**Transition Metal Organometallics in Catalysis and Biology**
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**Module No # 01**
**Lecture No # 02**
**Reppe Synthesis (Introduction)**

Welcome to this course on transition metal organometallics in catalysis and biology. Continuing in our discussion in the previous class where we are talking about applications of transition metal organometallics in catalysis particularly in the areas of homogeneous as well as heterogeneous catalysis. We had observed that this application had been developed not only the laboratories of the academia, but many have also been parallelly developed in the laboratories of industry.

And you know one thing about this field of transition metal organometallics that this is a special bond that academia shares with industry and parallelly the development of the field has been attained in both of these platforms. Now with that in mind we were going to continue the discussion further and take up some more examples which have been developed in industry which is not so common in other fields where most of the developments or new ideas are developed in industry.

So today I am going to talk about another such important development which has primarily or exclusively had been done in the industry in the form of Reppe synthesis. Now there are several reactions of which are been developed at the industry like these for hydroformylation, the water gas shift reactions and so on so forth which has went on to become a big development in the industrial world oliphant polymerization metathesis polymerization to some extent.

So there has been a lot of contribution from the industry in the development of a particular area and here is another such important discovery that we are going to be taking up in today's lecture and this is on a Reppe synthesis. So Reppe synthesis or Reppe chemistry refers to conversion of acetylene to a different form of compounds functionalized versions of acetylene which has been carried out by Walter Reppe in an industrial setting.

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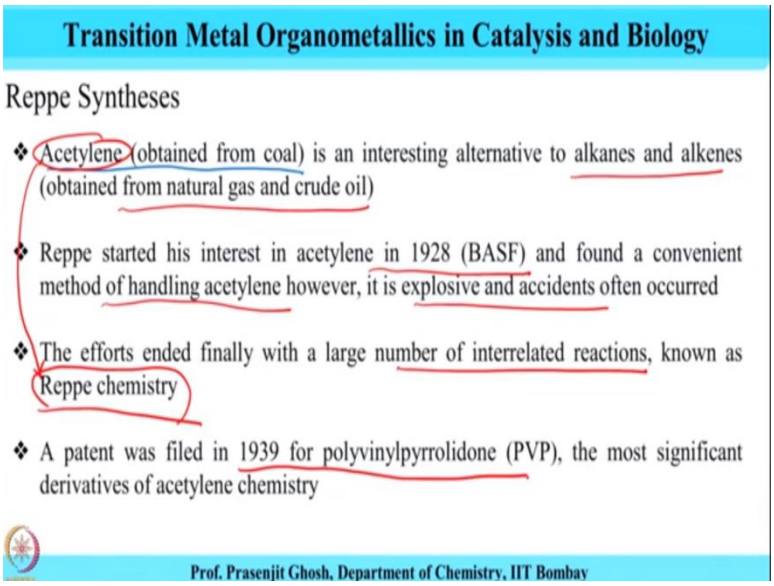


Now one of the major challenges about acetylene or conversion of acetylene to other functional compounds is the fact that acetylene is highly explosive and is extremely difficult to handle. And that the reason being acetylene in presence of oxygen is used for welding purpose and they form fuel gas which can be ignited very easily and is used and also a lot of heat is generated and it is a perfect gas for carrying out all the welding type applications.

And hence because of this explosive and flammable nature of acetylene in presence of air any reaction or industrial scale utility of conversion of acetylene into another chemicals became a primary challenge. And more so this was more difficult and more formidable a challenge about a 100 years back when the understanding as well as handling ability of organometallic compounds were even not as developed as it is today.

So Reppe he was a chemist at BASF Germany. So most of the chemistry of Reppe synthesis that I would be taking about today had been developed about 100 years back in an industrial setting in Germany. The goal of these Reppe is was in being able to handle acetylene under safe condition and so far most of the time people were using acetylene in small scale under low pressure even though there were explosion.

And that time in acetylene chemistry explosions was quiet common and to take up this challenge what Reppe did is Reppe successfully studied the decomposition of acetylene in ignition experiments. So this is something that he took up in order to understand in order to overcome the

difficulty associated with handling of acetylene. What he studied is the reactivity of acetylene under the ignition conditions.

And then designed a special test tube called Reppe glasses which are stainless steel sphere with screw caps and that allowed high pressure experiments with acetylene that could be carried out. And finally he succeeded in handling acetylene at a very high pressure of about 200 atmosphere. So these is the very important contribution of Reppe in that led to the development subsequent development of Reppe chemistry.

And now acetylene the primary source of the acetylene is from the coal not like other alkanes or alkynes which comes from natural gas and crude oil. Acetylene is exclusively obtained from coal. So the source of acetylene is different from that of the crude oil and but however like alkenes and alkynes acetylene also can be used for fuel as well as because of its unsaturation can also be used for conversion through other chemical.

Now one thing at this juncture I should note that these utility of acetylene or other alkanes alkynes for as fuel for energy purpose is still something which representing becoming obsolete as these are source of energy from non-renewable resources and finally at some point our earth is going to be depleted of all of these natural resources from where energy could be made and hence right now the focus is more on developing energy as a source from renewable resources which going to be lasting even forever as compared to that from the natural non-renewable resources.

However one should also understand the time when this chemistry of Reppe was developed that was about a 100 years back or so when the perspective was different and hence so much of discrimination as to what is the source of energy it was not as stringent as it is today. And that time there was a significant interest in developing energy from non-renewable sources like crude oil or from coal.

So Reppe let me give a big background historical background. So Reppe interest in acetylene started in in 1928 in BASF and where he actually found a convenient method for handling acetylene because the accidents and the explosion where quite common at that point of time. And

what this allowed was that it opened door to a large number of interrelated reactions and all of them finally consolidated wise was termed as Reppe chemistry.

So Reppe chemistry it refers to a large number of compounds under different conditions which could all be obtained from the source of an apparent source of acetylene and all of it together is what is known as the Reppe synthesis of Reppe chemistry. And of the several process that were part of the Reppe chemistry the most important one is the discovery in 1939 of polyvinyl pyrrolidone or PVP which is a significant derivative in acetylene chemistry and has been synthesis using Reppe method.

So what this Reppe synthesis did was open door to a large number of rich chemistry in many of which are had industrial importance and hence was extremely useful for carrying out these reactions. So now let us just take a look at some of the interesting conversion which fall in the (()) (10:39) of Reppe synthesis.

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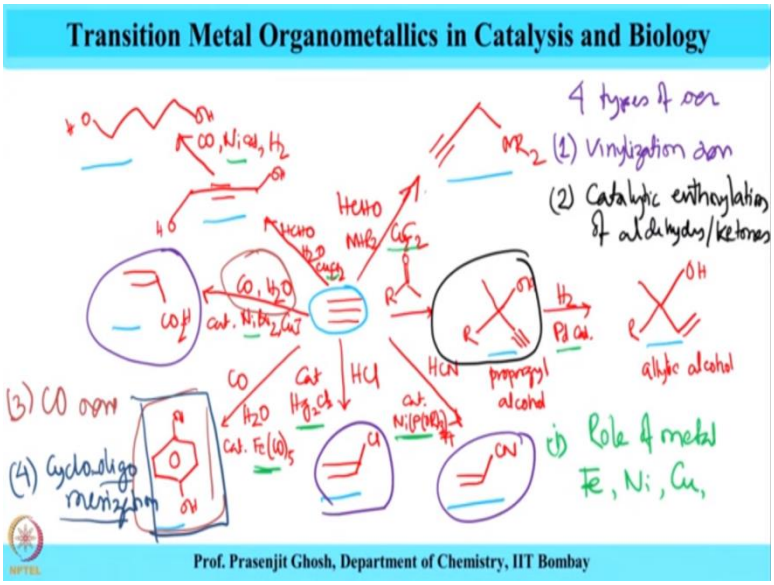


(refer time: 10:40) So for example reaction of acetylene with HCl and catalyst would give vinyl chloride. Similarly the reaction with HCl and catalyst nickel phosphide whole 4 would give vinyl cyanide with carbon monoxide water in present of iron catalyst feco5 would give this phenol with alkoxy group in the para position with aldehyde with ketone will give propargyl alcohol. And then with hydrogen palladium catalyst will give allylic alcohol proper.

How the reaction of acetylene with formaldehyde I mean in presence of copper catalyst copper to CO2 copper carbide would give this acetylene with inner to amine again with carbon monoxide water catalyst nickel bromide and copper iodide would give CH2 CH CO2H with formaldehyde, water and CO2C2 copper iodide would give the reduced product that when hydrogenated with carbon monoxide nickel catalyst and hydrogen would give the alcohol.

So what is amazing about this is that so many different chemistry or so many different product is emerging out from this simple acetylene. So as if acetylene has given away opened doors to the formation of so many different compounds starting from the same acetylide source. Another interesting thing to note is that all of this chemistry is a catalyst by transition metals and there are different metals for example that ranges from iron to mercury to nickel to palladium to copper nickel copper.

So what we see is that there are transition metal which are playing an important role in in expanding this chemistry of acetylene to different specialty chemicals. So obviously the role of metal which gives a flavor of organometallics chemistry and these have been catalyzed by various transition metals like iron, nickel, copper that successfully carryout or participate in this whole range of catalysis.

And all of these have been achieved using this acetylene which is explosive in nature. Now we are going to look at another interesting correlation part form the role of metals that we had observed which is the type of reactions that is mainly observed over here. Actually Reppe chemistry has 4 types of reactions mainly a starting with vinylization we will discuss in more details 4 types of reaction one is vinylization of alcohol.

So what are vinylization reaction? The formations of vinyl chloride or vinyl cyanide or acid these are examples of vinylization reactions. The second type of compound are reactions that is observes that ethnylation catalytic ethnylation of a aldehydes or ketones. And the example of these are formation of these where these acetylene moiety is making a alkenyl derivative. The third type of reactions are reactions with carbon reactions with carbon monoxide co reactions and they are part of the formations of a products like these where the CO is forming.

And the fourth type of reactions are cyclo oligomerization. And this also is an example of cylo oligomerization reactions were like a benzene moiety has been formed this acetylene. There are more examples of cyclo oligomerization reactions whereby benzene derivatives can be synthesized from this acetylene. So what we see is if we step back and look at the different utility that has emerged from Reppe reaction is that tremendous amount of different functionalized chemicals which can be obtained through functionalization of acetylene which have been achieved through Reppe synthesis.

The primary difficulty in carrying out this reaction had been able to handle acetylene safely because acetylene is highly explosive and in presence of oxygen forms of fuel gas which we all of us know is extensively used as welding gas. So being able to handle acetylene safely is the primary challenge which had been overcome by Reppe. And then having done that it opened door to a wide variety of different chemical reactions with different functionalized specialty chemicals that can be converted or obtained from acetylene.

What is more important we have seen that all of these require some sort of metal catalyst and they are where the organometallic chemistry it comes into play and the metal catalysts that are used in Reppe synthesis are extremely important ones like iron, nickel, copper these are first row transition metals very economic cheap and they are the ones which carry out all these transitions. Secondly if one so that one sees that these are all organometallics catalysis.

Also if one step backs and sees the type of compounds reactivity which has been obtained out of acetylene one cans see that there are 4 types of reactions first is vinylization where you make the vinyl derivative from acetylene. Second is catalytic ethnylization of aldehydes or ketones which is shown over here. Third is carbon monoxide reactions 2, 3 examples of the same is so on and last but not the least about very important outcome of Reppe synthesis is cyclo oligomerization where one can form benzene derivatives or even higher cylco octa tetraene derivatives from acetylene through this oligocyclo merization reactions.

So I think these the picture gives a capability and capacity of Reppe reaction and how these had been very important in making different chemicals about a century back and all how all of these were developed in industry about a century back. However having said that the bottom line is

that acetylene is obtained from coal and again the coal is a non-renewable resource and in today's context at some point or other we have to move beyond non-renewable source of energy and hence we have to go beyond looking for alternatives for carrying out these reactions. But having said that these presents an exciting domain of chemistry exciting domain of organometallic compounds.

The utility of organometallic compounds in carrying out this synthesis in being able to convert acetylene to different chemicals and then use it for industrial good. So with these I come to an end of today's lecture where we have looked at and important applications of organometallic compound particularly with respect to this Reppe chemistry which was solely a developed in industry about a century back.

Whereby acetylene was converted into several different important chemicals. So the Reppe chemistry is important as mentioned earlier not only from the perspective of being able to convert acetylene to different feedstocks. But also from the perspective of the fact that this has been an industrial contribution to the field of organometallic chemistry which also says highlight the important of organometallic chemistry in the area of catalytic utility.

So in this particular reaction we have in looked at today how Reppe was successful in designing Reppe glasses or the containers which can handle acetylene at very high pressure and overcome the challenge of explosion as well as ignition of handling acetylene. And he did so by studying the ignition of acetylene under different conditions so as to come up with the solution to be able to handle acetylene at very higher pressure.

Now the outcome of such a diligent study is a open for all to see and here in this slide as has been rightly shown that acetylene can be converted to different feed stock using transition metal catalysts and all of these we have also observed in this lecture can be grouped into 4 kinds of reaction primarily namely the vinylazation of acetylene. Then catalytic alkylation of aldehydes and ketones this is just an addition reaction vinylation also is an addition reaction then cyclo oligomerization reaction and the reactions with carbon monoxide.

So the we are going to take up these interesting examples in more details as we go through these applications of Reppe chemistry and there you said in industrial world in terms of developing a

some of the large scales industrial processes which has come out of the application of Reppe synthesis. So more of this and some more developments of Reppe chemistry as we take up the topic in the next lecture till then good bye and I look forward to being you in the next lecture where we take up Reppe synthesis in a lot more details thank you.