Transition Metal Organometallics in Catalysis and Biology
Prof. Prasenjit Ghosh
Department of Chemistry
Indian Institute of Technology – Bombay

Module No # 01
Lecture No # 04
Reppe Reactions

Welcome to this course on transition with organometallics in catalysis and biology. We have been discussing about a very important reaction which is called Reppe synthesis particularly that involves conversion of acetylene to various chemical functionalized feedstocks and was developed in early 1900 by Walter Reppe. Now we in the last lecture we have looked into the context in which the Reppe chemistry was developed.

And based on the need of the hour of the day looking for the application or utility of acetylene which was produced from the coal as its major source the Reppe reaction become relevant. A great deal of developments in Reppe Chemistry had been performed or obtained at under industrial conditions and that is why the Reppe synthesis can be called as a gift of industry to the field of organometallic chemistry.

Now this discussion that I have covered in the last lecture as well as part of what I will be covering now has been nicely reviewed in a American chemical society ACS review article which I am going to give the reference today for people to look up.

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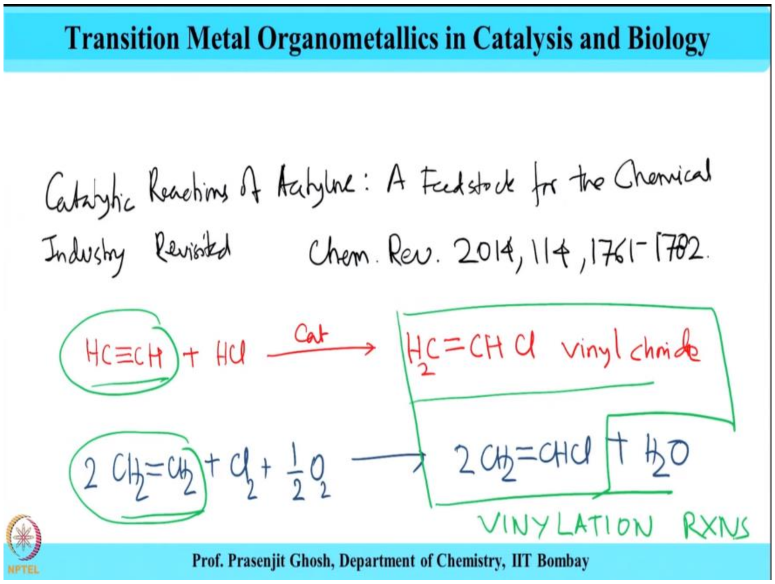

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Catalytic Reactions Of Acetylene: A Feedstock for the Chemical Industry Revisited Chem. Rev. 2014, 114, 1761-1782.

$HC\equiv CH + HCl \xrightarrow{Cat} H_2C=CHCl$ vinyl chloride

$2\,CH_2=CH_2 + Cl_2 + \frac{1}{2}O_2 \longrightarrow 2\,CH_2=CHCl + H_2O$

VINYLATION RXNS

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

The title is catalytic reactions of acetylene feedstock for the chemical industry revisited and the reference is chemical review 2014, 114, 1671 to 1782. So this is a nice review which sort of discusses the importance of Reppe chemistry not only at the time when it was developed even the relevance of the development of Reppe chemistry even under today’s context and is the beautiful review through which I have also covered in the last and part of last lecture and part of the present lecture and would request all the viewers of this course to look up if they want to look read about the developments of Reppe chemistry in much more details.

Now what we had earlier also discussed that Reppe chemistry involves a set of large number of reactions and the most common or the most important type of Reppe reactions are vinylation reactions. And what we have seen that in this vinylation reaction acetylene is converted to various vinyl derivatives and in our previous class we have discussed about how acetylene getting converted to vinyl alcohol by reaction in presence of base like potassium hydroxide.

As well as another example of vinylation which we had read about or spoken about in the last class was about reaction of acetylene with hydrogen cyanide HCl in presence of catalyst giving a acrylonitrile nitrile for the vinylation reaction. Another example of vinylation reaction which we are going to be taking up today is the reaction with HCl and this is called vinyl chloride. Now if you remember as I had said in earlier class that there was a parallel development about accessing all of this products which were obtained through Reppe using other methods particularly from that of the feedstocks from natural gas and crude oil which is ethylene.

For example I had spoken about how focus of the industry shifted on conversion of acetylene to acetaldehyde in presence of what it by reaction of water with acetylene in presence of acid and mercury plus to that of conversion of ethylene to acetaldehyde the same product acetaldehyde one obtained from acetylene in Reppe chemistry and the other obtained through wacker oxidation which also is the industrial process developed for consumption utilization of ethylene which are obtained as a product in petrochemical industry from natural oil and crude oil.

So similar to the development for acetaldehyde which could also be obtained from acetylene and ethylene. Similar development also has been obtained from ethylene for the current purpose and the corresponding development is in presence of chlorine and oxygen it gives. So these as I said is an interesting development whereby one could see that the same product was obtained from two different substrates one from acetylene and another from ethylene as the time progressed.

And the focus shifted from utilizing ethylene source to that of utilization it is a olefin olefinic ethylene source to that of using acetylene source. The focus shifted as a result the technology shifted, the reaction shifted. However the product obtained from both of these reactions remains the same. So this is the beautiful example where one can see that how chemistry accommodated different transformation from different sources to give the same product as per the need and the demand of the time.

So this is a beautiful example another example we had also seen similarly acetaldehyde could be obtained from acetylene as well as could be obtained from ethylene and both have been developed technology for large scale industrial productions. So we continue further on this vinylation reactions we are going to take up the reaction with carboxylic acids.

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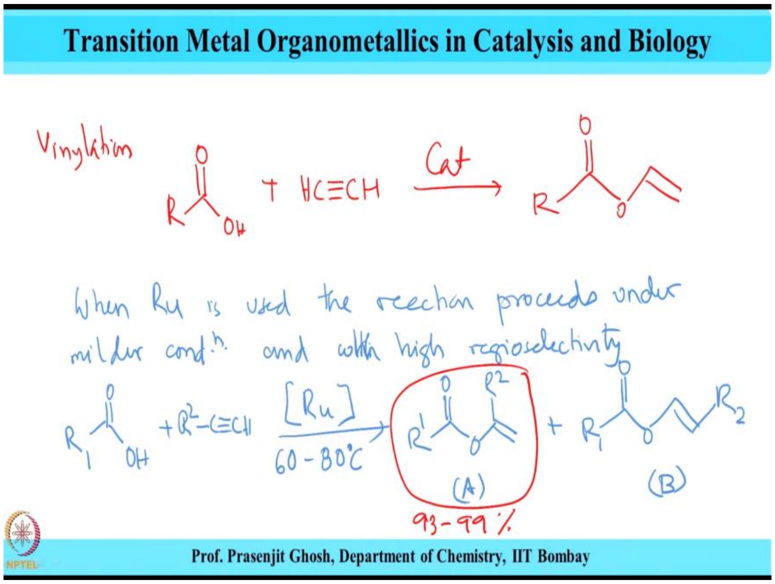

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When Ru is used the reaction proceeds under milder cond.n and with high regioselectivity

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

And interesting thing about is that this also requires metal catalyst and if ruthenium is used as the catalyst then the reaction proceeds at much milder conditions and with high selectivity ruthenium is used the reaction proceeds under milder conditions and with high regioselectivity. I will explain this with this example R1 COOH reacting with R2 CH it is a terminal acetylene in presence of ruthenium as a catalyst more milder conditions about 60 to 80 degree centigrade resulting in 2 product R1O R2 + R1O R2.

So one can see that 2 different kind of olefinic bonds are here where O and R2 are seize and where O and R2 were trans we designate these as A and B and with ruthenium being the catalyst the selectivity is primarily A and which is formed about 93 to 99 %. So what we see is that ruthenium brings in great amount of selectivity in the formation of these 2 compounds. And also ruthenium brings in these milder reaction condition which this reaction proceeds.

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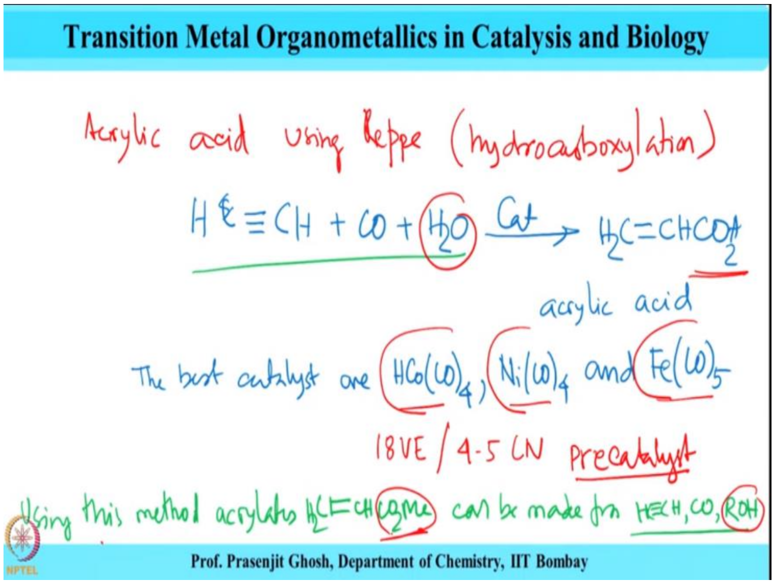

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Acrylic acid using Reppe (hydrocarboxylation)

$$HC \equiv CH + CO + H_2O \xrightarrow{Cat} H_2C{=}CHCO_2H$$

acrylic acid

The best catalyst are $HCo(CO)_4$, $Ni(CO)_4$ and $Fe(CO)_5$

18VE / 4-5 CN Precatalyst

Using this method acrylates $H_2C{=}CHCO_2Me$ can be made from $HC{\equiv}CH$, CO, ROH

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

So this we are going to move on to see another very interesting synthesis of acrylic acid using Reppe method and this involves hydro carboxylation. What is the meaning of hydro carboxylation? It means that simultaneous addition of HX as well as CO and this is given by the reaction in presence of catalyst to give these acrylic acids. Now, as mentioned earlier in case of acryl, vinyl cyanide as vinyl alcohol acrylic acid to is an important (()) (13:29) for variety of polymerization processes and hence is of great demand in the industry.

Here one can see the base catalyst user homoleptic as well as heterolytic iron carbonyl complexes. So like metal carbonyl complexes like cobalt tetra carbonyl hydride nickel tetracarbonyl or iron pentacarbonyl are extremely good catalyst for these Reppe synthesis. Now one should or may argue that how come these are behaving as a catalyst because all of these complexes are both electronically saturated as well as coordinatively saturated.

Now we have had an elaborate discussion on electronic saturation and coordinative saturation in our previous course where we said that preview is it for behaving as a catalyst is the requirement of electronic unsaturation as and as well as coordinative unsaturation. Now if one were to look at all of this complexes one would see that they have 18 valence electron count and also have about 4 or 5 coordination number.

So what does that mean tell us that these are not the real catalyst but most likely are obviously are the pre catalyst for the reaction. What is it mean is that they lose carbon monoxide one or two of them to become electronically as well as coordinately unsaturated when they participate in the catalytic cycle as the active species active catalytic species for carrying out this transformation? So we see that these complexes metal carbonyl complexes like cobalt hydride tetra carbonyl nickel tetracarbonyl and iron pentacarbonyl are very good catalyst for converting acetylene to acrylic acids.

And for the same using these methods acrylates can also be made from acetylene CO and alcohol using these method acrylates can be obtained from acetylene CO and alcohol. So what it says that this method is a very a common generic one where once can replace water with alcohol and in presence of forming acrylic acid one can also form acrylics acrylic ester using the same method.

So these further highlights the versatility of these transformation that we just spoke about.

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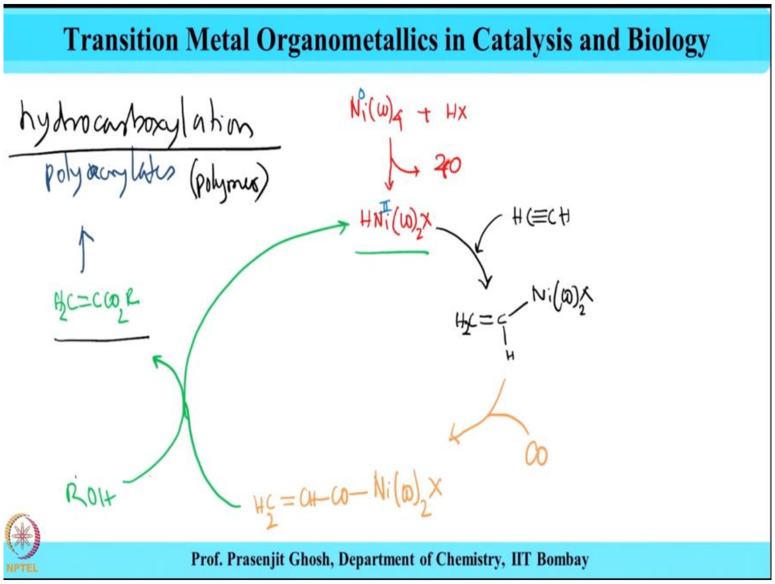

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Now we would like to give example of how this reaction proceeds in terms of the catalytic cycle time as mentioned earlier that nickel tetracarbonyl is both electronically as well as co-ordinatively saturated because it has 18 valence electron so it when it reacts with a Hx for let us say for this hydro carboxylation prior to that it loses to CO HX undergoes oxidative addition to give HNi CO2 X.

So as is a common for oxidative addition one can see that the oxygen state of nickel has gone from nickel 0 to nickel 2 by the addition of these Hx. Now once this is form then the acetylene reaction takes places with this species. And nickel hydride add across the acetylene giving these nickel vinyl bound nickel species which is drawn over here. Now once this is formed then one of the CO which is liberated comes in and undergoes the insertion into the nickel carbonyl bond this is sort of what is called migratory insertion to give this compound.

And then subsequent reaction with alcohol gives the vinyl ester and would give back initial starting catalyst that one started off with and this is a good monomer for acrylic acid or polyacrylate. So this is polymer poly acrylates and they can be obtained by polymerize saying this monomer are these acrylate esters and what we see is here is announced demonstration of hydro carboxylation nice demonstration of hydro carboxylation which had resulted in production of acrylic esters and they are important feed stock for polyacrylate or the polymer.

And these again highlights the importance of Reppe chemistry in terms of producing this important monomer through a large scale industrial process and by which also utilizing acetylene as one of the sources which a feedstock from coal to produce the monomer acrylates. And then they are also used for another industrial process of polymerization giving polyacrylates. With that we had come into discussing in the end of vinylation reactions that are used for making vinyl derivatives which can be halide ester acid and the cyanide from acetylene feedstock.

And then we move on to another interesting topic which in Reppe reaction or Reppe chemistry another set of reaction which are called ethyl ethynylation reactions.

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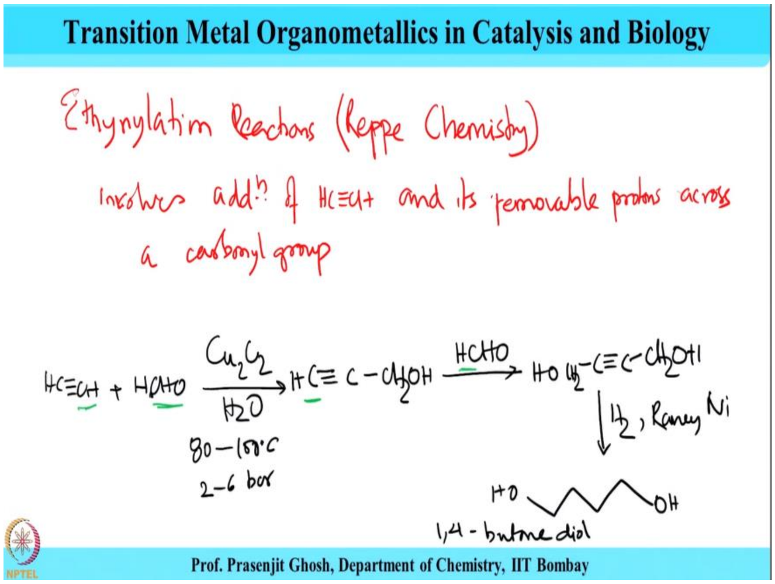

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Ethynylation Reactions (Reppe Chemistry)

Involves addn of HC≡CH and its removable protons across a carbonyl group

$$HC{\equiv}CH + HCHO \xrightarrow[H_2O]{Cu_2C_2} HC{\equiv}C-CH_2OH \xrightarrow{HCHO} HOCH_2-C{\equiv}C-CH_2OH$$

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And this reaction involves addition of acetylene and it is removable proton across a carbonyl group and these are similar to one to addition and implies copper for this chemistry CO2 C2 water 80 to 100 degree centigrade 2 to 6 bar pressure produces CH2OH that reacts with aldehyde to give CH2 C C CH2OH and that in presence of hydrogen and Raney nickel produces 1, 4 butene diol.

So these are important demonstration of how acetylene can be used to convert can be used to undergrow this ethynylation reaction like this acetylide CH adding across this carbon CO group and giving CH2H and then another reaction over at the other end to giving to CH2OH and that under reduction giving this one for butene diol. So in the current examples the addition of the alkenyl CH across one CO group as well as the second CH across the second CO group resulting in CH2H CH2H which under reduction gave important intermediate one for butene diol.

So with this we come to an end of today’s lecture in this we look into the reactive various types of reactions of Reppe chemistry particularly with regard to the vinylation reactions in which the acetylene a moiety has been reacted with a various kinds of reagent like HCl HCM acids esters to give various kind of vinyl acid cyanide esters acrylates. We have also looked into the mechanism in which how acrylates esters are obtained from reaction of acetylene carbon monoxide and HX.

These are called hydro carboxylation reaction. And then with that we are had come to an end of vinylation reaction and then in the end we have looked into another new type of reaction of Reppe chemistry which are called ethynylation reaction that involves the reaction of acetylene with the carbonyl group and which also resulted finally to the conversion of one for butene diol.

So with this we a come to our current discussion on Reppe chemistry in today’s class we are going to be looking into some more important of applications of Reppe reaction Reppe chemistry as we take up in the next class. I hope you have enjoyed these the content which has been discussed today in this with regard to Reppe chemistry we look forward to some more exciting reactions and developments on Reppe reactions as we cover the topic in bit more detail in the next class. Till then goodbye and see you in the next class.