Transition Metal Organometallics in Catalysis and Biology
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Module No # 08
Lecture No # 38
Oligomerization of alkenes and alkynes (Part – 4)

Welcome to this course on transition metal organmertallics in catalysis and biology in this series of lecture of (()) (00:22) we are discussing oligomerization of alkenes and alkynes topic and in that we have discussed about 4 kinds of oligomerization reaction.

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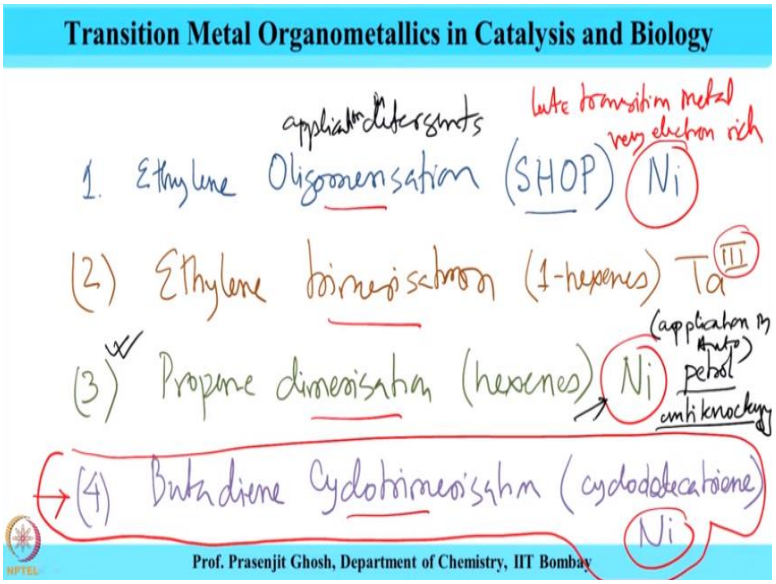

Transition Metal Organometallics in Catalysis and Biology

application detergents

late transition metal very electron rich

1. Ethylene Oligomerisation (SHOP) Ni

(2) Ethylene trimerisation (1-hexenes) Ta III

(3) Propene dimerisation (hexenes) Ni (application in Auto) petrol antiknocking

(4) Butadiene Cyclotrimerisation (cyclododecatriene) Ni

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Starting with ethylene oligomerization and these we have discussed with regard to shell higher olefin process or the shop process which uses the nickel catalyst for carry out this ethylene oligomerization the main drawback even though this is a industrial scale process the main drawback is that it is not selective in the sense that it produces the broad range of distributions of ethylene oligomers of various chain length. This shop is a industrial process that includes ethylene oligomerization along with olefin isomerization and olefin metathesis together they constitute the process of shop which is sell higher olefin process.

Subsequently we have also discussed another interesting reaction which is ethylene trimerization and these is done very selectively in which ethylene is trimerized to give 1 hexane and this is a process that use early transition metal tantalum 3 catalyst for carrying out these 1 hexane trimerization. The subsequent that we have also discussed another topic which is dimerization of propane dimerization and are these produces hexanes of different substitutions and these branched hexanes when hydro generated give high quality petrol of very high anti knocking attribute.

And this also uses for nickel catalyst for carrying out such kind of transformation now with these being discussed today we are going to proceed further or and then we are going to discuss another interesting reaction which is cyclo trimerization of butadiene or may we can call it for the sake of beta dine cyclo trimerization and these produces cyclo octa dodeca and uses also nickel catalyst.

Now one word to look we are going to be discussing about this topic in as a part of today's class. Now in this connection it is worth noting that if one were to look at all these oligomerization process for example oiligomerization, trimerization, cyclo dimerization all of these process then one would see that the metal of choice for such as process is in fact nickel which is a late transition metal and also supposedly very electron rich.

Now this is a interesting observation as well as correlation that comes out of these oligomerization reactions what it says that olefin oligomerization is usually favored by electron rich (()) (05:54) transition metals whereas olefin polymerization is favored by only transition metal electron deficient early transition metals. So this is a conventional wisdom in the area of olefin oligomerization and polymerization.

Now from this prospective this ethylene trimerization with tantalum 3 which is an early transition metal sort of in the sense there are some examples of even lower order or lower degree of polymerization like trimerization happening with electron deficient metal like tantalum. But note that oxidation state of tantalum is not fives and three's hence you know it not very electron deficient as it would have been if it were in the class 5 oxidation state.

Now with that we are going to focus on today's discussion which should be centered around this butadiene cyclo trimerization reaction and look at various ways that formed. One thing to note that the in terms of application before I proceed further in terms of application these shop is applied for where applied for preparing detergent in variants application in detergents industry.

Whereas this propene dimerization giving hexane branched hexane’s these are in automobile because they are used for producing petrol of high quality high knocking agents.

So this is application in auto industry and this ethylene trimerization is providing this selective one hexanes they are also used for commercial purpose also to note that this particular reaction which is propene dimerization having applications in high quality petrol of anti-knocking capacity the activity of these catalyst is extremely high the turn over number and is quite comparable to that of biological enzyme like catalyst that carry out these and transformations.

So having said that here we have system which is extremely efficient and has a very high turnover number with respect to similar to that or comparable to that of enzyme catalyzed reaction. So from that prospective this catalyst of this process is quite remarkable fit that demonstrate the capability of organometallic catalysis in the world of chemical transformation. ‘s Now with that discussion let us move on to this topic of today’s discussion which is cyclo trimerization of butadiene.

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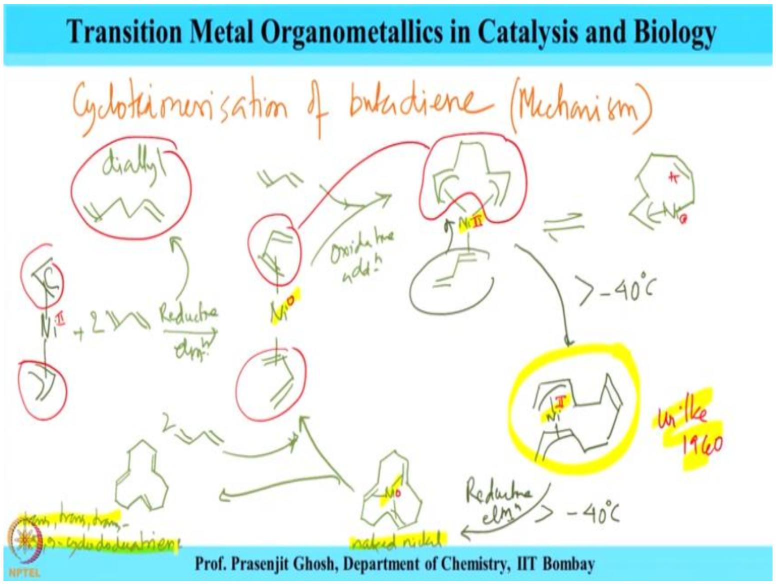

Transition Metal Organometallics in Catalysis and Biology

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So what we are going to primary focus on is the mechanism in which how it works. So the precursor is the nickel to allele complex that is the catalyst precursor and the oxidation state over here is nickel 2. Now that in presence of butadiene undergoes reduction elimination of the 2 allele moiety to give diallyl compound is shown here so the reduction elimination happens between these and this resulting in diallyl compound as it shown over here and it gives this nickel 0 species with nickel 2 butadiene.

So the oxidation state for this species is a nickel 0 now that subsequently reacts with butadiene to give the species which is shown over here. Now this is a oxidative addition reaction of 2 butadiene moiety to form this these allele ligand and the oxidation state of the nickel as become nickel 2 as a result of these oxidative addition reaction. Now these is in equilibrium with this species which is sigma bond this is the pi bond which are now separated and at very low temperature greater than -40 degree centigrade this the second insertion happens on to this ligand giving rise to this species which also is nickel 2 and then this is a important species which subsequently trimerizes at reaction about -40 degree centigrade to give the corresponding nickel 0.

So this is sort of reductive elimination process to give the nickel 0 species as it shown here and this is called naked nickel. And this is a nickel 0 species which finally eliminates the butadiene trimer to give this cyclic trimer this is called trans 159 cyclo dodecatriene. This gives cyclo dodecatriene and this butadiene 2 of them then enters the catalytic cycle. So this is a interesting mechanism which has been proposed by (()) (18:06) in 1960 and this involves the formation of nickel as is shown over here.

So the main feature is the transformation from nickel 2 in 2 of the catalytic cycle as well as nickel 0 as well as nickel in the 2 of the catalytic cycle. The other important thing is that these particular species was confirmed by preparing it separately and entering the catalytic cycle through these species so give the identical cyclo trimerized products. So this is indeed a very good reaction that as been successfully carried in which butadiene can be trimerized can be trans 159 cyclo dodecatriene and it shows over here.

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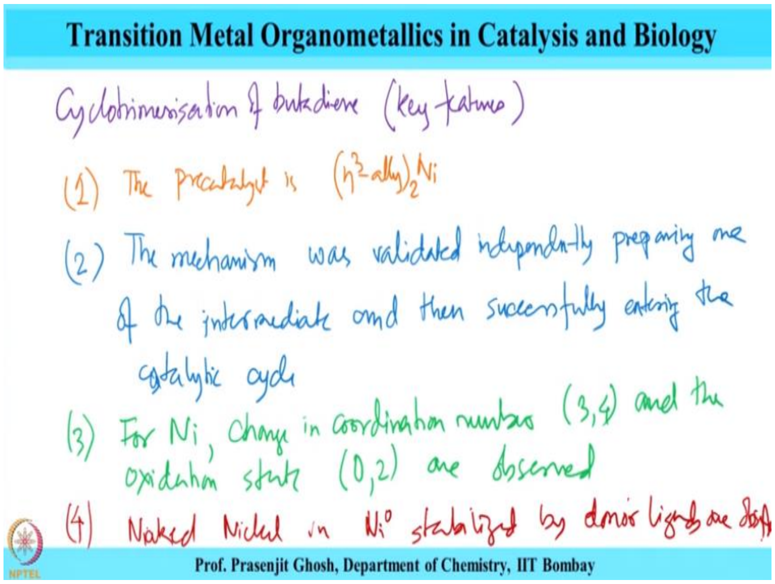

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Cyclotrimerisation of butadiene (key features)

(1) The precatalyst is $(\eta^3\text{-allyl})_2Ni$

(2) The mechanism was validated independently preparing one of the intermediate and then successfully entering the catalytic cycle

(3) For Ni, change in coordination numbers (3,4) and the oxidation state (0,2) are observed

(4) Naked Nickel in Ni^0 stabilized by donor ligands are obs

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So the key features of these cyclo trimerization reaction is given below the key features the number 1 pre-catalyst is (()) (20:02) complex of nickel then the second thing is the mechanism was validated by independently preparing one of the intermediate and then successfully entering the catalytic cycle. So another important attribute of these mechanism is of the change in metal for nickel change in coordination number from 3 to 4 and the oxidation state 0 to 2 are observed and the last but very important attribute is naked nickel in nickel 0 stabilized by donor ligands are observed.

So these are the key attributes of cyclotrimerization process which sort of shows the feasibility of these nice reaction through the metal undergoing flexible displaying flexible coordination more by changing the coordination number from 3 to 4 as well as flexible oxidation state by changing the oxygen from 0 to 2 in the process naked nickel stabilized by alkene donors are formed and they are part of the catalytic cycle.

Lastly the catalytic cycle is even validated by entering that catalytic cycle through one of the catalytic intermediates which were prepared independently. Now having said these even though this was very nice and beautiful reaction in terms of the applications of organometallic catalytic are concerned however these reaction is not being used in industrial scale for producing this cyclo dodecatriene or trimer of butadiene and this cyclo dodecatriene in industry is prepared by Ziegler Natta process as it shown over here.

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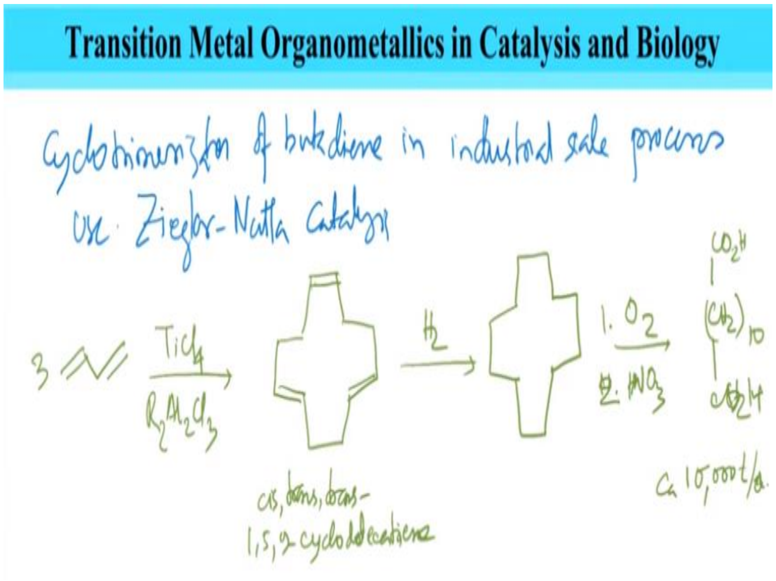

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Cyclotrimerization of butadiene in industrial scale process use Ziegler-Natta Catalysis

Cylo trimerization of butadiene in industrial scale process use Ziegler Natta catalysis and this is shown below 3 butadiene with titanium tetrachloride R2Al2 Cl3. And this give this C's trans 159 cyclo dodecatriene that is further hydrogenated and then finally in presence of oxygen and the second nitric acid this acid is produced. Now in large scale about 10000 ton part here annually. So even though this (()) (27:01) method of producing butadiene trimerization is a very nice beautiful method but this is not being used in industry probably because of difficulty in handling the air sensitive nature of nickel 0 intermediate that is produced in the process of cyclo trimerization of butadiene.

And hence the Ziegler Natta catalysis are used to produce these trans cyclo butadiene then which is then hydrogenated and subsequent oxidation and nitric acid produces this diacid about 10000 ton annually in a large industrial scale. So with these I come to the conclusion of today's lecture in today's lecture we have looked into the cyclotrimerization of butadiene in the context of various other topics where covering along the thing of olefin and alkyne oligomerization reaction.

We have looked into the mechanism as proposed by (()) (28:00) using a nickel catalyst and then we have also looked at the alternative pathway which is used in industry using Ziegler Natta catalyst using titanium tetrachloride to produce a this cyclo trimerization butadiene in large scale processes for making a diacid in about bulk quantity about 10000 annually. So with these I come to the conclusion again one more time to of today's lecture and I look forward to taking up this topic in bit more detail little bit remains on this early olefin and alkyne trimerization reaction. And subsequently will take I up olefin polymerization which reaction as we meet next till then good bye and thank you.