Transition Metal Organometallics in Catalysis and Biology
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Module No # 02
Lecture No # 07
Origin of Olefin Metathesis

Welcome to this lecture on transition metal organometallics in catalysis and biology we have been discussing olefin metathesis in continuation with the previous discussion of Reppe reactions in which we have looked the utility of acetylene to various chemical feed stock and how it was overcome using elegant organometallics synthesis. We had also observed in the previous lectures that both academia as well as in this industry had been in the fore front.

While contributing to the expansion of the field and we in that context we have noted that Reppe synthesis has had been development which has exclusively or significantly happened at the industry whereas the next one the olefin metathesis reaction that we have taken up in the previous class there we have noted that both academic world as well as the industrial world had been equally series about the development of olefin metathesis reaction.

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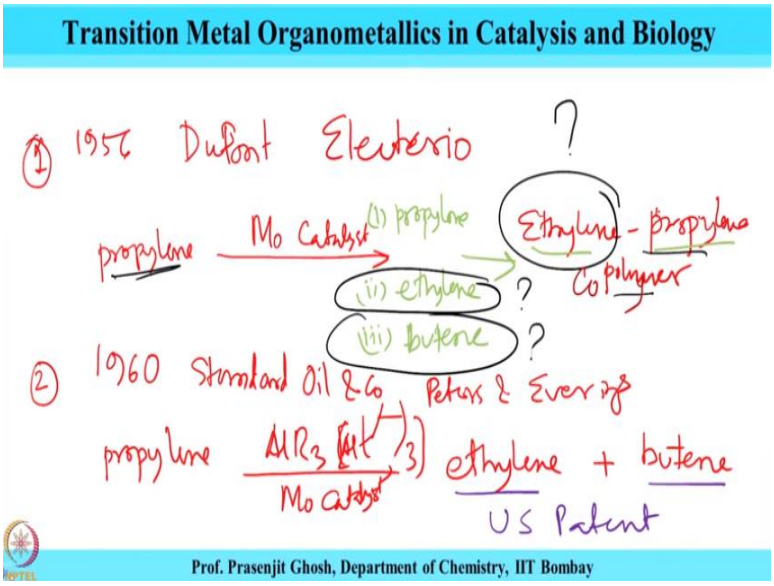

In the previous discussion we have also noted that both olefin metathesis as well as olefin polymerizations these are 2 seminal discoveries in the field of polymers and both had been awarded with Nobel prize in 1953 whereas for the other one is 2005 about 50 years apart and

both have been recognized as important development in the area of polymers. We have also noted in the previous discussion that even though both olefin polymerization as well as olefin metathesis had its origin in mid 1900's to 1950's.

You know elucidation and understanding staggered a bit with olefin polymerization being understood first followed by olefin metathesis and subsequently the application aspects of these 2 Nobel prize award winning discoveries were taken place in the chemical world. So with these we are going to focus more on today's topic which is on olefin metathesis and I am going to give an early prospective early developmental of this discovery and this is a best given by an article in chemical and engineering news 2002 volume 80 page 34 to 38.

So this article provides a fantastic description about the development of olefin metathesis in 1950's how this was taken up around at that time. So continuing further on our discussion on olefin metathesis let me being by saying that initial discovery had happened in the laboratories of industry particularly at a famous chemical industry laboratory which is at Dupont and it is what mentioning that olefin metathesis discoveries happened by chance by exploring the conditions for olefin polymerization reactions.

So it is sort of like the research in olefin polymerization accidently had led to the discovery of olefin metathesis. So olefin metathesis sort of can be seen as an off shoot of olefin polymerization with that said let me just talk about how olefin metathesis was born and it goes back to 1956 in Dupont is well known chemical industry which is on being and being more than about 200 years old and they have had some wonderful chemist which are have contributed to new research and development and lot of important compounds have come out of laboratories of Dupont.

The famous nylon was also developed in Dupont and there are many other important products which have transformed the world have also had its origin tracking back to Dupont laboratories. So in 1956 at Dupont a researcher called Eleuterio you know while polymerizing propylene in molybdenum catalyst observed ethylene propylene polymer. So this was a surprising result because if the propylene was polymerized then the polymer obtained should have been propylene

in polymer whereas this formation of the ethylene was a big surprise that how could ethylene propylene copolymer was obtained.

Now to investigate that what Calderon discovered further that this output feed of this propylene gas actually consisted of propylene ethylene and butane which eventually polymerizing to give this ethylene propylene copolymer. So that was kind of interesting observation which at that point remained unexplained and also what was unexplained over here are the formation of other gases like ethylene and butane how they were formed from the field which had only propylene to start with.

So this that point of time this was observation which was completely perplexing and subsequently again in another industrial setting in standard oil and company of Indiana this is in 1960's the scientist involves that Peter Evering's he observed that when propylene was passed over molybdenum catalyst in presence of aluminum component then they were obtaining ethylene plus butane and this is aluminum tri-isobutyl.

In presence of aluminum tri butyl propylene was giving ethylene and butane and this again was a result which was at that point of time unexplained that how could one get these 2 olefin's from propylene and they had field a US pattern regarding this discovery because they thought this much be something very interesting.

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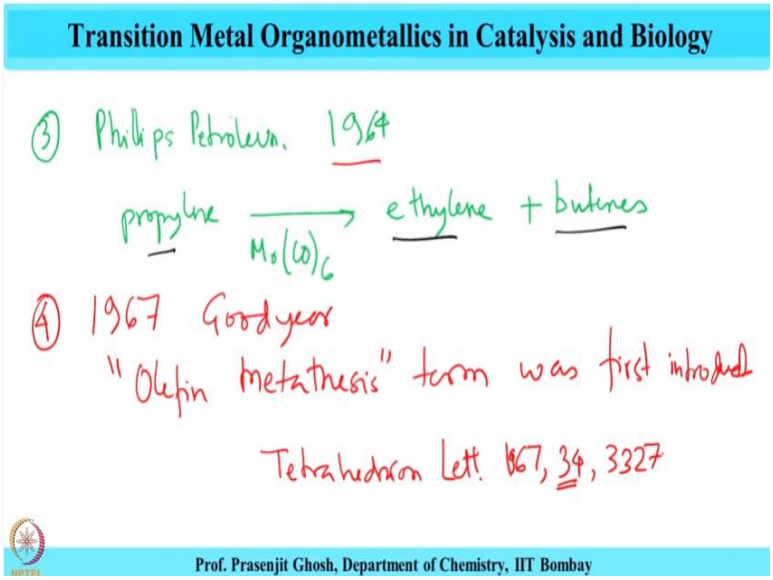

Subsequently again another observation was reported in another industrial company which is Philips Petroleum in 1964 where the disproportionation of propylene to ethylene plus butanes were reported on molybdenum hexa carbonyl compound. So what was observed over here there has been observations which remained unexplained as how other olefin's where forming from propylene and then in some cases that these olefin's where even went further polymerize to give ethylene, propylene, methylene, butane copolymers.

So this was a very perplexing discoveries and people in the industrial world as well as in the academic world were trying to figure out as to what was happening in conversion of olefin to other kinds of olefin it seemed to them as if somebody had stitched cut open the olefin from the middle with scissor and stitched end with the other fragments in a very neat fashion. So this at that time was very complex and intriguing observation which when the scientist at that time were unable to explain.

Indeed the name of olefin metathesis was coined at industry and this was given in 1967 about 3 more years later in Good Year Tyres were the researchers point the term olefin metathesis was first introduced. So this is an interesting thing that nomenclature of this type of reaction was happened about 10 years about 15 years from initial observation of what this reaction was meant to be.

The results of the term is first traced back to a tetrahedron letter publication in 1967, 3327 when the Good Year first coined the term olefin metathesis. Now once the name has been given to this olefin metathesis the mystery still remains as to how the reaction was happening or sort of what is the mechanism of this reaction. So the next focus of research was diverted towards understanding the mechanism.

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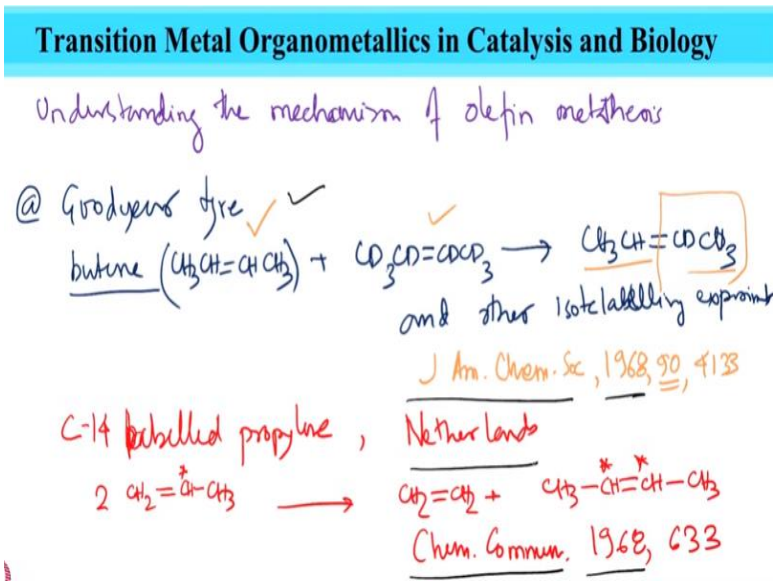

The mechanism of olefin metathesis and what is interesting to see that a lot of effort and lot of attempts and speculations were made as to arrive at the correct mechanisms with people as usual tired different things starting from isotope leveling experiments and so on and hence so forth are trying to arrive at the mechanism. And the most important interesting bit about it is that much of the speculative mechanism which was proposed at that time and were published got accepted in premium journals however did not turn out to be true.

Whereas a very non descriptive (()) (16:00) mechanism in a very non descriptive foreign language finally turned out to be correct and went on to win the Nobel prize. So one can see the excitement and unpredictability that science as to be offer. In this effort the first this set of experiments where indeed done at the Good year tyre using a homogenous catalysis where they experimented with butane at Good Year tyres research was done with butane and deuterated butane.

You know the combinations of and other isotope labeling experiments were performed to see how the to see the formation of olefins and what is interesting is the fact that they could see the various kinds of labeling where half of it due to deuterated other half limb is protonated and so on and hence so forth depending on the type of the isotope labeling olefin's. They took they arrived have at this and this was published in journal of American Chemical society in 1968 for 133.

So this is interesting paper contribution from Good Year tyres were they took on the path to elucidate the mechanism and the first thing they tried is to take butane an isotope leveled butane and to see what kind of isotope distribution happened in the olefin that is formed. And then based on that they had come up with the mechanism. The second interesting effort also on leveling experiments with C14 labeled propylene was used by a research group in Netherland where they looked at the distribution of C14 fragments and to describe the experiments.

This is the labeled C14 carbon so 2 of these gave the products and this was published in important journal of Royal society which is chemical communication in the year 1968 volume 633 so what is worth noting is the time of publication of these 2 references both are in 1968 one happened in Jacks and other happened in chemcom one was from US the other one was from Netherlands this also highlights how competitive are how intense was the efforts research efforts at that point of time towards elucidating this mechanism as to how this olefin metathesis reactions were happening.

And this way we see the same approach of isotope leveling studies one with deuterated olefin's the other with carbon13 laboratory olefin were studied to come out of the possible mechanism for these 2 types of reaction and indeed all of these studies lead to for the various kinds of hypothesis which you are going to be looking at it and what would be surprising to see that even though the number of hypothesis had been proposed for the mechanism only and they had appeared in very many important journals.

However the once that had that appeared in not so famous journal at was later proven to be correct and was recognized with Nobel prize. So that is sort of brings us to the prospective that you know the work is important and it does not really matter where it get published so along with published it will see the light of the day it is good effort. So the intense speculation as to how the reaction was proceeding late to the discoveries in various pathways that was resulting in the metathesis reaction.

With regard to the mechanism of metathesis what was more interesting to the community was how does or how is the metathesis reaction proceeding.

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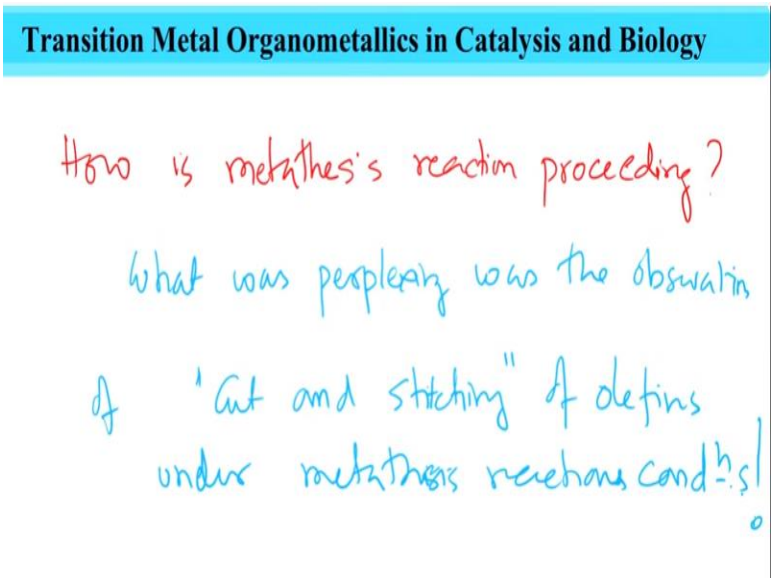

What the researches where sort of perplexed at was this cut and stitch phenomenon observing at the time. So what was perplexing was the observation of cut and stitching of olefin's under metathesis conditions. So this is something which was really intriguing at that point of time and this is what consumed much of the effort in obtaining and understanding of this reactions.

Now once that was obtained its full potential was explored with regard to developing various times of metathesis reaction for further development. Now with these the I would conclude today's lecture were we have looked into this olefin metathesis particularly from the time of its origin and how it was observed first in industry which led to baffling interpretations with regard to the formation of this we had also observed that the term olefin metathesis was indeed a coined in industry particularly at Good Year tyres where they have termed the coin olefin metathesis to this set of reactions.

We have also seen that this baffling observation of cutting and stitching of olefin's was observed while as off shoot of while studying or developing the olefin polymerization chemistry using propylene substituted olefin fades under molybdenum catalyst in presence or in absence of aluminum alkynes. So this is interesting thing to note that olefin metathesis has its birth in olefin polymerization and which as both of which has developed into their own field duly recognized with Nobel prizes by their own right and merit.

We had also seen in this discussion as to how industry has helped in first observing this reaction this new reaction and then getting started on it and trying to name and then understand this reaction with regard to what they were observing. So more of this discussion as we continue in the next class we look into the interesting aspect of the next phase of focus on metathesis reaction which is trying to sort of trying to elucidate the mechanism in which such cutting and stitching of olefins where effortlessly being done in under the gamut of this reaction.

So what we would see that intense effort across America and Europe at that time led to development of this interesting reaction and more on how this happened as we meet in the next class till that I thank you for being with me in this lecture where we had looking up a very interesting topic of olefin metathesis more on olefin metathesis has been made next where we look at the development of this reaction what has happened till today. So with this I conclude today's lecture and I look forward to being with you in the next lecture till then good bye and thank you.