# Advanced Transition Metal Organometallic Chemistry

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**Module - 10**
**Lecture - 50**
## Organometallic Catalysis Reactions: Olefin Oxidation

Welcome to this course on Advanced Transition Metal Organometallic Chemistry. Today we have been, we will be discussing 1 example of organometallic catalytic reactions, particularly olefin oxidation. Now, if we step back and look at the big picture and we try to find out that, why is organometallic chemistry or organometallic complexes based catalysis so important? The one thing which stands tall is the fact that this organometallic complexes catalyse many reactions which have gone on to become a large-scale synthesis taken up by industry.

So, that may be the prime reason as to why, what makes this organometallic complexes so special, because some of the catalyst can carry out reactions in really big scale which can help make a lot of chemicals, fine chemicals and speciality chemicals. So, it is this translation of laboratory research to industrial scale is what makes organometallic complexes so special. Now, we will step back further and take a look at organometallic chemistry from this industrial perspective.

So, from a industrial perspective one may think of the fact that, are asked the question is why are again the organometallic complexes so special. And the question which is more prominent from industrial prospective is the fact, is the question that, which metals or which component of organometallic chemistry is important to industry at the moment. So, to answer that, the answer vehemently would be palladium.

From a industrial perspective, palladium plays a great role in organometallic chemistry, because palladium we had seen a place significant effect or palladium probably is the one and only player in C-C bond forming reactions, in C-N bond, C-heteroatom bond forming reactions and so on and so forth. So, not only that, palladium is also seen in various kind of oxidation reactions.

So, not only palladium is important in bond forming reactions, they also participate very much in oxidation reaction. So, this versatility of palladium to carry out different reactions and that too as bigger scale as the industry requires, is what make palladium so special. So, from that perspective, it is quite important that we have spending this many time on palladium mediated catalysis.

And in this context, we had been discussing this Wacker palladium based oxidation reaction which is this occur Wacker reaction which involves conversion of ethylene to acetaldehyde. Now, the second question from a industrial perspective, the first one was of course, which metal in organometallic chemistry important to industry. The second thing is, which substrate in organometallic chemistry would be of importance to industry.

Now, this is also an interesting question. And the answer to this is molecules like ethylene is of importance to industry, as we had seen that reactions like addition reactions, hydroborations also hydrosilylations, hydrocyanation reactions, as well as oxidation reactions like Wacker reactions; all are used to carry out a conversion of ethylene to many other important intermediates.

Wacker reaction for example would convert ethylene to aldehydes. And then, acetaldehyde and aldehyde is a hub of access to many other important compounds like acids, alcohols and imines, amines, so on and so forth. So, what we see from industrial perspective, ethylene is of important substrate which can be translated to large scale transformations. Now, continuing on this, another substrate which is also important for synthesis of various chemical is carbon monoxide.

We are going to take a look at how carbon monoxide is converted to other important substrate in industrial scale through industrial processes. So, with this let me just start talking about this Wacker oxidation reaction. And what we had seen that, this is one of the first applications of organometallic chemistry in industrial scale and that the industrial synthesis goes back to more than 100 years ever since it was launched.

And this is uses palladium for conversion of ethylene to acetaldehyde. We have also looked at the various scope of this Wacker oxidation after looking at the mechanism, we had looked at how the catalytic cycle of Wacker oxidation proceeds. And then we had seen, we had observed in the previous lecture the regioselectivity in Wacker oxidation reaction. In particular, what we had seen that terminal olefins give methyl ketones selectively regioselectively produces methyl ketones as a part of this reaction.

We have also seen the chemoselectivity in terms of oxidation, if there is a oxidisable group like aldehyde in along with the olefin present on the substrate, it is the olefin which gets converted to methyl ketones. And the aldehyde does not oxidise further. And lastly, what we had seen that Wacker oxidation can be done in a variety of solvents including non-aqueous medium. And depending on the type of the solvent used, the products would be formed.

For example, if Wacker oxidation is performed in water, it gives acetaldehyde; in alcohol, it gives vinyl ether and in acetic acid it gives vinyl acetate. Now, proceeding further, we are going to look at the different other scopes of Wacker oxidation. And I must mention that, many of these scopes of Wacker oxidation are individual industrial processes by themselves. So, it is not just one industrial process that we are talking about, when you are talking about water oxidation.

But even the variant of it, a different scope of this reaction is also realisation of another industrial process. So, if we take a look at all of it, then one realises the importance and the worth of this Wacker oxidation to industry from a organometallic perspective. So, with this, what we are going to be talking about is this another scope of this Wacker oxidation which is this acetoxylation of olefins.

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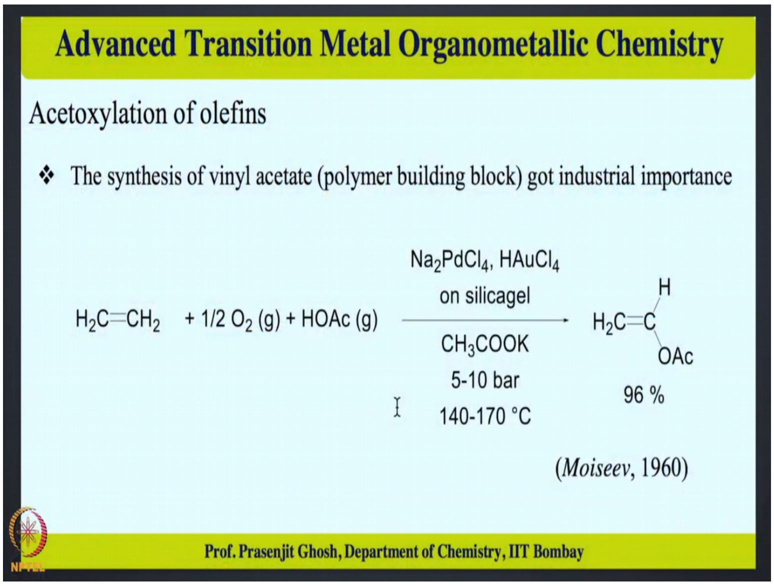

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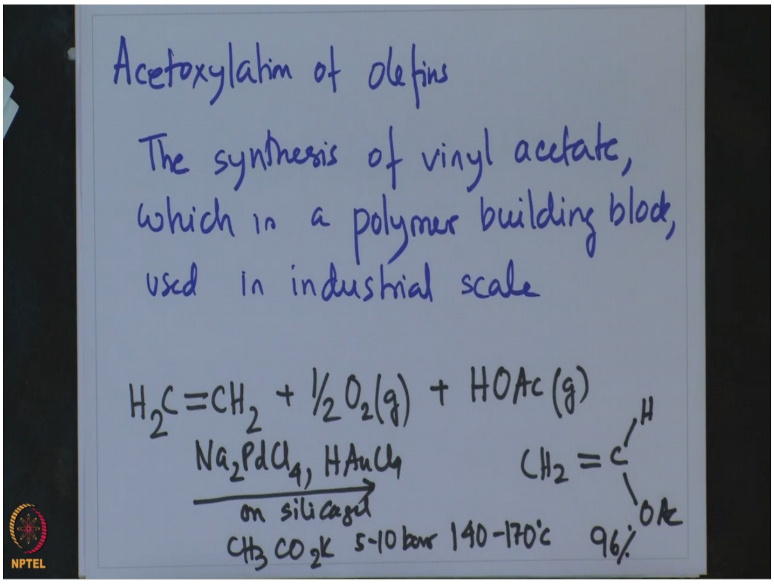


This reaction is used for synthesis of vinyl acetate which is a polymer building block in industrial scale, of vinyl acetate which is a polymer building block and used in industrial scale. And the reaction is given as; and vinyl acetate is produced in 96% yield in industrial scale this way. And these also reflects the importance of this Wacker oxidation process in this reaction.

So, instead of producing aldehydes, what it does is, in presence of oxygen and acidic acid, it produces acetox O-acetate. So, this is a acetoxylation reaction of olefins. So, this is a variant of this aldehyde Wacker oxidation reaction. I must mention that this reaction is also produced in a industrial scale through homogeneous catalysis like the ones we have been discussing before.

And these examples of this homogeneous catalysis, of the utility of homogeneous catalysis in industry. So, these are very important reactions which are carried using homogeneous catalysis in large scale in industry. The process can be extended to other volatile carboxylic acids and diolefin.

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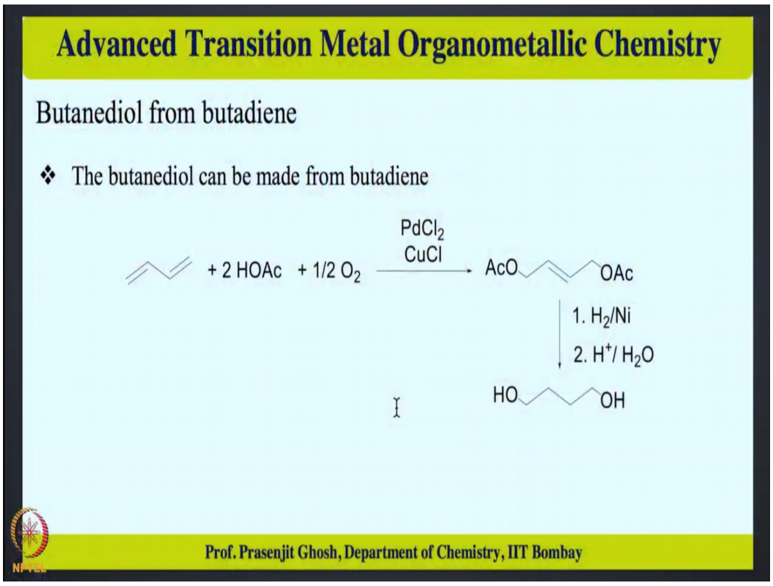


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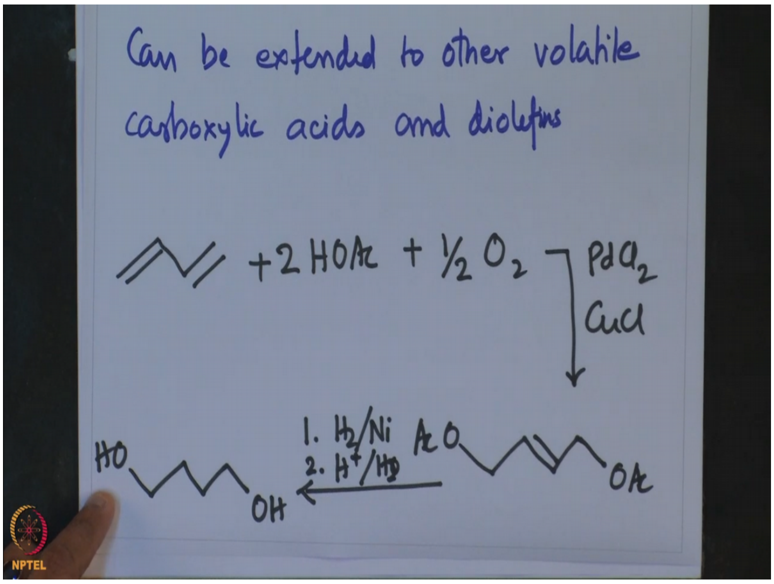


And the reaction is given as alcohol to give diols. So, this important intermediate 1 4 diol is obtained by hydrogenation of the diacetate which is in turn produced by this acetoxylation of olefin. So, this, one can see the importance of the scope of this reaction. Now, even another interesting thing is that, it can also be used to produce in presence of HCL to produce chloroacetylation.

So, in the chloroacetylation process, what will happen is, 1 side it will be acetate, the other side will be chloride. And this is done achieved by performing the reaction in presence of HCL and acetic acid.

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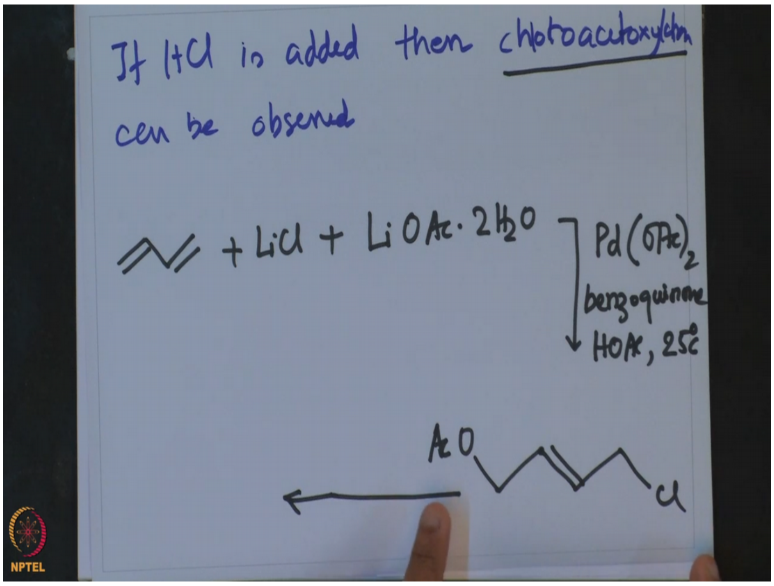


If HCL is added, then chloroacetylation can be observed. And this is done by this beautiful example where butadiene is reacted with lithium chloride + lithium acetate to water, palladium acetate and benzoquinone acetic acid 25 degree centigrade giving this chloroacetoxy product. So, here we see this example of chloroacetoxylation where instead of obtaining di acetate at the end of the butane linkage, one side is acetoxy and the other side is chloride.

And this is obtained by presence of HCL. The HCL is obtained by treatment of this lithium acetate in presence of acetic acid and lithium chloride in presence of acetic acid will give formation of lithium acetale and HCL. And in that case, what one see is the formation of a chloroacetoxylation which then would be reacted with R R dashed N H palladium phosphine THF 25 degree centigrade O Ac and N R R dashed.

So, what we see, 2 different catalysis of palladium is prevalent over here. The first one obviously is this chloroacetoxylation is an extension of Wacker oxidation reaction. So, first is oxidation chemistry being catalysed by palladium, followed by C-N bond forming reaction. Again, that C-N bond forming reaction is a carbon-heteroatom bond forming reaction. Again, that one is also catalysed by another palladium compound.

So, what we see that this particular example upholds the versatility of the catalytic applications of palladium and points out that palladium can not only do oxidation reactions, but also can do various kind of bond forming reactions. And here is a good example in which both the oxidation of olefins as well as a C-C bond C-heteroatom bond forming reaction had been performed by 2 different catalyst of palladium.

Now, with this we are sort of coming to end of the discussion on a, on the Wacker type oxidation of olefin using palladium complex. And we are going to, what we had observed that the scope of this Wacker oxidation is huge. Wacker oxidation is also a historically important complex which has been known in industry since more than 100 years and which utilises homogeneous catalytic pathway.

Now, what we had also seen that Wacker oxidation can be regioselective in terms of olefins, terminal olefins having more than 3 carbon atoms. It is the methyl ketones, they had been observed almost all the time. It is also selective in oxidising olefin. We have looked at a example where there is an aldehyde group and olefin. And the aldehyde group remains untouched during the course of the catalysis, whereas the olefin as expected gets oxidised to give methyl ketone.

We have also seen that Wacker oxidation is not only restricted or limited to aqueous solvent where Wacker oxidation of olefin gives acetic acid. It can be performed in alcohol where it gives a ethers and also can be performed in acetic acid where it can give vinyl acetate. One good example of Wacker oxidation what we had observed in today's lecture is the fact that, when the, as this Wacker type oxidation is performed in acetic acid, then, acetoxylation of olefin is observed instead of getting aldehyde.

Now, one gets an O-acetate moiety attached to the end of the carbon and by, if the one, this acetoxylation is an important route for producing vinyl acetate which is used in industrial scale. It can also be extended in butadiene and make a bis acetoxy terminal bis acetoxy compounds which can be deduced with nickel to give nickel hydride. It can, then what we had seen that, if the acetoxy reactions perform with HCL in presence of acetic acid, then one can obtain chloroacetoxylation in which one side it will be a chlorine moiety incorporated, the other can be an acetate moiety.

And the chlorine moiety can then subsequently be made to participate in a C carbon-heteroatom bond forming reaction to form the amine acetoxy moiety. So, what we had seen is some fine demonstration of palladium based catalysis which not only speaks on its versatility, but also on the depth and the breadth of the palladium catalysis, particularly from industrial point of view.

So, with this, we are going to take a look at another important oxidation reaction of olefin and this is called Halcon/ARCO oxirane process. And this is a reaction which produces epoxide and the catalyst for this reaction is molybdenum. So, this is an example of molybdenum catalysis.

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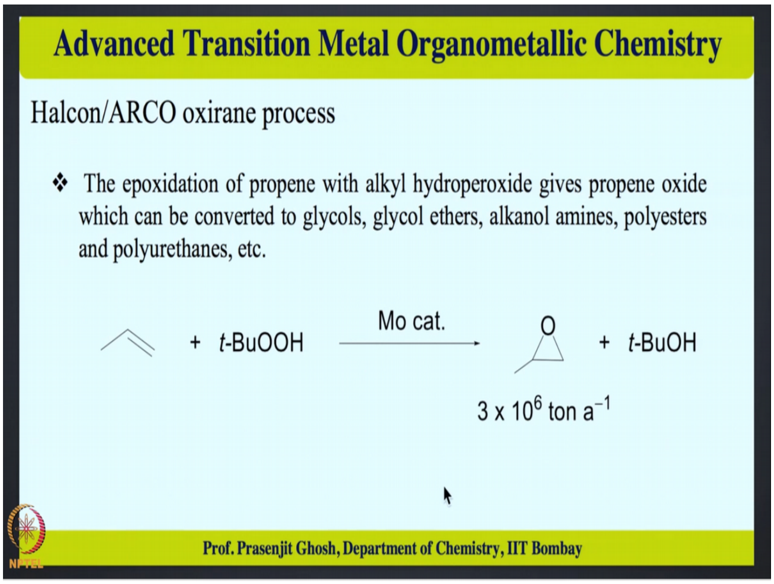


So, we sort of take up this new reaction which is new epoxidation reaction which is called Halcon/ARCO oxirane process.

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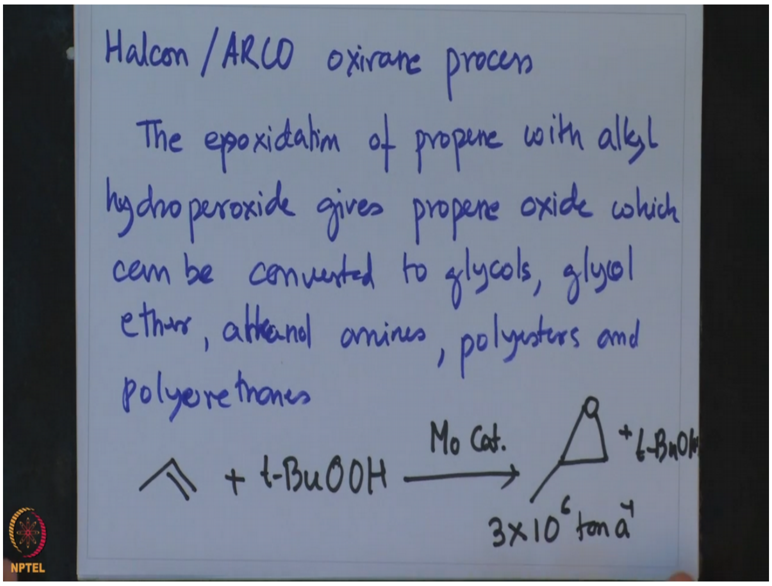

So, as one observes that Halcon/ARCO oxirane process is really an important process because this is a industrial scale epoxidation process of propylene with alkyl peroxide. Hydroparoxide in presence of a molybdenum catalyst that gives these propene oxides. Now this propene oxides are important intermediates for accessing glycols, glycol ether, alcol alconol amine, polyester, polyurethanes and etcetera.

So, one can see the importance of industrial scale entry to this epoxides. And these have been achieved by this Halcon/ARCO oxirane process. And the process utilises molybdenumised catalyst and the reaction is given over here. Molybdenum catalyst + butanol; and the reaction is 3, the turnover is very high, 3 into the power 6 ton per annum. So. this is really a large amount 3 million tons per annually is produced by this particular Halcon/ARCO oxirane process.

So, one has to realise that these process must be extremely effective not only in terms of their efficiency but also in terms of their catalysis if it were to make it to this scale of industry application. And one sees, one is evident from the fact that, about 3 million tons per year of this epoxide is produced by this particular process. Now, the molybdenum is the active catalyst and the molybdenum is formed from molybdenum 0.

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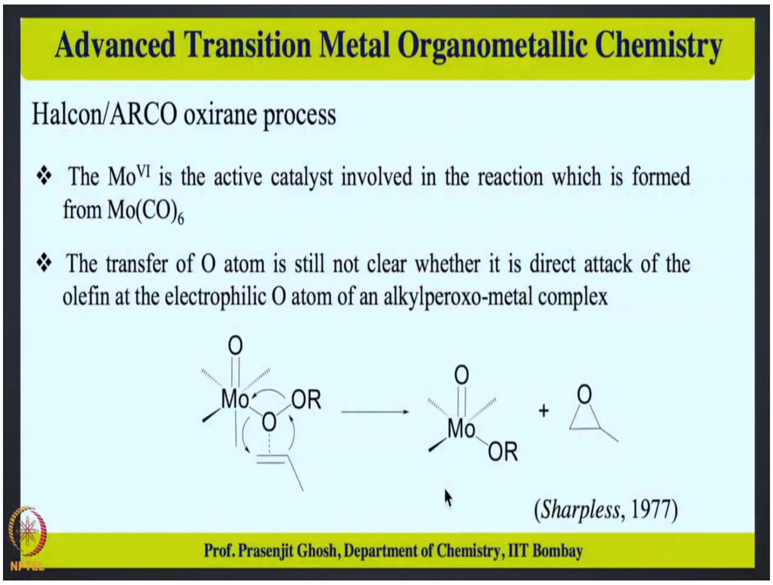


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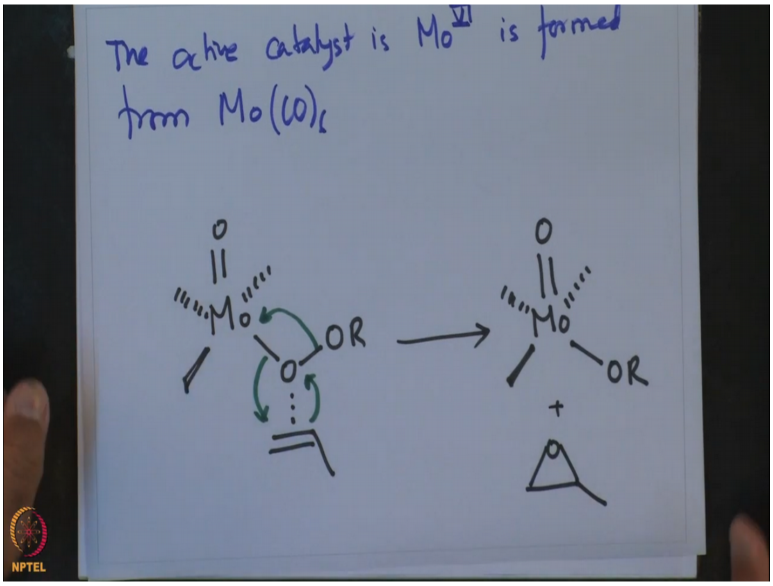


The active catalyst is molybdenum VI and is formed from Mo CO 6. And there is some difference in idea as to how the transfer of oxygen takes place. The one idea is whether if the transfer of the oxygen from molybdenum occurs directly by the direct attack of the olefin at the electrophilic to give the alkyl paroxo species. Whereas the other belief is that the adduct happens after the olefin gets activated by coordination to molybdenum.

And this the mechanism for each of these is explained below. OR, so this attack happens by this oxo attacking here and attacking there, the alcoxo going there to give this + the desired propylene oxide. And this is a belief where the oxygen is attacking to the, directly to the olefin and the other assumption is that it goes through eta 2 propene intermediate.

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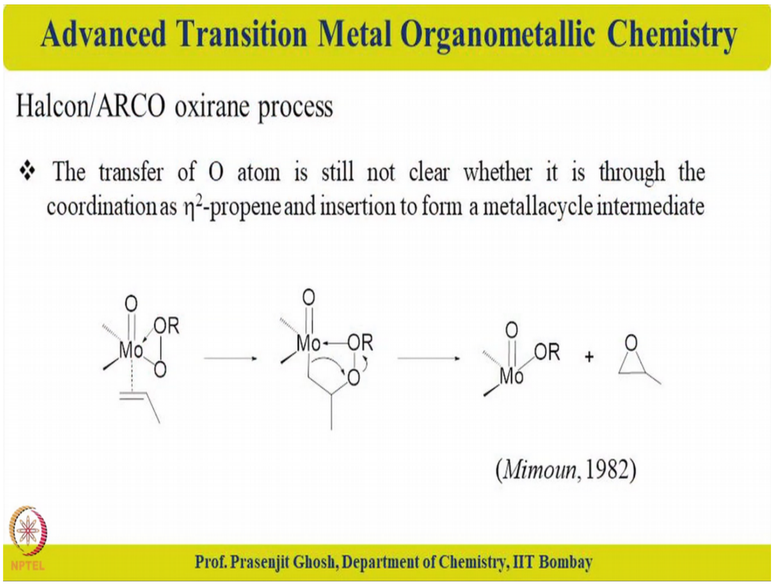


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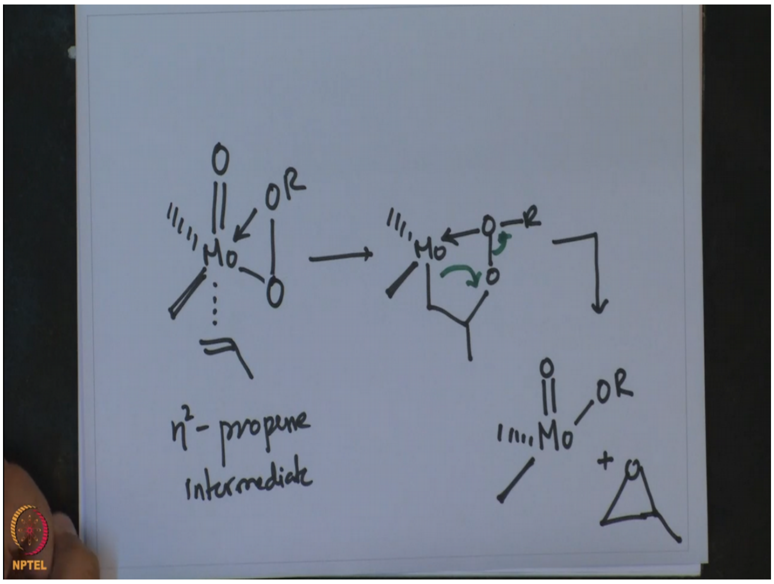


So, that is illustrated. This is eta 2 propene followed by this intermediate which is formed. And then, this attacks over here to give +, they produce propene oxide. So, with this, we come to the conclusion of our discussion of Halcon/ARCO oxirane process that use molybdenum for this epoxidation of propane. So, I would like to conclude today's lecture. In today's lecture we have seen the scope of a Wacker oxidation process, whereby we had seen that how the reaction if done under acetic acid produces acetoxylation of olefin.

We have also seen that this acetoxylation of olefin can be done on butadine. And then, one can make this diols which are important industrial intermediates by reduction with nickel of this diacetoxy compound that would be produced by acetoxylation of olefin. We have also seen that the, if the Wacker oxidation process if done, performed in presence of HCL and acetic acid one can produce chloroacetoxylation of butadine.

And then, the chloro group can also be replaced by amine moiety performed with N coupling with another palladium. And then, we have come on to discuss another oxidation type reaction, particularly the epoxidation reaction which is also extremely important. And in this case, this, we have started up by looking at Halcon/ARCO process, which uses molybdenum 6 compound molybdenum oxo compound.

And we have also looked at the various possible mechanisms that exist out there, trying to explain how this epoxide, propylene oxide is formed. This indeed is a nice fines demonstration of extension of translation of organometallic chemistry to industry, as propylene oxide to the amount of 6 million tons a year is produced by this method. So, with this, I again thank you, for patiently listening to me in this lecture and I look forward to take up more on this oxidation reactions as well as other important catalytic reactions of organometallic complexes in the next lecture. Till then, goodbye and thank you.