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Organometallic Chemistry-I

Prof. Debabrata Maiti
Department of Chemistry, IIT Bombay

Module No. 2

Lecture No. 6

OXIDATIVE ADDITION
[3. RADICAL MECHANISM]

Welcome everyone today we will discuss the last part of oxidative addition that is the radical mechanism we have seen in the last two classes oxidative addition by concerted mechanism and oxidative addition by SN2 mechanism of course obvious other option that is left is the radical mechanism is it possible of course it is possible radical mechanisms are possible for a number of cases specifically those substrate which will not undergo SN2 reaction for example that very easily then radical mechanism is one of the most viable offset.

Now how are we going to know that which is the radical mechanism of course there are few experiments which we can do to be sure as the name suggests radical mechanism will not get reproducible kinetics data that we have already understood while we were discussing the SN2 reaction so non reproducible kinetics data will be one of the proof in favor of a radical mechanism of course other techniques that we can utilize in this case is to use radical traps if we use radical traps and if a radical mechanism is prevalent then what we will see the reaction will either completely shut down or at least you know considerably shut down.

In case of the radical reaction in presence of the radical trap in addition we can have different initiator or you know sensitizer initiator mainly oxygen light as initiator or other initiator we can use for such reaction most importantly if you look at the stereochemistry point of view if a radical mechanism is happening the stereochemistry of the you know let us say halide the RX where the oxidative addition is occurring stereo chemistry will be lost in the concerted mechanism we have seen the stereochemistry is intact.

So if you are starting with a RX with which the oxidative addition is going to happen and the RX is having chiral centrein it the chiral centre will remain intact if it is a concerted mechanism so the chiral complex will give a chiral final product organometallic product for concerted mechanism if it is a SN2 reaction as you know it is a backside attack so the inversion of configuration will be observed but if it is a radical mechanism we will see that the chiral center will be maximized so the product final product will be a racemic product from starting a chiral RX spices. So these are the characteristics let me try to write down very briefly about this characteristic.

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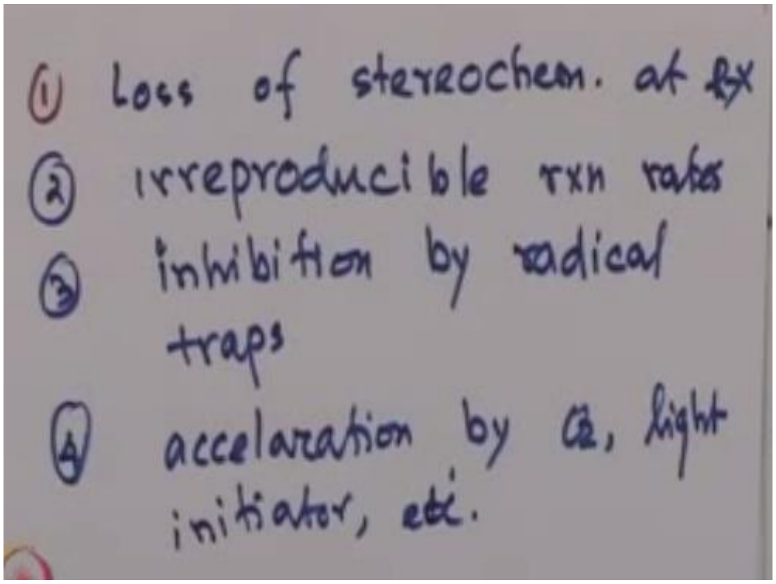

① Loss of stereochem. at RX

② irreproducible rxn rates

③ inhibition by radical traps

④ accelaration by O_2, light initiator, etc.

As we as we have discussed the characteristic of a radical mechanism will be loss of stereochemistry chemistry at RX if RX is having stereochemistry irreproducible reaction rates, okay. The fluctuates we will be there inhibition by radical traps finally we can also expect acceleration by oxygen, light, other initiator etc, right. Now of course for any radical reaction we can expect two type of mechanism, one is the non chain radical mechanism another is the chain radical mechanism.

We will discuss briefly the non chain radical mechanism where we will see the reaction starting material usually is an odd electron one often we see that for let us say 17 electron complex 17 electron organometallic species will gives rise to a oxidative addition that is undergoing a radical mechanism let us take one of the real-life example right now.

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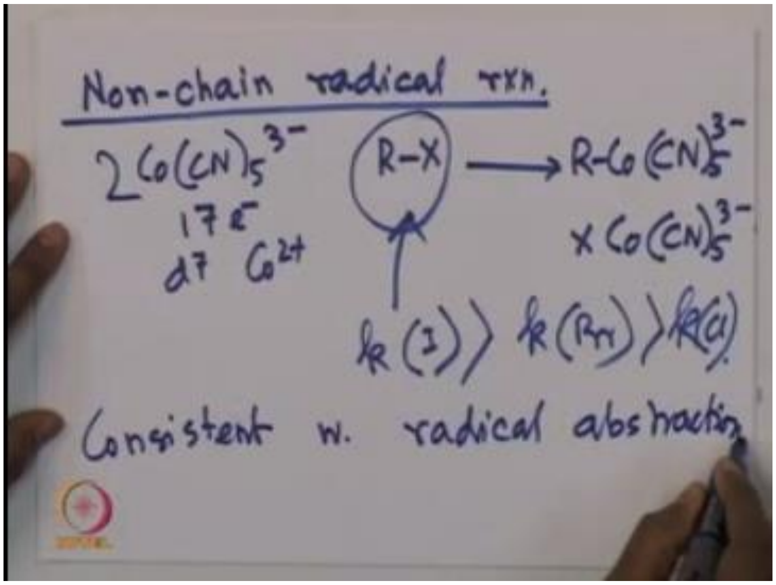

So we are discussing non-chain radical mechanism, now what could be better complex than cobalt for a odd electron species if you do the electron count you will find that this is a 17 electron species it is a d^7 cobalt 2^+ do the electron count it will be d ^{7} now this species two of these species will react with RX to give you $R\text{-}Co(CN)^{3-}_5$ and $X\text{-}Co(CN)^{3-}_{5,}$ now this RX if you are varying different RX.

Let us say iodide, bromide, chloride rate constant for the iodide will be faster than bromide then your fluoride and so on, again this further proves that it is a radical mechanism if iodide is faster than bromide and then chloride this suggestion that it is a radical mechanism therefore this is again consistent with radical abstraction right now of course it is a non-chain radical it happens in a stepwise manner so the cobalt complex which is the 17 electron species will react with RX in a stepwise fashion let us write down the step-wise reaction mechanism so c 0

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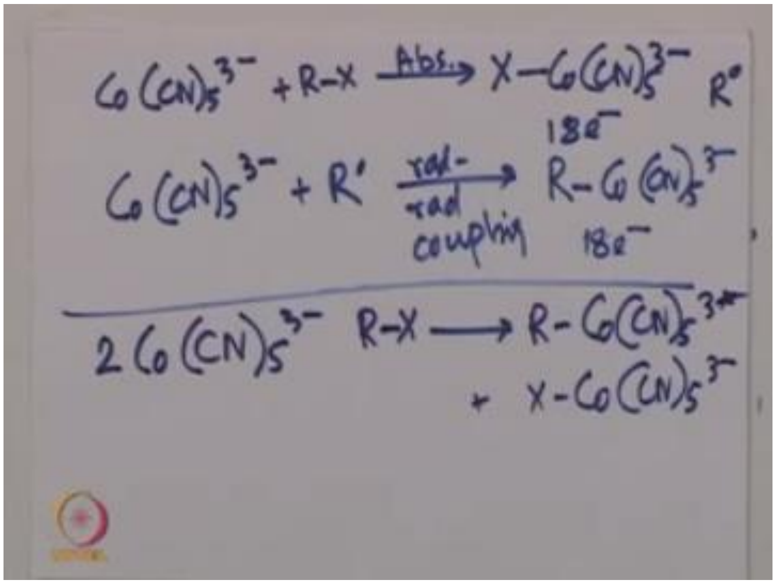

$$Co(CN)_5^{3-} + R\text{-}X \xrightarrow{Abs.} \underset{18e^-}{X\text{-}Co(CN)_5^{3-}} \; R^{\cdot}$$

$$Co(CN)_5^{3-} + R^{\cdot} \xrightarrow[\text{coupling}]{\text{rad-rad}} \underset{18e^-}{R\text{-}Co(CN)_5^{3-}}$$

$$2\,Co(CN)_5^{3-} \; R\text{-}X \longrightarrow R\text{-}Co(CN)_5^{3-} + X\text{-}Co(CN)_5^{3-}$$

$(CN)_5$ 3 - reacts with RX this is an abstraction step to give you X Co CN_5 3 – species which is an 18 electron species along with $R^{\cdot}$ now this another molecule of Co CN 5 3 – will react with that R dot to give you show called radical coupling and finally we will get R Co CN5 3 - of course this is again 18 electron species so what we have seen so far here Cobalt Penta cyanide species reacts with RX to give you X cobalt CO CN 5 3 - along with our radical formation this radical will combine with the cobalt which is again it is a kind of radical intermediates 17 electron species to give you radical coupling overall our CO CN 5 3 - both these species are 18 electron in count.

So if you combine these two steps overall will have two molecule of the cobalt species reacting with our X to give our CO CN 5 3 - sorry 3 - + X CO CN5 3 - right so this is this is how actually radical reactions are you have seen the radical reaction before the mechanism is rather straightforward you need to generate the radical somehow if your organic intermediate happen to be a radical intermediates such as 17 electron species in this case we have seen the cobalt species previously if you notice carefully for the concerted mechanism and also for the SN_2 mechanism we were mainly discussing the 16 or 18 electron complex never really.

We were discussing an odd electron species like17 electron species but for radical reaction either you are starting material is having odd electron or you have to create such atmosphere where odd electron is there okay now we will take one of the example which is a 16 electron species to start with but then it is undergoing a radical mechanism in this case what you need is a promoter or a initiator to initiate the reaction so 16 electron species will initially converted will be converted to a 17 electron species and then that 17 electron spaces will undergo the radical reaction overall to give you the oxidative addition by a radical mechanism.

So it is not necessary to have the organometallic species in a radical mechanism to have the odd electron like 17 electrons to start with we can start with an even electron organo metallic intermediate and then an initiator can initiate the reaction it can do the job to promote the reaction and then overall a radical reaction then follows let us take an example.

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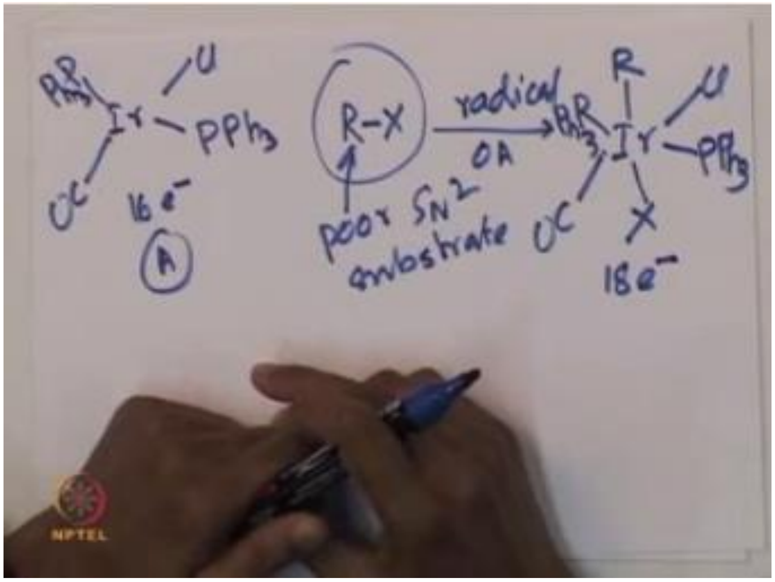

Once again our favorite complex this iridium complex it is a 16 electron species, now let us say this is the species A, this piece is A will react with RX let us say this is poor for your SN2 substrate let us say butyl, fluoride or anything you would understand that will not undergo SN2 reaction. Now this will undergo the radical oxidative addition overall to give you iridium RX species to give you the first form intermediate is the one which will have the initiator let me first draw the oxidative addition complex.

So the 16 electron species is undergoing oxidative addition overall to give you an 18 electron species, but in this case particularly we are emphasizing that the RX is not the one where SN2 reaction will be easily done, can these reaction go of course it can go a 16 electron species can undergo an oxidative addition by a radical mechanism but it will not be a straightforward one you need again initiator in this case the initiator will bind with the starting 16 electron complex once again the RX that we are using it is not a substrate where simple SN2 reaction will be possible. In such cases let us say tertiary butyl fluoride of course there is no way you can get in SN2 reaction what you can do to get the oxidative addition is to start with a initiator.

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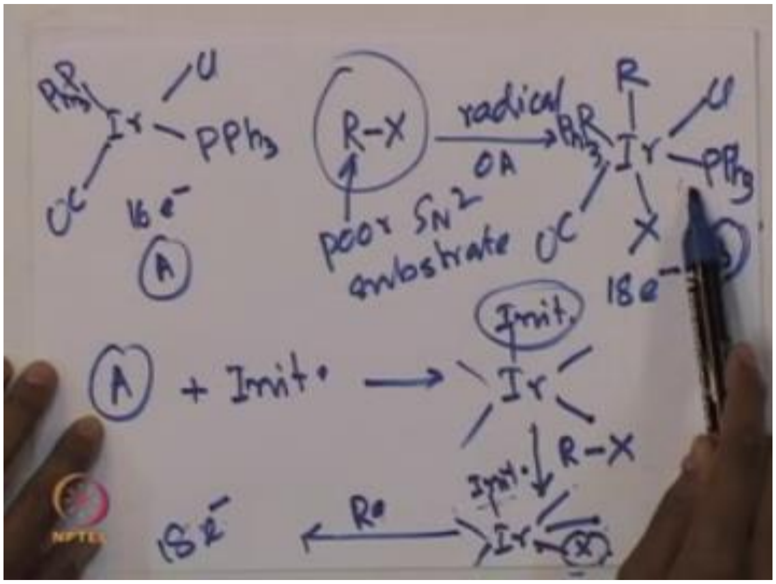

Met me draw then so the A the organo metallic intermediate A will react with the initiator to give you initially iridium initiated species, okay rest of the coordination remains same and then the RX will be the one which is getting involved to give you iridium complex where you will have X an initiator involved with it, okay,.

Now this intermediate we'll all other coordination then will react further with the r dot so the x is here r dot is there r dot will be replacing the initiator to give you the final this complex 18 electron complex let us say this complex B. So what we have seen the A is binding with initiator to give you iridium initiator complex from where r x will be combined with this to give you the first initiator x complex the other coordination four coordination remains exactly the same. And then the r dot will replace the initiator to give you the 18 electron final species okay, the propagation for this reaction will involve the R.

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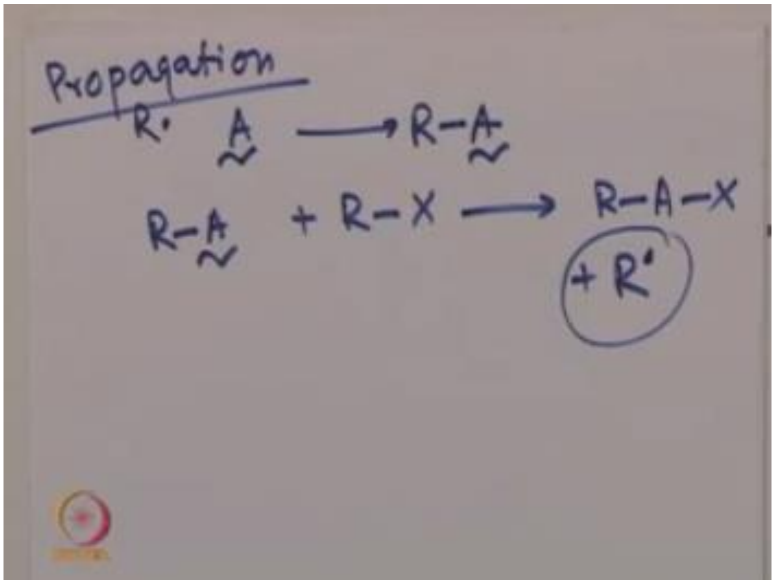

So the propagation let us say reacting with the initiator okay to give you RA now RA will react to give you RA + RX will give you RAX pcs + R. that is how the reaction will propagate so once you have a initiator to initiate this radical mechanism the reaction will take care itself because the next step will be the r dot that r dot will then react with A again it will go and do the reaction to give you the reaction in a step wise manner so what we have seen so far is two examples of radical mechanism in one case we have 17 electron complex that is the cobalt spaces cobalt species reacting the 17 electron species reacting in a radical mechanism to give you first an 18 electron species.

And then another radical gets generated that radical will again react with the metal complex to give you two species so two equivalent of the cobalt intermediate was giving one equivalent of the cobalt R species and another equivalent of cobalt X pieces both of those species where 18 electron when we have a 17 electron starting material it is good to have an odd electron spaces for the radical mechanism but it is not essential to have the odd electron species in case of even electron species such as 16 electron species the Iridium species the pass cage complex we were trying to discuss.

We need to have a promoter or the initiator to start kick the reaction once we have 16 electron complex converted to a 17 electron complex in presence of an initiator the initiator will bind with the Iridium complex in this case gaskin species and thereby the next radical reaction will start off once the radical reaction is start off you do not need the initiator anymore the radical generated from the reaction will take care of the progression of the reaction okay. So that is what is the radical mechanism of course if you try to look at the radical mechanism that standard characteristic for this reaction will follow as we are trying to discuss.

The radical scavenger you can add so radical scavenger will be able to stop the reaction we will not have a reproducible kinetics data and if the RX is having the choral Center the hilarity will be lost in the process, more importantly if it is a tertiary halide that will be reacting faster compared to the secondary halide that is once again proving that it is a radical mechanism if you it is a sn2 reaction you would expect the other way around that means the primary will be reacting faster than secondary the entire CD but for radical mechanism you will see that tertiary halide will be the fastest.

So that is all for the radical reactions or that is the conclusion for the oxidative addition reactions. to summarize oxidative addition, we have seen different types of oxidative addition over the last two classes, where we have seen oxidative addition by concerted mechanism, the RX and the metal interact in a concerted fashion, to give the SIS product and we have seen a number of examples for that, subsequently we have discussed the SN2 mechanism as much as you have seen in the organic reaction isn’t too similar to that organic reaction.

In case of concerted mechanism, if the RX is having chorale centre, will have the chorale centre remained intact for SN2 mechanism will have inversion in configuration, and for radical mechanism will have basically the resinization of the chorale centre. So essentially what we are seeing increasingly is the mechanism will depend on the type of our X, we are having that is most crucial, what type of RX we are having? That will kind of determine the course of the reaction, and of course the metal species that is involved in the oxidative addition will also be crucial, to judging which mechanism is prevalent.

So it is a combination of the metal species and the RX that will determine which mechanism will be followed. if you see usually if you see that RX, R and X after oxidative addition if it is trans to each other, then most likely it is SN2 or radical mechanism that is involved in. it if R X is stitch to each other then most likely it is a concerted mechanism that is involved.

And there are number of examples, that is there where we can see you know the oxidative addition is this key step, starting from let us say palladium complex we have seen a number of reactions, even 2010 Nobel Prize is given on the cross coupling reaction, where we have heck reaction, and aryl halide, let us say you know penile bromide, or promo benzene basically.

Reacting with a play Diem 0 species to give you palladium 2 plus oxidation state, and the aryl the and the iodide or halide is also interacting with the metal spaces, so play Diem 0 interacting with final iodide let us say or iodobenzene or bromobenzene to give you palladium aryl or palladium phenyl and the halide species, so both final and the halides are attached with the palladium species, this is the first oxidative addition intermediate species then for the heck reaction will see we will discuss that olefin will interact with the palladium and then insertion of that aryl intermediate will involve to give you the final product.

This is one of the reaction that got Nobel prize in 2010, another famous reaction is the Suzuki reaction which got the Nobel Prize again share Nobel Prize in 2010 with heck, there we do see that you know it's again a oxidative addition that is happening over there, the first step is the oxidative addition and then oxidative addition into, let us say a different aryl halide or alkenyl halide or even alkyl halide and subsequently we will see that oxidative addition intermediate will undergo trans metallation and then reductive elimination to form the product.

Another reaction that actually also shared the Nobel Prize is the Negishi reaction again all these reaction 2010 got the Nobel Prize combined, so heck legacy and Suzuki reaction these are of very fundamental huge of the organometallic intermediate, organometallic principle that we will be discussing shortly in the classes. So in the next class we'll discuss the reductive elimination, reductive elimination as one can imagine is the opposite of oxidative addition.

Whatever is happening in the oxidative addition is the increase of electron count by 2, so 16 electron complex is undergoing a product formation where 18 electron species is formed, now for reductive elimination just to tell, if you take the 18 electron species it will give you the16 electron species. It is almost the microscopic reversible intermediate so, till then for the next class we will see for the reductive elimination in the next class keep on studying and if you have any queries please let us know. Thank you very much

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IIT Bombay

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