Transition Metal Organometallics in Catalysis and Biology

Prof. Prasenjit Ghosh
Department of Chemistry
Indian Institute of Technology – Bombay

Module No # 01
Lecture No # 03
Reppe Reactions (Part -1)

Welcome to this course on transition metal organometallics in catalysis and biology we have been discussing and very interesting reaction which is Reppe chemistry with regard to this particular topic. Now Reppe chemistry stands very relevant in today's context and we are going to be looking at the development of Reppe's chemistry in the overall scheme of the developments that happened in transition metal organometallic chemistry.

In this context in today's lecture we are going to take a look at the chronological sequence in which the Reppe's chemistry evolved under conditions and requirement that was the need for the day. Now what we had seen in the earlier class is the fact that this Reppe's chemistry allows access to large number of functionalized chemical feed stocks are compounds all originating from acetylene chemistry and it was as if the acetylene serves as feed stock for various different functional chemistry.

And today we are going to see this development in light of the overall development of transition metal organometallics in the scheme of things and we are going to see how the need of the day resulted in the development of Reppe chemistry. Much of the research that goes on in the present day as well as it relevant in earlier times depends on the need of the day and is guided by the economics and the need of the time.

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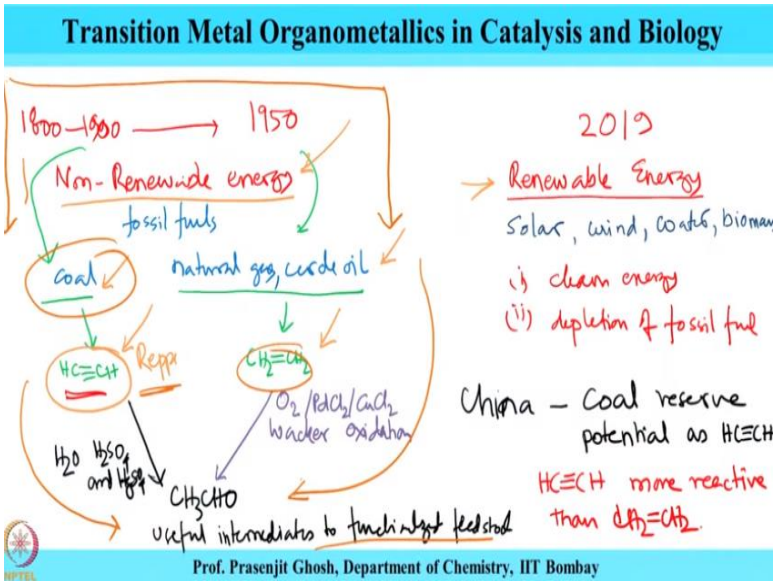

And hence in current context for example the much of the research is about development renewable source of energy. And this involved looking into options like solar, wind, water, biomass so and hence so forth. The reason for more need for the development of renewable source of energy arises from the fact that these are clean energy that mean no carbon foot print or no carbon-di-oxide and so on and hence so forth.

So these are the reason which allows us to focus more on renewable energy the other reason to have this synthesis on renewable energy arises from the fact that depletion of the carbon foot print from the phase of the arc in terms of the so called non-renewable energy like petro coal and petroleum of fossil fuel. So the way that things the focus had been on renewable energy in the current century if the things were however different if we back just about a 100 years or so.

For example around 1800 to around 1900 till around 1950's are the focus of energy source had been primarily on non-renewable energy. And these involve fossil fuels which would include sources like coal, natural gas, crude oil. Now chronologically if one were to look at that these emphasis of the energy from this sources had been in the order shown here that petroleum as well as natural gas crude oil sources were probed in mainly 1950's whereas the 1 those are coal or coal driven energy sources where more in even before that is in 1800's and 1900.

Now to see the connection between with respect to acetylene is that from the coal is the major source for production of acetylene and whereas from natural gas or from petrochemical industry.

What people get is ethylene or propylene. Now the way in current times the focus had been on generating energy from renewable sources about 100 years or so that the focus had been on gathering energy from non-renewable sources which were for example from that of coal or from that of acetylene or to be more accurate that in early 1900 or so the focus had been on getting it from acetylene which is a product from the coal.

Whereas may be about 3 or 4 decades later in 1950's the focus shifted from on to acetylene to more economically feasible source like ethylene and propane. Now the whole gamut of Reppe chemistry starts from here that we talk about it is about utilizing acetylene. Now Reppe chemistry as we had seen in our previous discussion that acetylene could be converted to large number of functionalize products and that had solely been because of the efforts of Walter Reppe who found out how to deal with acetylene.

And elaborate further on that for example one can convert acetylene to acetaldehyde which is a useful intermediate aldehyde is a useful intermediate for other functionalized chemicals functionalized feedstock the conversion from ethylene to acetylene can be achieved by treatment with water in presence of sulfuric acid and mercuric sulphate and this has been one of the major exploits of acetylene so that one can see the need for developing acetylene as a feedstock for carrying our chemical reaction.

However and that had been the reason that had led to the development of Reppe chemistry however with time the focus shifted from acetylene to ethylene which was more easier and more cheaply obtained from natural gas and crude oil and then that had led to sort of exploring the possibility of using ethylene to for making acetaldehyde. So that again the useful intermediate for accessing other functionalized feedstock could begin.

And for this also resulted in very important process which is called Wacker oxidation. So Wacker oxidation involves reaction of ethylene in presence of palladium dichloride catalyst and copper chloride catalyst which results in formation of acetylene and these process from obtaining acetaldehyde from ethylene become more prevalent in 1950's and over took production from that from acetylene which were more prevalent in 1920's.

So what we see is that the shift sort of technology for obtaining functionalized feed stock moving on from acetylene to ethylene. Now these were the stories which were more invoked about 50 or 60 years back whereas now we move on to more unconventional but more permanent solutions that is exploring energy from a renewable sources like solar, wind, water, biomass so on and hence so forth.

And the primary reason is that at some point of or other the whole of these non-renewable sources would depleted from face of the earth and then our energy requirement has to be made from this sources available from the renewable energy. Now even under the current scenario there is a larger argument still prevalent in favor of developing this Reppe chemistry which sort of makes comparative estimates of how long is fossil fuel like coal or natural gas or crude oil would last on earth.

And based on the estimate it is still suggested that probably the natural result of coal will outlive that of petroleum products and hence still would require to focus on getting energy some amount of energy using the Reppe chemistry. And this brings us to the relevance of Reppe chemistry in today's context even though both coal and natural gas crude petroleum at some point or other would get exhausted but coal reserve would outlast or outlive the natural gas and the crude oil reserve and hence the energy potential rising from coal should also be exploit even under today's context even the focus is shifting towards more renewable energy.

Now another point mentioned over here is that in this would where everything is still yet to standardized or people does not have a standardized opinion on several issues there are countries pursuing each of the technologies depending on their reserves. For example china has a large coal reserve and China still explores the potential of acetylene as a fed stock. Now with these being the scenario there is a lot of thrust in looking into the acetylene chemistry and as far as the chemical nature as the chemical intuition is concerned acetylene as a high reactivity more reactive than ethylene.

And hence would require less step in reactions to reach the intermediates then what would one would require from that of acetylene. A another last but not the least but important argument however in favor of non-renewable energy is that unlike renewable energy for example like that

of the solar energy a there is a depending on the strength of the vain there is a huge fluctuation in the power that is generated arising out of this wind.

Whereas in contrast to that energy from non-renewable sources like coal provides a steady supply of energy in terms of the electrical power that is generated and hence there is still demand as well as argument in favor of exploring the non-renewable energy sources as an option for making our energy needs. Now with these background I think now we would have understanding of the reason as to why Reppe chemistry which was developed so early on in 1900 is still relevant in today's context and that those reactions as lead to so many different products because of its various chemical exploits and that have been carried out by very dedicated scientists.

For example in the form of Reppe was developed this chemistry and the name suggests so. Now with that I think I have provided you a picture how relevant is acetylene and conversional of acetylene to other feed stock and the challenges involved in this which was the need of the day in early 1900 when the energy options where from non-renewable sources where explored and even now about 100 or more years later the Reppe chemistry is still of relevance because of reasons just mentioned now.

Now with these we come back to the central of Reppe reaction which is acetylene and then we are going to sort of look into the utility of acetylene apart from what I have been talking about on Reppe kind of conversion in our daily need. Now acetylene as I mentioned apart from the Reppe chemistry has been long used for welding purposes.

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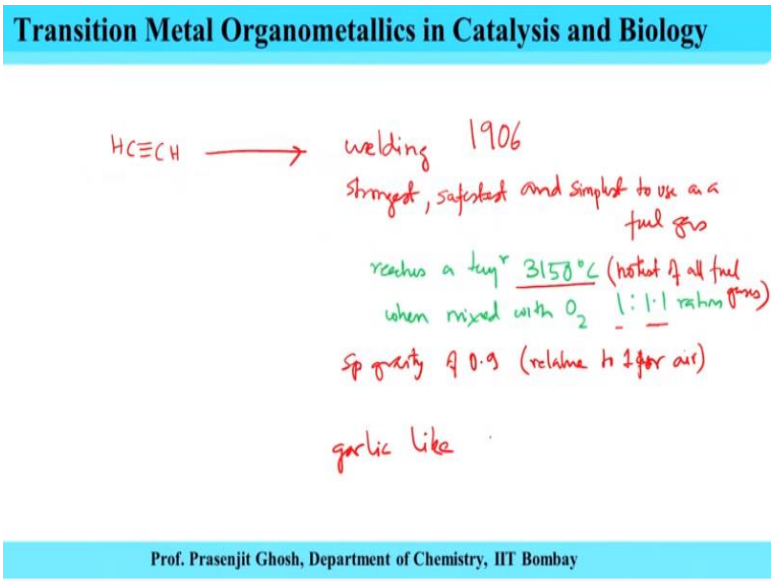

And the first use of acetylene in welding is noted as early as 1906 and the reason being the applications of acetylene in welding is because this is the strongest, safest and simplest to use as fuel gas. Now why is so useful because it gives a temperature of around 3000 degree centigrade when mixed with oxygen in 1 is to 1.1 ratio. So these by enlarge is a very important aspect that you reach a temperature of about 3000 degree centigrade.

Now if you compare this temperature this is almost about half of the temperature of that in some may be 6000 or 7000 degree centigrade. So this is very higher temperature in which most of the metals would melt. So applications wise these temperature is by far the highest or the hottest of all fuel gases and hence it can easily melt all of them and hence it is not a surprise that acetylene is a can is find the extensive applications in welding purpose.

Now it has a specific gravity of about 0.9 relative to 1 for a year so that means acetylene is lighter and hence would move up if unused. So it is not going to sort of you know sync or stay low if there is unused acetylene is still there. So in that way it is kind of very safe to use and also the oxygen ratio that it requires is very less which is about 1 is to 1 many other fuel gases for example ethylene, propylene would require more amount of oxygen to burn then what acetylene would.

And because of this reason because of it is light nature because of it is low oxygen consumption ratio and because of very high temperature that it can attain when burning with oxygen acetylene

is the best safest, strongest and simplest fuel gas to use and has found applications in various welding type applications. So apart from conversion of acetylene to feed stock acetylene as also tremendous application in welding industry.

Lastly it has also a smell that of garlic so if there is any leak or anything that can also be easily deducted garlic like odor. And all of these provided over view of as to why acetylene as important in context of application as early as beginning of 1900 and why so much research activities as centered around acetylene which has led to the development of Reppe chemistry which we are talking about. With these you know we are going to be looking into some more reactions some of the reactions relevant to Reppe chemistry as we go on.

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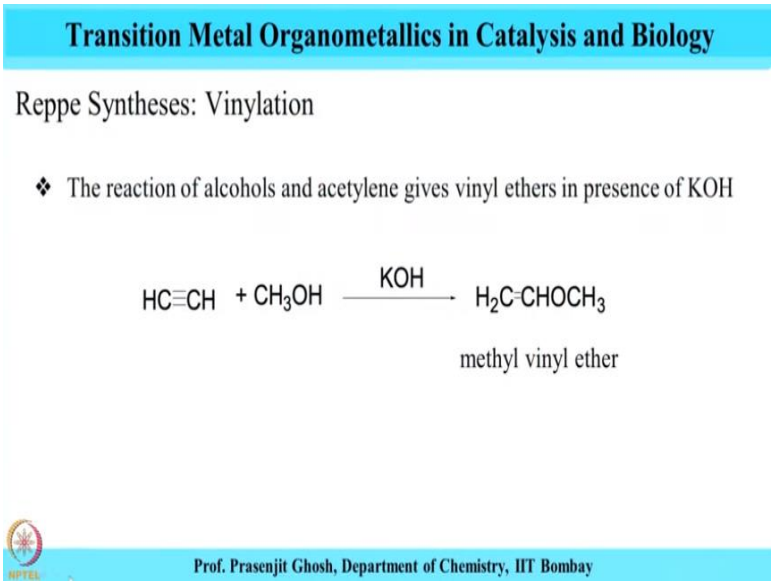

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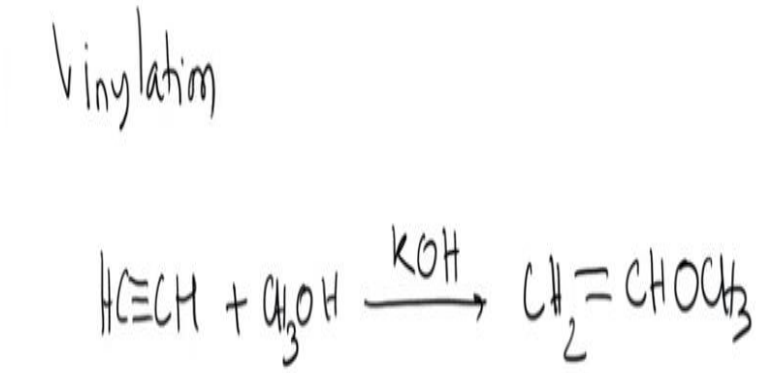

For example the reaction of acetylene with alcohols results information of methyl, vinyl, ethane. So this is the reaction when vinyl functional group is formed and is a part of the reaction called vinylation.

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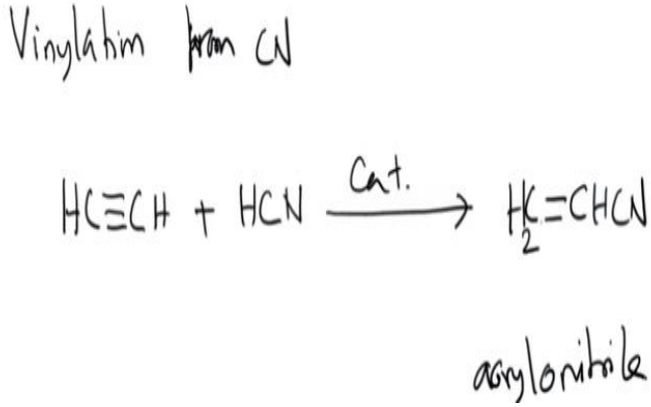

Similarly another example of vinylation involves reaction with cyanides involves a catalyst which gives acrylonitrile. Now this kind of intermediates are very important intermediates are monomers for various polymerization reactions including polymerization to produce functionalized polyethylene's that they have this functional moiety cyanide attach to this poly olefin's. So these intermediates has lot of put application as monomer for various polymerization reaction.

So with these we come to the end of today's lecture on Reppe reaction in which we have looked into the prospective of the development of Reppe reaction in the context of the energy need as a function of time. And what we had seen that with the passage of time from 1800 to 1900 to the present scenario the demand for energy have been made from non-renewable sources to that of the renewable or more technologically cleaner sources of energy.

And this has led to shift in the energy sources on moving from coal, fossil fuel particularly from coal to natural gas and crude oil in 1950's which was that time invoked because of the olefin polymerization discovery and because of the petro chemical development at that point of time to the current scenario of clean technology involving solar beam, biomass water so on hence so forth.

So the acetylene have been produced largely from coal and hence the conversion of acetylene to other feedstock has been explored and successfully demonstrated by Reppe through is wonderful set of reaction has well as the development of being able to handle acetylene in higher pressure but unfortunately in 1950's with economic taking over the ethylene and propylene obtained from a crude oil and natural oil where much cheaper.

And here is the development of ethylene chemistry particularly from ethylene to the that of acetaldehyde using Wacker oxidation took over as opposed to the conversion of acetaldehyde using mercury and in sulphuric acid in water which was sort of taken over by Wacker oxidation were one could convert it ethylene to acetaldehyde and which could then finally be used for synthesizing or accessing other functionalized chemical feed stocks that eventually came round however given the fact that the coal reserve on fossil fuel is going to outlast the oil reserve of natural oil and crude oil.

So still even after 100 years also there are important argument in favor of developing the acetylene chemistry has been initiated by Reppe. In this context we have also looked at 2 vinylation reaction particularly the reactions of alcohol with acetylene in potassium hydroxide and that of hydrogen cyanide with acetylene presence of catalyst given acrylonitrile. With these we come to an end of today's class and we are going to look into some more reactions on Reppe

in subsequent lecture that we are going to be taken up in the next class so till then good bye and thank you.