

Advanced Transition Metal Organometallic Chemistry
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Module - 11

Lecture - 51

Organometallic Catalysis Reactions: Enantioselective Sharpless Epoxidation

Welcome to this course on Advanced Transition Metal Organometallic Chemistry. As a part of our discussion on various organometallic catalysis reaction, we have been looking at oxidation reactions of ethylenes or olefins in the last 2 lectures. We have started off by looking at Wacker oxidation which is a long-known reaction, has been known in the industry for over a century now and in which ethylene is converted to acetaldehyde in presence of palladium catalyst and copper catalyst in presence of molecular oxygen.

We have also seen another important industrial process in the form of Halcon/ARCO oxirane synthesis in which epoxides or propylene oxides were formed using a molybdenum catalyst. Now, in our last lecture, we have discussed about the possibility of this molybdenum 6 oxo species transferring the oxygen from molybdenum onto propylene by possibly 2 pathways. The one involve direct transfer of oxygen to the olefin and the other involved the transfer of the η^2 type propene peroxo species to coordinated olefin resulting in the formation of propylene oxide.

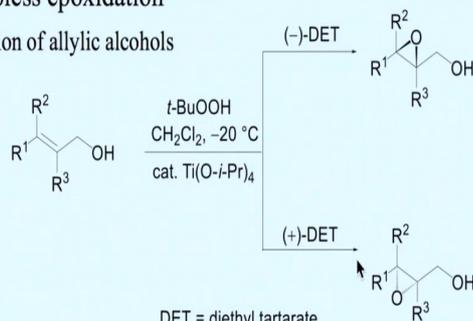
So, continue further on this epoxidation reaction, we are going to talk of another interesting epoxidation reaction which is better known as enantioselective Sharpless epoxidation reaction.

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Enantioselective Sharpless epoxidation

❖ Ti-catalyzed epoxidation of allylic alcohols



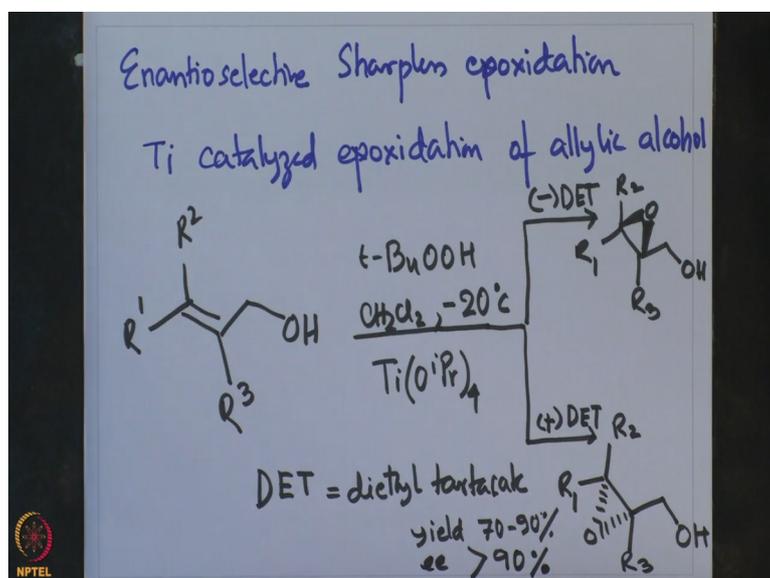
DET = diethyl tartrate

(Sharpless, 1987) yield 70-90 %
ee > 90 %



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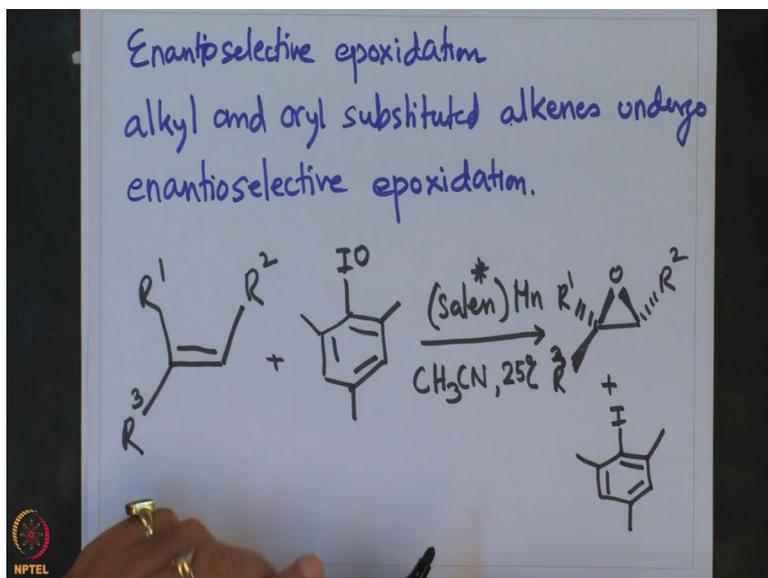


And this is catalysed by titanium and does performs the epoxidation of allylic alcohol. And this is beautifully represented by this example, R^1 , R^2 , OH, R^3 , t-butyl hydroperoxide CH_2Cl_2 20°C . And this is catalysed by titanium tetra isopropoxide. And the reaction in presence of a diethyl tartrate, gives 2 different forms of epoxides R^2 , R^1 , R^3 , O. And the opposite form is obtained with + diethyl tartrate.

The yields are extremely high, 70 to 90%. And enantioselectivities more than 90%. Now, this is a very nice example of enantioselective epoxidation reaction reported by sharpness in which one can see that by different, by taking 2 different chiral ligand and celery, that is, with $-$ DET they get epoxides where the oxygen is attached from the top and where with + diethyl

tartrate the opposite enantiomer is obtained. And so, one can see the scope of this epoxidation reaction extending to asymmetric catalysis.

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So, another example of enantioselective epoxidation involves alkyl and aryl substituted alkenes undergo enantioselective epoxidation. And this is given by R^1 , R^2 , R^3 , with an oxidising agent IO in presence of a chiral salen manganese compound in acetonitrile at 25 degree centigrade yields this chiral epoxide R^1 , R^3 , R^2 , oxygen + iodine. And this was reported by Jacobson. And the active species, by of this is consistent is thought of as a manganese oxide compound. And this can be act as a catalyst.

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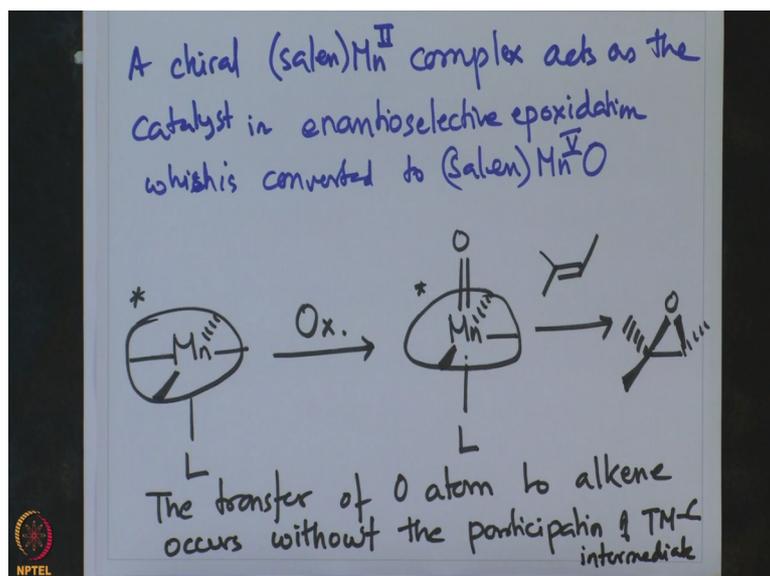
Enantioselective epoxidation

- ❖ A chiral $(salen)Mn^{III}$ complex acts as the catalyst in the enantioselective epoxidation which is converted to $(salen)Mn^{VO}$

- ❖ The transfer of O atom to the alkene occurs without the participation of an TM-C intermediate

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So, chiral salen manganese 2 complex acts as the catalyst in enantioselective epoxidation which is converted to salen manganese 5 oxide. And this is beautifully represented by this schematic mechanism Mn, star, L, presence of oxidant giving Mn, star, manganese oxo species. And that reacts with this olefin to give the desired propylene oxide. So, the transfer of oxygen atom to the alkene occurs without the participation of the transition metal carbon intermediate.

The transfer of oxygen atom to alkene occurs without the participation of TM C intermediate. Now, this is a very interesting observation in the sense that highly enantioselective epoxidation can be carried out with chiral salen manganese complex, which can transfer the oxygen functionality onto the olefin, without the olefin formally getting activated by binding to the transition metal.

So, with this, we come to this important closure of this important epoxidation reaction in the form of Halcon/ARCO oxirane epoxidation reaction. To sum up, what we had observed is that, this epoxidation reaction is a important industrial method for producing propylene oxide and this uses a molybdenum 6 catalyst which carries out this conversion of propene to propylene oxide.

The utility of this reaction can be gauged from very high annual turnover of around 3 million tons per year of propylene oxide being produced by this method. Now, we have also seen the scope of this extension being extended in form of enantioselective epoxidation reported by

Sharpless where titanium tetra isopropoxy catalyst in presence of chiral ligand like diethyl tartrate produced different isomers of epoxides depending on the chiral ligand they used.

And these reactions were carried out in large-scale high yield and high enantiomeric excess. And then, we have also seen the development of a chiral salen type catalyst that also carried out these epoxidation of olefins trisubstituted olefins using a manganese chiral salen compound in high enantioselectivity. So, with this, one can sort of see how this important reaction of epoxidation have been used not only in industry but also have been extended for carrying out the epoxidation in enantioselective fashion.

So, with this we come to the closure of this oxidation of olefin reaction. And we are going to take up 2 more important reactions which are water-gas-shift reaction and Fischer-Tropsch in reactions.

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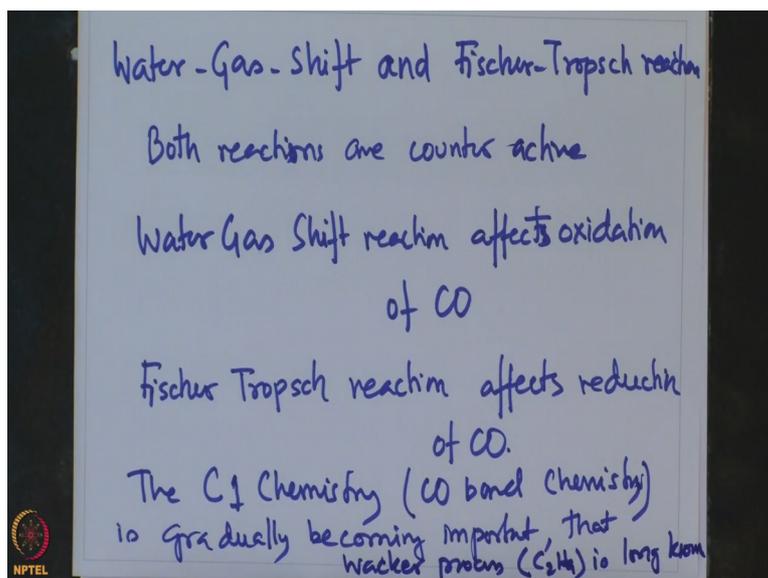
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Water-Gas-Shift and Fischer-Tropsch reactions

- ❖ Both the reactions are counteractive
- ❖ Water-Gas-Shift reaction is the oxidation of CO
- ❖ Fischer-Tropsch reaction is the reduction of CO
- ❖ Though the Wacker process opened up the doorway for the organometallic chemistry, later the field was mostly based on CO (C₁ chemistry) ↗

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Now, before we start discussing this reaction in detail, it is important to know that the industrial perspective on these 2 reaction. As mentioned earlier in couple of discussion back, we had looked at industrial perspective of the field of organometallic chemistry in terms of the metals that would be used in carrying out many of the industrial scale reactions. And what we have observed that, by and large palladium stands tall on the front, in the sense that palladium is quite in this principle with regard, not only with regard to C-C bond formation, but also can be used in industrial processes for oxidation reaction.

And a growing example of that is that of Wacker oxidation where ethylene is converted to acetaldehyde in presence of molecular oxygen and a co-catalyst in form of copper. So, what we see that from industrial perspective, palladium is the metal of choice for organometallic catalysis. And as far as the feed stock being concerned, ethylene is also a important substrate in terms of various industrial processes.

Particularly, with respect to ethylene we have seen addition reactions hydroboration, hydrosilylation, hydrocyanation reactions. We have also observed oxidation reactions like the water process. So, what it turns out that the ethylene is the important substrate from the perspective of industrial transformations, as ethylene can be converted to various intermediates like aldehydes, alcohols, acids.

And depending on further utility, they can also eventually be used for making important target molecules. Now, as far as the substrates are concerned, after ethylene what is the focus of industrial perspective is that of carbon monoxide. Now, it is, and this context of carbon

monoxide that water-gas-shift reaction and Fischer-Tropsch reaction becomes relevant. So, this carbon monoxide can be converted to useful chemicals using redox chemistry which might involve reduction of carbon monoxide or oxidation of carbon monoxide.

And the chemistry which comes out of it is thus called C1 chemistry. So, this C1 chemistry of carbon monoxide gradually becoming important as raising concentration of carbon monoxide has got on to be a global nuisance. And there is active research in finding out ways and means to use carbon monoxide for some gainful purpose. So, in this perspective, the utility of ethylene chemistry in terms of Wacker and other industrial processes, there is of emphasis of those getting substituted by that of C1 chemistry.

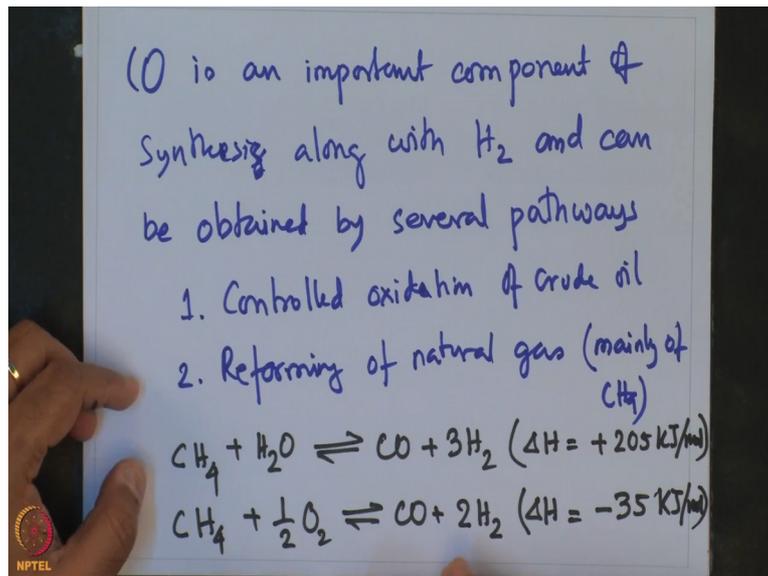
And from this standpoint alone, this water-gas-shift reaction and Fischer-Tropsch reaction does become intuitive. So, it is important to mention that, these 2 reactions are counterintuitive. Water-gas-shift reaction is the oxidation of CO, affects oxidation of CO. And Fischer-Tropsch reaction affects reduction of CO. And as mentioned earlier, though Wacker process has opened up the door way for organometallic chemistry, later the C1 chemistry or the chemistry used with CO is becoming important.

The C1 chemistry or CO based chemistry is gradually becoming important, though Wacker process; this is with ethylene C_2H_4 is long known. So, this is an important paradigm shift in terms of utility, in terms of the perspective of industrial chemistry because as the natural gas gets depleted the source of ethylene becomes less. And then, one needs to find alternate route for making all these important chemical using the oxidation chemistry of olefins or other forms.

And in the, from that perspective, this water-gas-shift reaction as well as Fischer-Tropsch synthesis provide a viable and attractive alternative as there is a acute need for utilising the increasing concentration of CO in the form of its oxidation and reduction to give the oxidised and reduced products. So, from this perspective alone, we are going to take up these 2 reaction. And to begin with, we are going to first look at the water-gas-shift reaction.

Now, before doing that, this CO is an important, CO and hydrogen are important constituents of synthesis gas and these synthesis gas are used for various industrial processes.

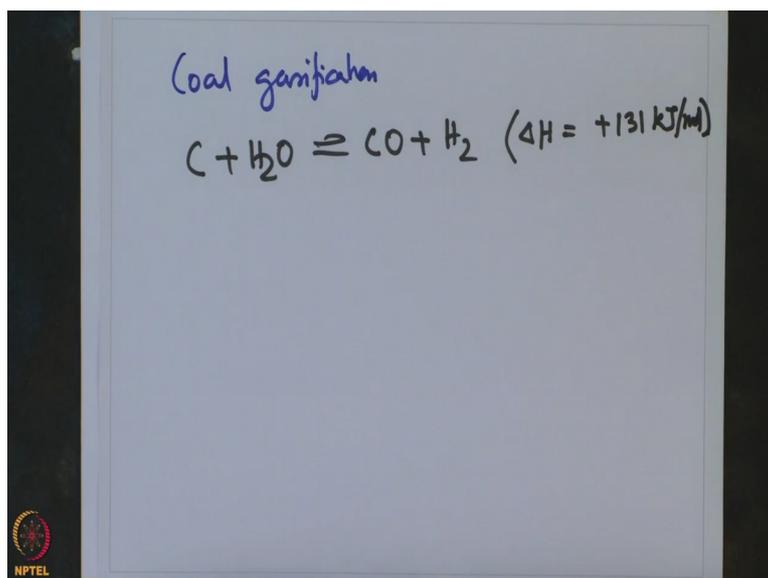
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CO is an important constituent component of synthesis gas along with hydrogen and can be obtained, and synthesis gas can be obtained by, with several pathways. 1, the controlled oxidation of crude oil. So, in this, when a crude oil contains several mixtures, so when the controlled oxidation of the crude hydrocarbons CO and hydrogens the syngas is obtained. Reforming, second is reforming of natural gas, gases and this is which can essentially consist of mainly of methane.

And this is illustrated by the equation $\text{CH}_4 + \text{H}_2\text{O}$ giving $\text{CO} + 3\text{H}_2$ $\Delta H = +205$ kilojoule per mole. And $\text{CH}_4 + \frac{1}{2}\text{O}_2$ $\text{CO} + 2\text{H}_2$ $\Delta H = -35$ kilojoule per mole. Now, so, one can see that the reaction of methane with oxygen can generate carbon monoxide and hydrogen which is nothing but synthesis gas or direct oxidation of methane with oxygen can also give carbon monoxide and hydrogen.

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And the last method for this is gasification coal gasification which is given by $\text{C} + \text{H}_2\text{O}$ giving $\text{CO} + \text{H}_2$ $\Delta H = +131$ kilojoule per mole. So, with this, I would like to conclude today's discussion on water-gas-shift and Fischer-Tropsch synthesis. To summarise, in today's lecture what we had done is we had looked at the various scope of this epoxidation reaction, particularly with respect to enantioselective epoxidation reaction.

And in this regard, we had looked, we had discussed about Sharpless epoxidation reaction using titanium tetrakisopropoxide catalyst and a chiral auxiliary and which is diethyl tartrate which in 1 enantiomeric form give 1 kind of epoxide and with the other it gives another form of epoxide. Moving on from Sharpless oxi epoxidation, we have also looked at the epoxidation process reported by Jacobson in which are a chiral salen manganese compound in presence of benzene iodine oxide derived reagent, could affect enantioselective epoxidation reaction.

Now, after finishing off with the olefin epoxidation reaction, we move to initiate discussion on a very important part of the, part of a chemistry which is called C1 chemistry or the chemistry of utility of carbon monoxide. And in this context, we had discussed water-gas-shift reaction and Fischer-Tropsch reaction. And what we noted is that these 2 reactions are nothing but oxi redox chemistry of CO with the water-gas-shift reaction affecting oxidation of CO and Fischer-Tropsch reaction affecting reduction of CO.

Now, this CO chemistry is important with respect to this synthesis gas in which it is a component of. And then, one looks at the various reactions which leads to the formation of

CO in the synthesis gas. And this can be obtained by 3 reaction. First can be controlled combustion of crude well. The second is reforming of natural gases and third is coal gasification reaction. So, these 3 reactions contribute to CO in syngas.

And we are going to look at various methods particularly water-gas-shift reaction and Fischer-Tropsch synthesis that would focus on utilising the CO of syngas to convert some valuable industrial chemicals. So, with that, I conclude today's lecture. I once again thank you for patiently listening to me in this lecture and I look forward to taking up this topic of water-gas-shift reaction and Fischer-Tropsch synthesis in bit more detail when we meet next. Till then, goodbye and thank you.