Transition Metal Organometallics in Catalysis and Biology
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Module No # 08
Lecture No # 37
Oligomerization of alkenes and alkynes (Part – 3)

Welcome to this course on transition metal organometallics in catalysis and biology we have been discussing alkene and alkyne oligomerization reaction in the past 2 lectures in this context we have covered 2 main reaction one is alkene ethylene oligomerization.

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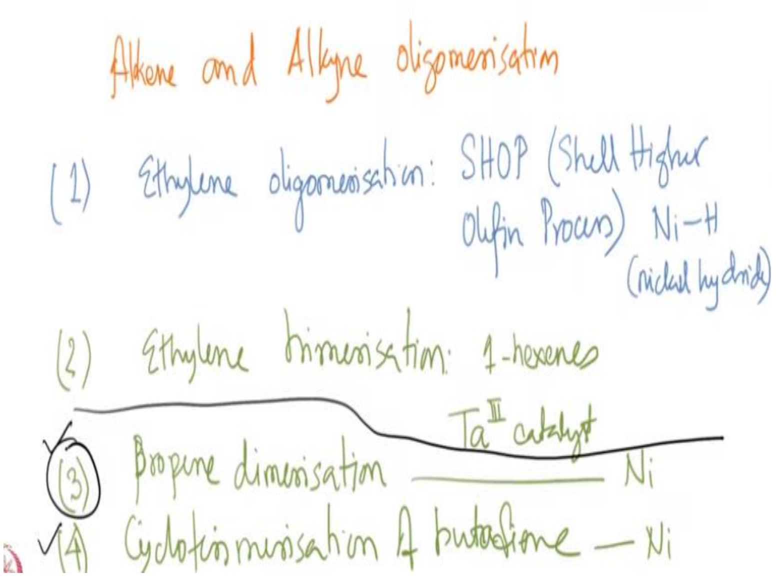

Alkene and Alkyne oligomerisation

(1) Ethylene oligomerisation: SHOP (Shell Higher Olefin Process) Ni–H (nickel hydride)

(2) Ethylene trimerisation: 1-hexenes
Ta^{II} catalyst

✓ (3) Propene dimerisation —— Ni

✓ (4) Cyclotrimerisation of butadiene — Ni

Alkene and alkyne oligomerization and in this context we have covered 2 reactions first one is ethylene oligomerization this we have covered from the prospective of shop process shop is shell higher olefin process and this we have covered using the nickel catalyst nickel hydride is the active species is an active species for the catalyst for ethylene oligomerization and this ethyl ilogomerization came into prominence with regard to the shop process.

But particular for finding a synthetic root to producing detergents and this was achieved by oligomerization of ethylene with a nickel catalyst followed by 2 other important processes which were added to it one is ethylene alkene isomerization and alkene metathesis reaction which together oligomerization isomerization and metathesis all together constitute the shop process shell higher olefin process and this was primary used for preparing the starting material for synthesis of detergents you know.

And this has been discussed in great detail with respect to both ethylene oligomerization as a part of this topic as well as with respect to olefin metathesis which was the topic which that was discussed in the earlier lectures. We had also discussed ethylene trimerization this ethylene trimerization is primarily used to produce 1 hexane using tantalum 3 catalysts and which was obtained by from tantalum 5 salts by presence of alkylating reagent and this also we have discussed in details particularly the mechanism of its formation highlighting the main advantage of this process which is about the selectivity of this reaction.

Today we are going to discuss about 2 other reactions 1 is a propene dimerization and the fourth one is cyclo trimerization of butane butadiene these 2 are very interesting processes that we would be talking about today and both involves nickel catalyst that carry out these 2 trimerization of propene and cyclotrimerization of butadine reactions. So today main lecture with this highlight on these 2 reaction one is propene dimerization as well as cyclo trimerization of betadine diene.

Earlier on in a previous lecture we have discussed above 2 reaction ethylene oligomerization using again nickel catalyst again second one that we had discussed in earlier reaction was ethylene trimerization to 1 hexane using a tantalum catalyst. So with this we are going to focus on first reaction which is propene trimerization reaction using nickel.

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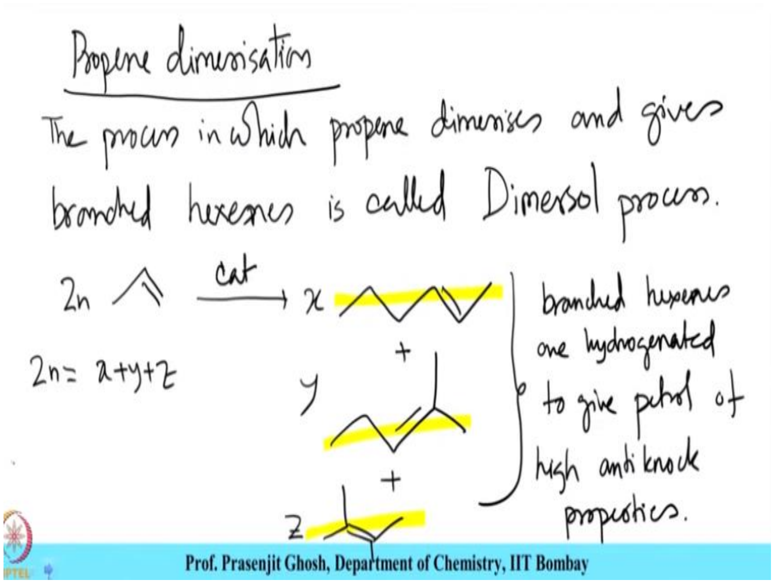

Propene dimerisation

The process in which propene dimerises and gives branched hexenes is called Dimersol process.

2n = x+y+z

branched hexenes are hydrogenated to give petrol of high anti knock properties.

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And reaction using nickel now this process in which propene trimerization to give hexane’s various types of branched hexane’s this is called dimer solved process the process in which propene dimerises and gives branched hexane is called dimersol process. And the reaction is depicted as follows to 2n using a catalyst gives where 2n equals x + y + z x gives x moles of hexane of this type +y moles of +Z moles of.

Now these are important intermediates as they can this branch hexane’s this can be hydro generated to give high grade petrol of anti-knock property branched hexane’s are hydrogenated to give petrol of high anti knock properties to give petrol’s of anti-knock properties. Now let us take a look at the mechanism for this dimerization of the propene reaction.

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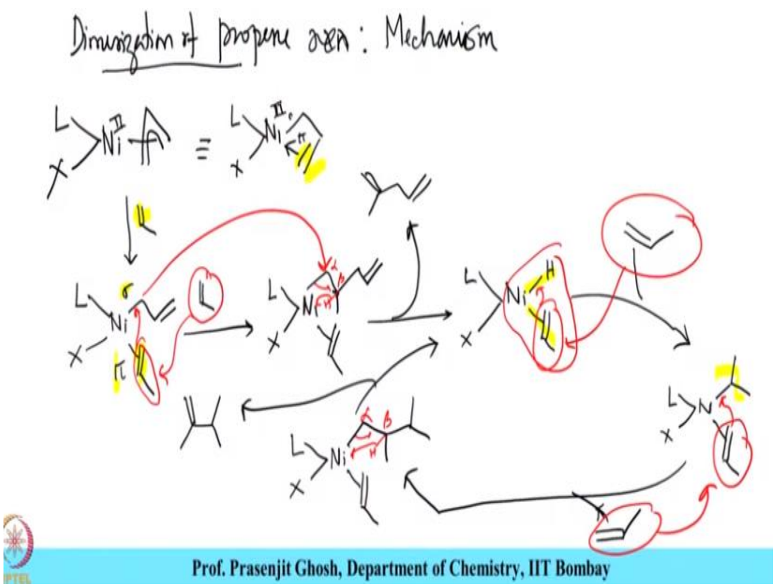

The mechanism of it and that is given as follows the catalyst prickles is of the type nickel L X type ligand with a allele. Now allele moiety bound to nickel so this is nickel 2 complex and an allele moiety bound to nickel can be viewed as such given over here one sigma bond another pi bond as is the one shown over here that react with a propane to give nickel x sigma pi complex. So what really happens over here is that these pi bond of the allele gets replaced by these olefinic pi bond and this beta 3 becomes sigma and pi over here as its shown over here.

So now this reacts with an olefin to give this nickel 2 complex x where this olefin first undergoes migratory insertion into the nickel alkyl sigma bond to give the following complex as it shown over here. Actually to be more accurate these undergo to migratory insertion and this comes under coordinate that is the more accurate representation and these undergoes this to give this inserted complex which then better eliminates this is alpha and beta and there is hydrogen over here.

Beta eliminates to give the corresponding alkene branched hexane as it shown over here and that then reacts with another propene molecule. Again a similar kind of coordination insertion happens were this insert into the nickel hydride bond and this comes an coordinates to give the product as is shown with the nickel bound now to an isopropyl moiety and then alkyne note that isopropyl moiety is obtained by insertion of this hydride into insertion of this into this hydride gives you the isopropyl moiety.

Now the reaction of these with propene gives nickel now again as observed in earlier case these undergoes insertion into the isopropyl moiety and these olefin coordinates there giving rise to this compound as is shown here and these further beta eliminates to give this nickel hydride complex with alkene and the product which are formed is these branched alkene as is shown over here. So trimerization of propene then leads to deformation of variety of alkyne through this process as is shown over here.

Now to note L for the catalyst is phosphine and x is to note over here that L is L and X are shown here L these effect phosphine and X is a ethyl tri aluminum chloride moiety. So with these we show how these dimerization of propene gives rise to branching branched hexane's which when hydrogenation gives this anti knock rate high petrol. And this involves a nickel hydride as the active species that carry out these dimerization of propene process efficiently.

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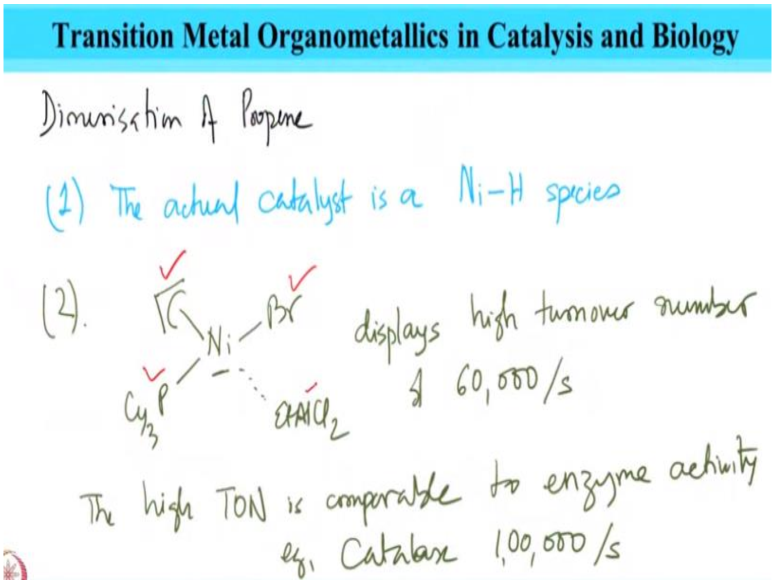

Transition Metal Organometallics in Catalysis and Biology

Dimerisation of Propene

(1) The actual catalyst is a Ni–H species

(2). displays high turnover number of 60,000/s

The high TON is comparable to enzyme activity eg, Catalase 1,00,000/s

So the actual catalyst is a nickel hydride species the catalyst the one which is eta 3 allele nickel Pcy3 Br EtALCl2 this is the active catalyst have shows displays high turnover number of around 60,000 per second and these numbers the high turnover number is comparable to enzyme activity. For example catalyst exhibits high turnover number of 1 lakh per second. So this is a interesting compound where nickel is bound to 1 liter allele 1 cyclo hexyl group 1 bromide and this (()) (23:40) Cl2 and these sort of is an effective species for dimerization of propene and that gives various kinds of branched hexanes which upon hydrogenation gives high quality petrol having anti knock properties.

So today we have looked into mechanism as to how these branching of how this propene occurs and these mainly go through these nickel hydride active species the forming the coordinated propene with then undergoes insertion into the metal alkyl bond to give the branch propene. So with these we come to the conclusion of today’s lecture which was primarily on this important reaction of dimerization propene.

We have also looked at this reaction in context of the other 2 alkene oligomerization reaction for shop process as well as these ethylene trimerization reaction to give 1 hexane now with these we move on to the next reaction which is cyclo trimerization of betadine we are going to be looking at how these catalyst is used for making these betadine trimer when we take this discussion in the next class.

So with that I conclude today’s lecture in which we had discussed about these one particular reaction which is propene dimerization reaction and these is called the dimersil process and is used to make branch takes in which upon hydrogenated give high grade anti knocking and quality of petrol and has used in automobile industry. So with these we come to the end of today’s lecture and I thank you for being me in this lecture and I look forward to discuss more on this olefin oligomerization reaction as we meet next till then good bye and thank you.