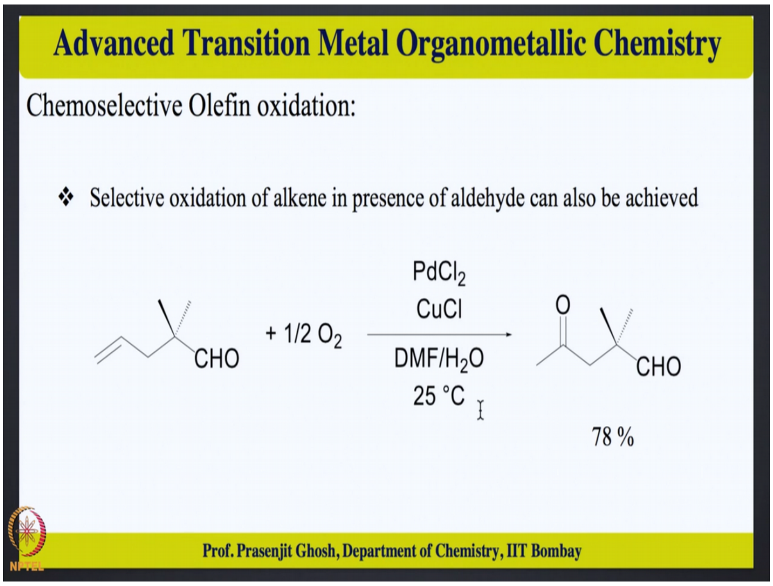

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Chemoselective Olefin oxidation:

- Selective oxidation of alkene in presence of aldehyde can also be achieved

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Example, so alkene in presence of aldehyde can also be achieved.

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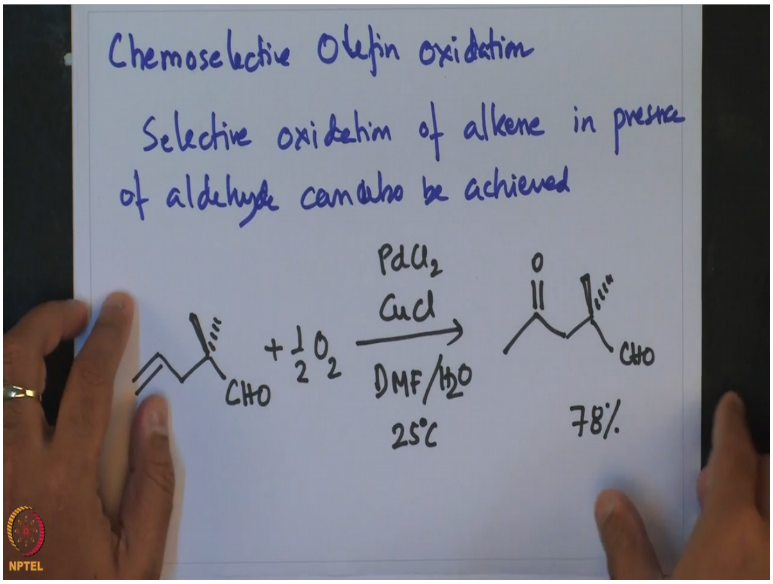

Chemoselective Olefin oxidation

Selective oxidation of alkene in presence of aldehyde can also be achieved

Chemoselective olefin oxidation. Selective oxidation of alkene in presence of aldehyde can also be achieved. So, this is illustrated by this beautiful example in which this olefin CHO in presence of half oxygen Pd Cl 2 Cu Cl in DMF water 25 degree centigrade giving the oxidation of this olefinic internal ke methyl ketone CHO in 78% yield. So, this shows that this, the selective oxidation of olefin to give methyl ketone and this aldehyde remaining untouched.

So, this is an example of chemoselective oxidation was observed. We had also seen that this can be performed in a regioselective fashion and also in a chemoselective fashion. Another important application of Wacker oxidation is that, it is not only restricted to aqueous medium occur, oxidation can also be carried out in non-aqueous solvent.

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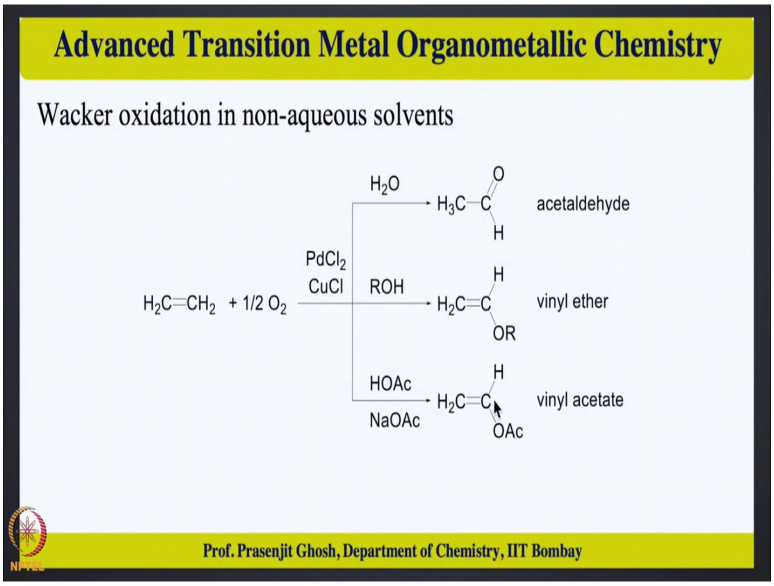

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Wacker oxidation in non-aqueous solvents

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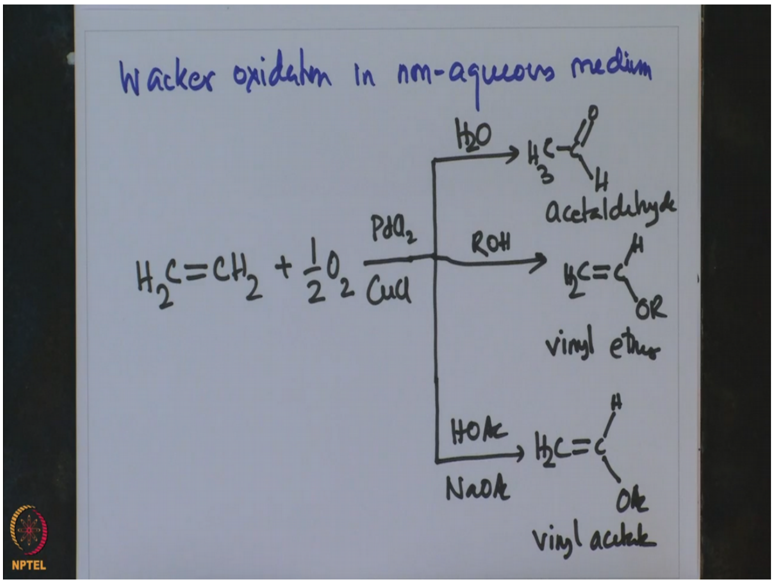

Wacker oxidation in non-aqueous medium

In non-aqueous medium. And this is given by H 2 C CH 2 + half O 2 with Pd Cl 2, Cu Cl in water giving acetaldehyde. Acetaldehyde with alcohol giving H OR vinyl ether and with acetic acid and sodium acetate. It gives C, H, OAC vinyl acetate. So, this also is a important demonstration that Wacker oxidation can be extended beyond aqueous medium. And as a result, depending on the type of solvents the people use, it, they can produce aldehydes in water, in alcohol, vinyl ether and then in acetic acid, it produces vinyl acetate.

So, this is a interesting reaction which sort of highlights the scope of this Wacker oxidation in non-aqueous medium. So, with these I would like to conclude today's discussion on olefin oxidation reaction. In particular, we have looked at a very industrially important, one of the first organometallic examples of organometallic catalysis making it a big way in the industrial scale up processes is this olefin oxidation.

Now, to begin with, we had observed that, though palladium is primarily known for their C-C coupling and cross coupling reactions, the palladium had also been long known for over 100 years for its ability to oxidise ethylene to acetaldehyde and that too in a very catalytic fashion. So, from that perspective, historical perspective too, Wacker oxidation is among the first few examples of organometallic compounds making it big in industrial processes.

So, this Wacker oxidation requires a palladium but also requires a palladium copper 1 copper 2 couple, to oxidise back the palladium 0 to palladium 2. Then now, this reaction proceeds with multiple elementary steps. Here the first of all the involves the coordination of olefin. Then the attack of the water, then beta hydride elemination, finally the hydride migration, followed by the elimination of the acetaldehyde.

We had also seen that, despite the complexity in mechanism, the reaction is extremely useful in producing value added chemicals like acetaldehyde, which can be used for producing many other commodities. We have seen the Wacker oxidation reactions can also be performed in regioselcetive fashion. Not only that, it can also be performed in chemoselective fashion in which it can oxidise the olefin in presence of an aldehyde, where the aldehyde remain untouched.

And lastly, if the Wacker oxidation can also be extended to non-aqueous medium, thereby highlighting the scope, the importance of this reaction, and the scope and the breadth of the utility of this oxidation process. So, with this, I conclude today’s lecture on olefin oxidation, particularly the Wacker oxidation process. We are going to be continuing some more discussion on oxidation process, Wacker oxidation as well as, we are going to take up other examples of organometallic catalysis.

So, I again thank you for patiently listening to me in today's lecture and I look forward to taking up more on Wacker oxidation and subsequent other catalytic examples of organometallic complexes in the next lectures to come. Till then, goodbye and thank you.