Industrial Inorganic Chemistry
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Lecture – 09
Chloramine and Hydroxylamine

Hello good morning everybody. So, we were talking about some important nitrogen compounds which are interestedly important. And, one such compound we have seen that is Chloramine.

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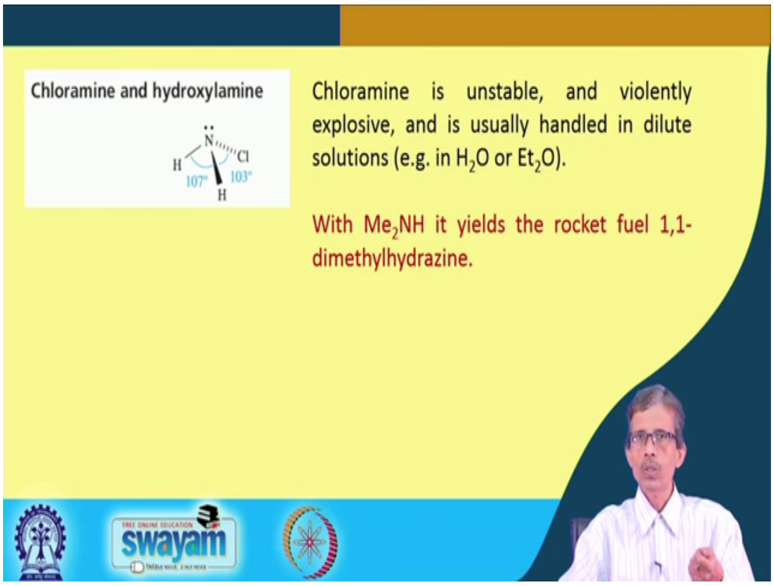

And, as we see that the chloramine structure is this one not the hydroxylamine because the hydroxylamine we will talk also along with this. So, if we consider a typical 3 nitrogen hydrogen bond bearing ammonia; that means, your NH 3, that we all know very well, that from ammonia if we are able to substitute; one of the NH bond by NCl bond we will get the compound which is known as the chloramine.

Because, this is a very important compound, where we have already functionalized like our typical organic chemistry thing, that we have substituted this NH bond by NCl bond and as we all know, that this particular NCl bond will be very much reactive in nature. And, if we go for these all these reactions already we have seen that the production of hydrazine also, we will also can go through this particular pathway; that means, producing chloramine; that means, substituting one of the NH bond by NCl and then again further you can react it with the free ammonia molecule.

So, how good this particular molecule is that we should know particularly that particular compound; that means, chloramine which is a very unstable compound; that means, at a very low temperature and in a very dilute condition, because whenever some compound is explosive in nature. We should go for stabilizing that particular compound, it can also be a gaseous one like your hydrazine, what we have seen that hydrogen can be very well stored in a dilute solution and in presence of water, that is why we get the hydrogen hydrate.

Similarly, this chloramine is also a unstable compound because is highly reactive why we consider some compound as unstable, because it is highly reactive also. So, when we consider that high reaction or high level of reactivity of that particular compound, we can consider that it can immediately react with moisture, air or any other readily available chemical reagent what we all know, that from atmosphere it can react with some of the gaseous molecules. Similarly, if the compound is present in a solution then it can be very much reactive with the water as well as some other species, which may or may not present in the water medium.

So, it is a violently explosive compound. So, is usually handled therefore, in a dilute solutions; that means, a dilute solutions of this chloramine in water or in ether is available as a chemical reagent also. So, laboratory available chemical reagents like these; that means, the chloramine can also be available in terms of its solution in water, or in terms of its solution in ether, which can be bottled in a nicer way; that means, diethyl ether containing chloramine or the corresponding hydrate of it is chloramine.

And, in terms of it is reactivity pattern when this particular compound; that means, NH 2 Cl the reaction of NH 2 Cl will be very much interesting. Particularly for the production of 1 1 dimethyl hydrazine, which is well known that it can go for a controlled oxidation process in presence of air or presence of excess supply of O 2; that means, 0 2; that means, oxygen from that cylinder as a gas.

So, which can be very quickly burnt away, but the substitution from one end of the hydrazine; hydrazine is your NH 2 NH 2. So, substitution from one end basically; that means, that particular end; that means, the 1 NH 2 N is getting stabilized by making it as

N M e 2. So, if we can go for stabilizing this particular part by converting NH 2 species as N M e 2 it is little bit stabilized compared to your free hydrazine.

So, it can be used for controlled burning process that mean can be used for a fuel because controlled burning of any material give us it is character as a fuel. So, this can be very easily prepared, how we can prepare because previously we have seen that hydrazine we can prepare from the reaction of chloramine with ammonia; that means, NH 2 Cl plus NH 3 is a very simple reaction giving rise to your hydrazine plus HCl.

Similarly, if we go for a reaction with this particular amine is the organic amine now, when we go for a typical substitution of ammonia molecule by methyl 1 methyl which is your methyl amine. And, 2 of the NH groups we can substitute by 2 of these methyl groups giving you the corresponding dimethyl amine compound. So, this dimethyl amine compound if it is allowed to react with your chloramine, it can give you the corresponding 1 1 dimethyl hydrazine molecule that hydrazine molecule is a very useful rocket fuel also. And, it definitely since we are using is a rocket fuel it should be a costlier one.

So, production of this particular molecule will be interesting one only thing that how cheaply we can produce and how safely we can produce. Because, it had some hazard also the related hazard related to this particular molecule making is also should be considered. So, that way if we go from this particular NH 3 to NH 2 Cl; now, if we substitute one of that same NH function by NO H; that means, we are getting NH 2 O H, which we all know from our school days that is known as your hydroxylamine.

Because, hydroxylamine is a very useful compound for our laboratory purpose also, because it can give you a very useful reaction with that of your aldehyde or ketone forming the corresponding oximes. And, oximes also industrially important that we will see so, it can be considered this hydroxylamine can be considered as a very useful starting material for some industrial purpose like, that of our making some oximes and those oximes can be industrially also important that we will see.

So, now how, we can get this particular hydroxylamine?

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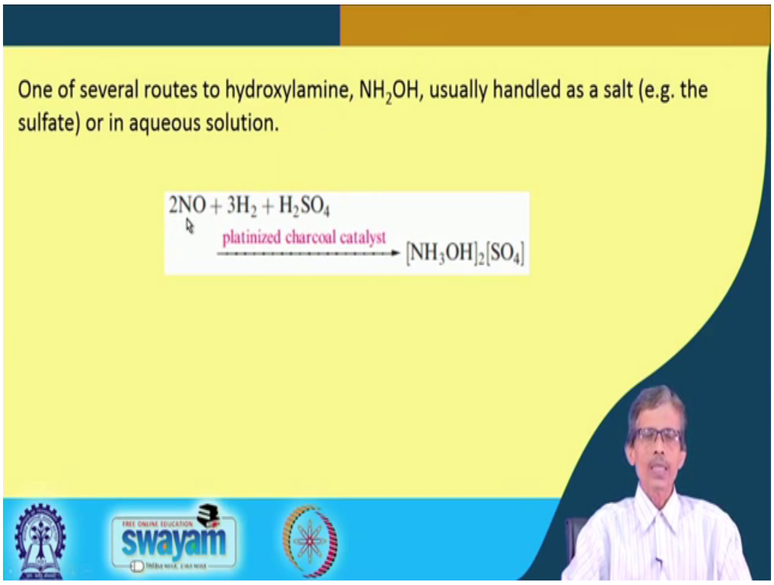

So, this hydroxylamine what we will get basically is our thing that how we can prepare this NH2 OH. So, different production routes or different synthetic routes or different preparative routes are available for hydroxylamine. And, it can be handled as salts because again the consideration of your stabilization like your hydrogen, we considered hydrogen as the corresponding hydrogen hydrate.

Similarly, since this is a basic compound, it can be stabilized at a corresponding sulfate salt; that means, it is protonated and then it is corresponding anion if it is available as sulfate we get the hydrogen sulfate. Like hydroxylamine hydrochloride or hydroxylamine bisulfate similar to these all these and in aqueous solution to keep yourself away from it is reactivity; that means, it is dangerous attitude for this particular reaction.

So, one such reaction if we consider that if we take the very basic reaction instead of taking ammonia. Now, we can go for NO the nitric oxide because there are large number of oxides and we are not able to cover all these in detail in this particular class. Because, the intended course is huge one, because we will only go for some of the very interesting and very useful molecules only; so, nitrogen oxide preparation is a very again a schooldays preparative stuff, but industrially these are also important.

So, how we immediately go for that particular conversion? So, we can have these; that means, NO we have only addition of hydrogen only. What is the difference between these NO and NH 2? This is you can compare by addition of 3 hydrogen atoms. So, those hydrogen atoms if we can transfer to the nitric oxide molecule NO in plus 2 oxidation state of nitrogen, we get the corresponding hydroxylamine sulfate. So, hydroxylamine sulfate the formula of that particular compound is NH 3 OH whole 2 S O 4.

So, this particular hydroxyl amine sulfate can also be obtained for this particular hydrogenation reaction, if we consider hydrogenation reaction in presence of sulfuric acid which is providing the corresponding sulfate anion as the corresponding anion of that particular salt which can be isolated from the reaction medium from the reactor whatever it is. So, this particular hydrogenation reaction is not a straight cut hydrogenation reaction and it should be also in catalytic in nature.

So, if we can have the catalytic nature of this particular compound, we can go for some optimization of the temperature, optimization of your pressure for the typical use of your hydrogen this hydrogen is not an typical one atmospheric pressure, it should be pressurized from the cylinder or some other source also. So, if we can have so, platinum would be therefore, a good catalyst if we just simply this reaction scheme, that tells us that platinum will be a useful catalyst, but we are taking it as a platinum charcoal catalyst. What is that that you can have a base; that means, the charcoal powder or charcoal dust if we get it?

So, you can have the corresponding carbon surface. Nowadays, we consider as the carbon particle that different types of different carbon particles, the nanoparticles of carbons are also nowadays available in the market, before that we can have the simple charcoal powder. So, charcoal powder you can have and on the charcoal bed if we can have the platinum in the metallic form not any other form the platinum metal itself.

So, if your charcoal surface is completely covered with the platinum metal powder, we can consider it as a platinized charcoal catalyst and that platinized charcoal, because we are increasing the corresponding surface area of that particular platinum. And, that platinum will be responsible for corresponding hydride formation or in some weak form the hydrogen atom absorption.

So, hydrogen atom absorption or the corresponding hydride formation on the platinum will be useful for transferring that hydrogen atoms to your NO molecule. And, that transfer of hydrogen we consider at is as a typical hydrogenation process. And, that hydrogenation process will be useful for making or converting your nitric oxide molecule to NH 2 OH your hydroxyl amine.

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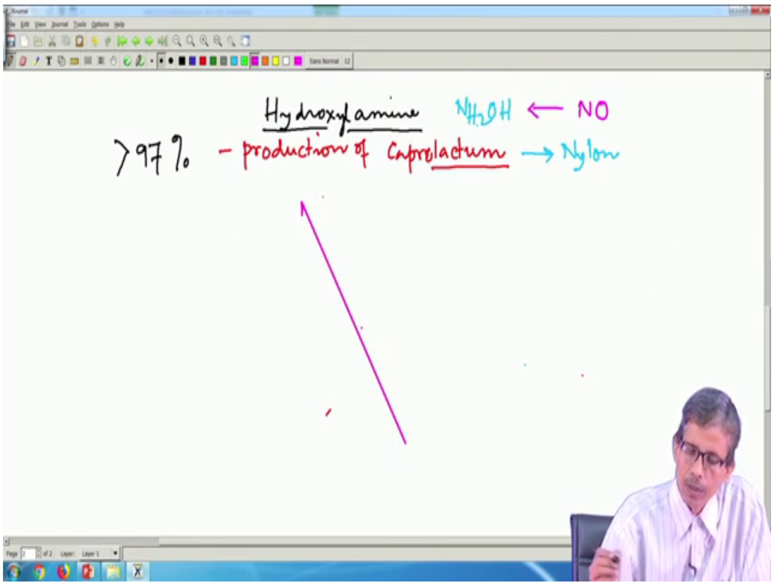

So, this hydroxyl amine and if we are consuming a large amount see 95 percent of your production; that means, industrial production of hydroxylamine how good it is for the different purposes. So, more than 97 percent of it is production is utilized for the production of Caprolactum is the industrially important compound that we also see for making the nylon or polythene making thing; that means, it has a typical Lactum ring. So, as I told you just now that you can have oxime from hydroxylamine reacting with your ketone or aldehyde. So, that particular one if we can convert it to a typical caprolactum and that caprolactum can be useful for making your nylon.

So, this particular course is therefore, very important in understanding that, if I ask you that how nylon is dependent on industrial in organic chemistry. You can have a very simple answer from there I know now that how the production of nylon is dependent on the caprolactum production. And, that caprolactum production is highly dependent on the availability which is cheaply available and readily available, it is cost should not be very high to that of our production of hydroxylamine.

So, making that hydroxylamine; that means, your NH 2 OH is important therefore, is a typical inorganic compound, which is directly related for to the production of your nylon. So, we can have the different processes; that means, just now in a previous way case we have seen that we can use NO for hydrogenation and the production of your hydroxylamine. How you get NO? Because, NO is not a typical compound which we get from your atmosphere, only thing we know that we can get a nitrogen based compound is your typical dinitrogen molecule N 2 molecule. And, we have seen that during the production of your ammonia if we can go for your typical reduction of your ammonia by hydrogenation reaction we get plenty of your ammonia in your hand for making your urea also.

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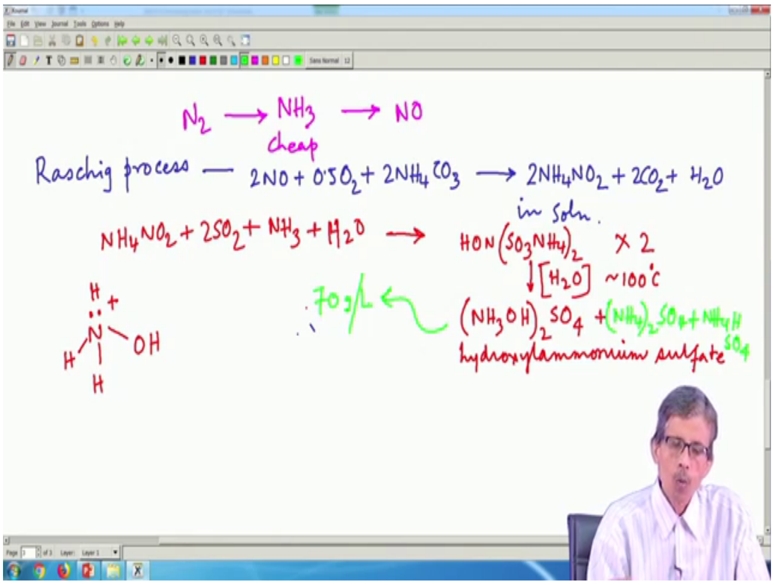

So, that should be your clue that if we can have available NH 3 and which is also that NH 3, if we can have and if we are able to convert that NH 3 to N O; that means, the typical oxidation process which this NH 3 should be cheap in your hand and which we all know can be produced from your dinitrogen which is available in air. So, this NO the production of this NO that this is the corresponding one for your production of hydroxylamine, one such process is known as raschig process, that process making our ammonia to nitric oxide conversion and then we have in our hand the NO.

So, 2 molecules of NO if we oxidize it further by 0.5 molar of your O 2; that means, oxidation with oxygen in presence of ammonium carbonate. So, if we write this simple reaction what we can see that NO is there and NO is further getting oxidized forming something in presence of that ammonia and giving you that correspond ignited ion formation; that means, we will be getting ammonium nitrite. So, typical ammonium nitrate formation in this is in solution. So, ammonium nitrate will be formed in solution and that ammonium nitrite along with 2 C O 2 and H 2 O.

So, we are not getting typically the hydroxyl amine at that particular point, but we are having now ammonium nitrite. So, this ammonium nitrate which is formed in solution can be utilized for the corresponding conversion, where we use it this ammonium nitrite; that means, your NH 4 NO 2 is allowed to react with sulfur dioxide now. Because, we are having some intention that we can have this sulfur dioxide in our hand and that sulfur dioxide with ammonia and water; so, you can have this with that of your water.

So, this we are giving that we are getting something which is related to that of your ammonia; that means hydroxyl amine. And, sulfur dioxide is supplied that we can have to have the corresponding sulfate salt. So, what do we get as the intermediate one intermediate one is forming as H O N and SO 3 NH 4 type of thing? So, this particular production is directly related to the reaction of your nitrite your sulfur dioxide and ammonia. So, this is our intermediate now. And, this particular intermediate if we can go; that means, the formal reaction with these 2 molecule of this can be hydrolyzed so, hydrolyzed in water.

So, is basically a water hydrolysis as we write water in square bracket at about 100 degree centigrade? So, at about hundred degree centigrade what we can have this particular one getting hydrolyzed giving you NH 3 OH twice of this, because sulfate is a having a charge of 2 negative charge. So, what we are having. Now, therefore, that we already seen that this is your thing this is your hydroxylamine. So, when this particular one proton is getting this is getting potronated. So, we get NH 3 O H.

So, if we have this NH this will have the charge; that means, if it is further protonated like ammonia gives the ammonium ion. So, hydroxylamine give you the corresponding hydroxyl ammonium ion. So, this is your hydroxyl ammonium sulfate hydroxyl ammonium sulfate what we can produce in our hand. Along with that we can have also ammonium sulfate and ammonium hydrogen sulfate is S O 4. So, these are the side products that we should be also be carefully controlled such that we get a production of these having a concentration of 70 gram per liter.

So, we will be able to produce a 70 gram per liter of that compound from this particular very simple reaction. So, this particular one is a very important one where we get these because this particular pathway for the formation of this one; that means, the formation of this oxidation and that oxidation giving us the corresponding nitric oxide.

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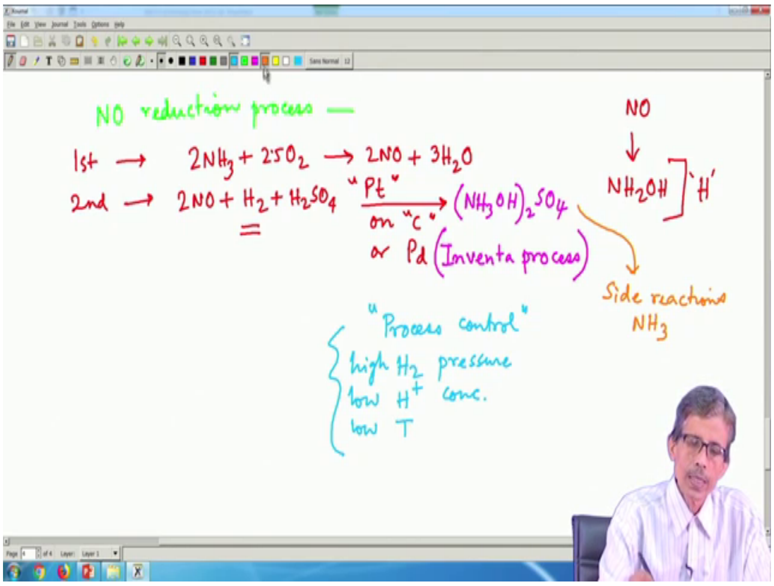

So, if we can go also a related process which is the process number 2, which is a NO reduction process, NO reduction process; what we get is therefore, that in the first step what we can have ammonia again can be oxidized by 2.5 O 2 giving 2 NO these reactions are mostly balanced, whenever you try to write any reaction. You try to balance it such that you can have the corresponding idea in your mind, that how you can go for the atom balance such as your atom economy; that means, whatever side product is forming is here you see that only water is forming.

So, this is your first step of reaction. So, first step is giving you NO in your hand and in the second step what will you do as we have seen that it is a NO reduction and we have already seen that how we convert no 2 NH 2 OH, that I told you from the very beginning, that you have to add several number of hydrogens on it hydrogen atoms addition of hydrogen so, 3; hydrogen atoms if you add on NO we will get NH 2 OH. There is a very simple reaction for forget about your corresponding configuration how the bonds are there, how many bonds are there, and what are those different bonds you can have?

So, the this particular NO so, this NO basically then is react with that of your hydrogen; that means, their hydrogen gas in presence of your sulfuric acid, because all the time we are using this sulfuric acid, because we are trying to get is or isolated as the corresponding sulfate salt. So, we will take the help of a catalyst for this hydrogenation reaction utilizing hydrogen as the elemental hydrogen or hydrogen gas. So, the platinum as the catalyst earlier we have seen that the platonized charcoal bed is also useful. So, this particular case the platinum again this platinum on C that means; on charcoal bed or sometimes we use the platinum as the corresponding one for the formation of these and that gives rise to a different process, which is known industrially also Inventa process.

So, you see that one industrial people or the industry is utilizing one particular catalyst and the second or the third one is changing only the catalyst, but they are simply using the same process of reactions, but they patent it they go for it is corresponding copyright for that particular one because the palladium catalyst when we can use it instead of your platinum (Refer Time: 24:06) it can have certain advantages. Particularly the it is cost effectiveness as a low price you can produce the material or the time consumed for their particular reaction is also less and the corresponding yield for the reaction can also be higher.

So, modification in terms of the catalyst which is a very huge area for the development of the different catalyst for this industrial processes are still very interesting area of research and development. So, if we just simply change one particular catalyst to other you can change the typical process and you can go for the corresponding changing or utilization of this particular process for making that particular molecule. So, this particular one giving you that particular hydroxyl amine sulfate. So, you have NH 3 OH whole 2 S O 4 this hydroxylamine sulfate and there we can have certain side reactions also.

So, this can have certain side reactions such as we should also be very much careful that you can have ammonia production, because we are talking about the reduction of NO. So, you can have the ammonia production over there.

So, this particular thing can be taken care of through a particular process we call that chemical engineers to basically call it as the process control. So, we should go for process control how you can change the particular chemical process for the production of this particular molecule. So, we can have that hydrogen what we are taking; that means the use of your hydrogen at a particular pressure.

So, if you use a high hydrogen pressure you can optimize that you can increase the corresponding rate of production or corresponding yield of that particular production of that material. And, the low hydrogen ion concentration it can have also thermodynamic implications, because the heat of the reactions and all these things if we can go for detailed calculations of these things. So, these are the parameters standard parameters, what can come out from this particular process control for this particular reaction and; obviously, the low temperature.

So, these 3 things if we can control we can utilize a very good amount of production of your corresponding hydroxyl ammonium sulfate. Next, we will just see that how we can utilize the third step the third step is the nitrate reduction process.

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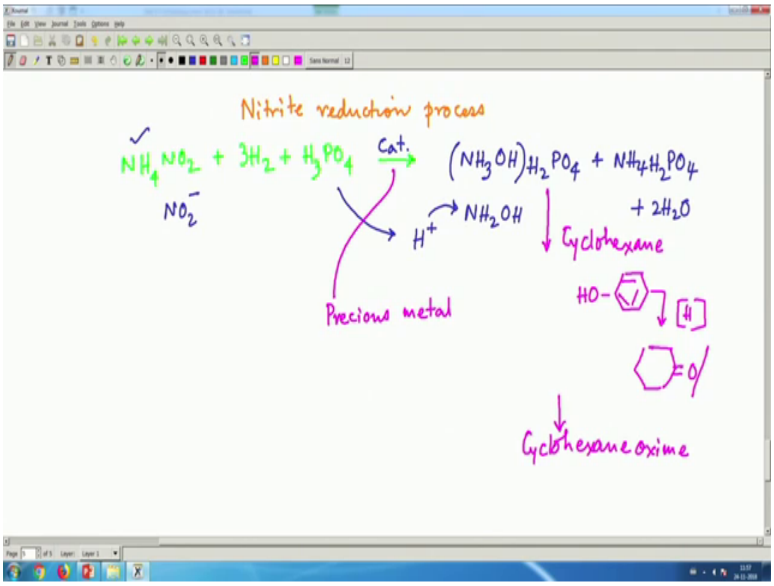

So, as in the first case we have seen that we can use that corresponding formation of the nitrate and ammonium nitrite formation we have seen. So, directly if we take that particular nitrate because it is readily available, sometimes it is a naturally occurring material the chilli, salt, (Refer Time: 27:17) we all know the sodium nitrate or sodium nitrite, sodium nitrate or nitrite if you can have in your hand.

So, nitrate reduction process can be a very useful process for the production of your hydroxylamine. So, this particular one starting from your thing that your ammonium nitrite. If, we take which should be reduced by hydrogen, and in presence of other inorganic industrial acid, or mineral acid is your phosphoric acid not sulfuric acid now.

So, what we get now is that the formation of these again you can utilize a catalyst we can consider that, what sort of catalyst we can use. So, what do you get there for that the NO 2 now instead of NO now NO 2 minus will be reduced by elemental hydrogen or hydrogen gas.

So, this will directly be converted to NH 3 OH; that means, your NO 2 minus is converted to NH 2 OH which is further protonated from the acid of the phosphoric acid giving rise to NH 3 OH plus. So, this NH 3 OH plus is a cation giving the corresponding anionic part of this acid where you fail if you lose of one of these h plus. So, we will remain with H 2 P O4. So, this particular salt you can have and that particular salt when you can utilize for this particular one you can get it as instead of sulfate salt you get it as a corresponding phosphate salt.

So, hydroxylamine preparation can also be controlled; that means, through that particular process and again is a industrially important process, and that industrially important process what we get is that your these thing that can be stabilized in presence of your phosphate. As the corresponding mineral acid source and that phosphate can be utilized along with your some other compounds ammonium, what other we can get if you just go for typically look at these thing that typical balance of these thing, that you have this ammonium ions group available.

So, ammonium dihydrogen phosphate H 2 PO 4 is also forming plus water molecules. So, this particular one so, we can have this particular catalyst in your hand. So, again this catalyst is your corresponding metal based catalyst and not all other metal ions, but some precious metal ion catalyst or metal catalyst not ion precious metal catalyst can be utilized. So, directly the industry people they are very happy that if we can make these without going for it is isolation, because if you go for isolation you have to think of it is packaging and selling in the market, but if this can be utilized for some other production of other material, people can utilize this particular one in situ whatever is formed.

So, in situ proper production of this particular phosphate salt appear hydroxylamine can be utilized by through trapping of cyclohexane. So, this cyclohexane can be utilized as we have seen that you can have the cyclohexane as we all know, that cyclohexane is this one is this is the benzene ring, this is the corresponding benzene one, and it is OH is the phenol. So, this if we can reduce it to this cyclohexane you get.

So, this cyclohexane can be utilized for giving you the corresponding oxime of this particular co function. So, we get cyclohexane oxime, which is again we will see that for the production of nylon the cyclohexane molecule will be very useful that we will see afterwards. So, we have seen in this particular class that how we can get this important compound like hydroxylamine. And, this hydroxylamine how industrially we can prepare and how good they are for making some other value added molecule like cyclohexane oxime ok.

Thank you very much.