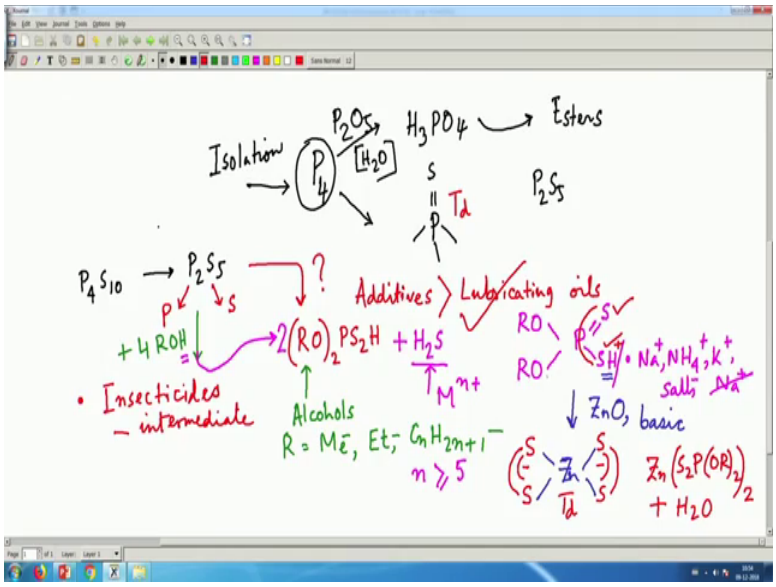
Industrial Inorganic Chemistry
Prof. Debashis Ray
Department of Chemistry
Indian Institute of Technology, Kharagpur

Lecture – 15
P4S10 and Phosphide Preparation

Hello, good morning everybody. Today we will just continue the last part of the phosphorus bearing molecules which are very important industrially.

(Refer Slide Time: 00:37)



So, we have seen that if we can have simple for us as P 4 and that particular P 4 how we can utilize? Because, we have already seen that this particular process where we get P 4 molecules whether you get a lead phosphorus or white phosphorus or some kind of black phosphorus. So, the first part was basically your isolation.

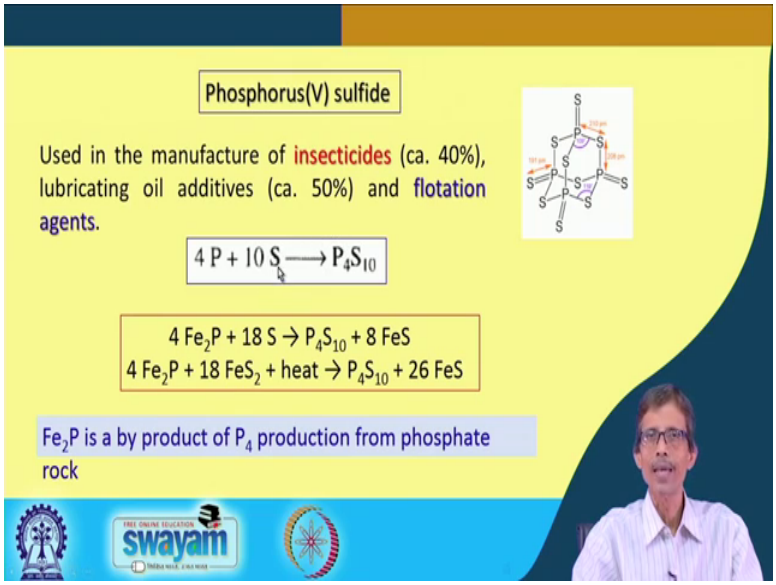
And then how we can convert this particular molecule to some other also industrially important molecules such as simple making of your phosphoric acid. So, today we will just see how we can introduce something related to some bond which is nothing but a phosphorus sulfur bond, because the presence of phosphorus is very important industrially as well as pharmaceutically. So, if we can have some more connectivity from phosphorus to sulfur we can get some more interesting molecule and which we can produce industrially quite easily. So, here also basically this particular conversion along

with these goes via the formation of P 2 O 5; that means, is a very simple process of oxidation.

That if we have elemental phosphorus in our hand we can oxidize to some kind of oxidized form of it and the highest level of oxidation beyond your P 2 O 3 molecule we get P 2 O 5; that means, phosphorus in the plus 5 oxidation state. That means, is the pentavalent phosphorus is present giving you P 2 O 4 and this particular P 2 O 4 when react with or absorption of water molecule giving you the corresponding phosphoric acid molecule.

So, similarly now we will see that whether it is possible from same part; that means, whether we get it from a particular part which will have a phosphorus sulfur bond. That means, corresponding analog as compound which is your P 2 S 5 that can also very important molecule, because we know that these can also give you the different esters; esters of the corresponding acid. So, we will see now that how we can get these particular one as the corresponding formation of P 2 S 5.

(Refer Slide Time: 03:11)



How we get that? So, you have the corresponding phosphorus 5 sulfide we consider it as the corresponding one as the phosphorus 5 sulfide. And in terms of its typical inorganic chemistry the textbook inorganic chemistry what tells us it is a very interesting molecule, because the shape of the molecule is also very much industry from your typical inorganic chemistry point of view it has no relationship with that of your production, industrial

production, its application and the uses. But we should know how this particular process of making this molecule is going. That means, as I told you just now that if you have phosphorus which can be oxidized to P 2 O 5. That means, typical oxidation process is taking place.

And where the elemental phosphorus which is also a P 4 molecule and having a tetrahedral shape; that means, the 4 phosphorus atom are in a space connected through some connectivity link; that means, phosphorus link if we come to consider it and the geometry of the overall molecule is a tetrahedral molecule. So, during the oxidation what we have seen that it has a similar structure that is P 2 S 5. If we start simply from the structure which tells us immediately that; whether we can correlate it with that of our P 2 O 5 or the dimeric form of it which is also the P 4 O 10.

So, in this particular molecule which is again the still 4 phosphorus centers are still present and we had this particular structure; where 2 types of phosphorus sulfur linkages were present and that will see afterward that how we can utilize it some useful conversion.

So, we have the sulfur as a sulfide ions as the bridging groups and some of them are the terminals. So, 4 on force phosphorus groups at the terminal sulfur we can consider it as a double bonded sulfur or a coordinate bond from phosphorous to sulfur. That means, if those sulfur centers are easily available we can transfer those centers from this molecule to some other molecule, where this particular network involving this particular sulfide bridges these are all sulfide bridges which are very useful to know also.

Because, in the different sorts of biological molecules where we have the ion and if we consider that iron sulfur protein molecules. We have this sort of linkages; that means, sulfur functioning as a sulfide ion and that sulfur ion is bridging to metal ions centered. Similarly for this main group element or the nonmetallic part of the phosphorous we have the same sulfur is present and which is bridging two phosphorus centers.

So, simplest way of writing this particular conversion is that P 4 or if we can at elevated temperature that is getting atomized. So, you can have the phosphorous atoms or you can write it as a P 4 simple P 4; P 4 is reacting with sulfur and those sulfur's are also coming from S 8 molecule because, the sulfur when we talk in terms of the corresponding sulfur

isolation of sulfur and industrially important sulfur production as the sulfur compounds when we talk in our next few classes will be considering sulfur.

So, there we will see how we can use this S as S 8. So, which is the molecular formula P is at the S 8. So, this basically giving you typical sulfide form as P 4 S 10 and it has a huge amount of uses. So, it is used in the manufacture of insecticides so, 40 percent of the production of this P 4 S 10 is utilized for making insecticides.

So, what are those insecticides basically? So, that can have definitely those are phosphorus bearing compounds as well as sulfur bearing compounds. So, if we have both these two together we will find there are a large number of applications and industrially those molecules are also interested in the huge demand in the market also. And from the business point of view also knowing this particular information that how you make very quickly, because always we have some intention that how cheaply or how we can produce all these at a very low cost.

Because most of these things are getting from the natural sources as the rock material the phosphate rocks or the phosphate rocks. What I told you in several cases that the naturally occurring mineral type of thing or ore type of thing the phosphate rocks are utilized for making phosphorus and that particular molecule if we are able to make it to some insecticides.

So, the procedures the processes will be very much helpful in understanding the value added molecules which are functioning as a typical insecticide. Similarly the lubricating oil additives; so, after 40 percent remaining 50 percent of the production of phosphorus 5 sulfide or we can consider also phosphorus penta sulfide. But it is the P 2 S 5 or P 4 S 10 is the lubricating oil additives and the remaining. That means, remaining 10 percent as the florescent agents.

So, these are the applications we will see also that how this lubricating oil additives can be prepared how whether we are able to use it directly from the P 4 S 10 molecule or we can have some other modifications that we will see. So, that information basically a challenging information to everybody that whether a phosphorus bearing compound, we are putting sulfur in it now that can be converted to a lubricating oil additive.

So, how we make it basically because I told you as that the typical phosphate rock you can utilize it as the phosphate rock and that phosphate rock and also be offset from the ferrous phosphide that Fe 2 P type of molecules these are all different types of solid state molecules and the molecular formula is basically a Fe 2 P.

So, like that of a burning of this particular phosphorus in presence of elemental sulfur we get this particular molecule similarly the ferrous phosphide or Fe 2 P. So, this pyrite we consider it also that pyrite ore. So, Fe 2 P when it is burnt in presence of 18 sulfur so, 4 of these will be utilized to react with 18 sulfur giving us back to that P 4 S 10 molecule.

So, when we get this P 4 S 10 molecule as a byproduct we also produce something which is very useful also this ferrous sulfide simple ferrous sulfide molecule not that iron pyrite rock material or the mineral material, but we will be producing ferrous sulfide. So, while making this particular thing; that means, the P 4 S 10 we are also producing FeS the ferrous sulfide as the byproduct.

So, if we are very much careful enough that whatever amount of iron present in the molecule while burning with sulfur we convert it to ferrous sulfide as well as P 4 S 10. So, sulfur is reacting both way with iron centers and with the sulfur centers giving you that ferrous sulfide and this phosphorus the remaining phosphorus present in that particular ore material is reacting then with that of your sulfide or sulfides giving you that P 4 S 10.

So, the procedure of making this particular P 4 S 10 molecule will be cheaper and cheaper if we can take care of the byproduct molecule or the byproduct compound what is forming over here. So, if we can take also; that means the production of FeS if we consider the price of FeS also the ferrous sulfide cost also. And if we can purify this particular ferrous sulfide and if we can use that particular ferrous sulfide very easily. Then we can subtract the price which will be required for the production of P 4 S 10 minus the production of this particular molecule which will also be useful. Because, we know that from our laboratory days, from our school days or college days; we know that these ferrous sulfide which are available in the market as the typical sticks ferrous sulfide sticks which are used for the production of H 2 S the hydrogen sulfide.

Because, we use keep separators and in the keep separators the bottom part of the keep apparatus we put this ferrous sulfide sticks. And then we put sulfuric acid to produce H 2

S gas the hydrogen sulfide gas as and when required by opening up the stopcock of the keeps apparatus. So, this is a very useful molecule because whenever you require this particular gas in a very small amount because is a poisonous gas basically it can pollute the environment also.

But you should be careful enough while handling this in the laboratory fume hole that your stopcock is in your hand. And you open that stopcock your ferrous sulfide will be reacting with sulfuric acid producing H 2 S and the chamber it has 3 chambers in the keeps apparatus and one of the chamber is filled with that particular gas and we are taking away this amount of gas. So, when the gas pressure is high it is just detaching that sulfuric acid level from the ferrous sulfide and the production of H 2 S is stopped.

So, we are not producing the excess amount of H 2 S when it is not required. So, this ferrous sulfide production so, always we should think of about the corresponding production of the byproducts. So, typical reaction also the 4 of these will be reacting with this also this another step basically because this is the elemental sulfur step and if we can have this iron phosphide the pyrite ore with that of your another ore iron sulfide that FeS 2 ore. So, these are very cheaply available starting material the ore molecules or the ore materials.

So, ores if we can directly combine them and direct reaction of these two ores first is phosphide based ore another is sulfide based ore and if we heat it. So, definitely that temperature, the pressure of the reaction and the reactor is also important, but the interesting thing to know is that what we are handling is one is the iron phosphide and another is the iron sulfide to make some compound where you can have a the composition of phosphorous and sulfur.

So, we can take out both these together; that means, phosphorous from this ore and sulfur from this ore we can take out and we can produce P 4 S 10. And along with this also we still can produce ferrous sulfides. And those ferrous sulfides are useful again for making these sticks or you can make some powder or you can convert it directly to the ferrous sulfate or ferric sulfate or some alarm of the ferric sulfate or by preparation for the preparation of more salts. So, these are the basically avenues where you can utilize this not only the production of P 4 S 10, but also the production of FeS and which we get basically from your phosphate rock. So, what we will see now that this.

Particular process what we are talking about thus now we just moved here from this to your P 4 S 10 which is giving us P 2 S 5 and our intention is that we should have the lubricating oil additives. So, we will be going for making additives which is which additives? The lubricating machine lubricating we call common terminology the mobiles the mobile oils which are additives for the lubricating oils. And here you see that you have both phosphorus and you have sulfur. Now we get something which is a typical salt basically and that salt will be making as RO twice of this RO P S 2 H.

So, how we make it from this particular system so, you have RO and this RO if we can get it from alcohols. So, large number of alcohols we can use it from there; that means, if your R can be methanol or methyl alcohol it can be ethanol or ethyl alcohol or a very long chain alcohol such as some number of n values. So, CnH 2 n plus 1 that alkenes functions ethyl methyl and long chain alcohol functions.

So, this particular P 2 S 5 or other P 4 S 10 will be highly reactive in nature. So, if we just simply react with plus 4 of your ROH the alcohol the 4 of that ROH giving us the corresponding species; that means, this will be formed. So, we can go there directly twice of this will be forming and what else will be forming, because if you have the hydrogen over here and that hydrogen will be taking care here only. So, one will be coming with this particular molecule.

And like that of your production of ferrous sulfide. Now we are also producing hydrogen sulfide. So, we should take care of this hydrogen sulfide when we go some reaction that hydrogen sulfide is forming as a byproduct and it should not be allowed to go in the environment such that it can have the corresponding responsibility that you are polluting the environment. So, we should have a closed chamber of thing and the gas whatever gas produced from there it should be taken out in a nozzle or any other mechanism that you can store it somewhere or you can utilize it some point making some other sulfide salts.

Because, if you put in water and if you add something; that means, if you add some metal ions over there the simplest way of making these Mn plus where n value is equal to 2; that means, you can have the nickel ion, you can have the copper ion, you can have the cadmium ions over here.

So, a water sample containing those ions those by bivalent ions can react with this H 2 S giving you the corresponding metallic sulfides. So, what about this particular one so, this

particular one is therefore, what is this how we write from here this molecule basically is giving now is a P double bonded S because we are making it from P 2 S 5. So, P double bonded S is there and another group is SH and we have two RO groups. So, the modification is such that we are moving from your P 4 P 4 to your P 2 S 5 or P 4 S 10 then we are putting oxygen over here from the alcohol. So, these particular molecule have phosphorus as sulfur as well as the oxygen and this H is there.

So, definitely we will be getting something where we get this particular S H as the corresponding sodium or ammonium salts or sometimes potassium salts if you use a some medium which is alkaline with respect to sodium hydroxide with respect to potassium hydroxide. So, you will also get as the potassium salt or the sodium salt sorry sodium salt is they are already. So, this salts basically the corresponding sodium salt ammonium salt or potassium salts will be soluble in water.

So, this particular one is not still your additive for your lubricating oil and this n value if we consider for this particular purpose, n value is greater than equal to 5, then these are very much useful in nature. So, this particular molecule when if we now allow it to react with directly with not any other metal ion salt, but zinc oxide because, zinc oxide when we will study the zinc oxide or zinc based materials it is also industrially important very much useful molecule. So, zinc oxide is a white powder material. So, it can also be used as a pent material.

So, when we will study zinc oxide. So, industrially it is very easy to make because this particular material when we go from zinc ore or zinc mineral making zinc oxide will be cheaper compared to the preparation of zinc sulfate or zinc chloride or zinc acetate. So, any metal ion salt will be costlier, then you are corresponding oxides carbonates or any other thing which is very close to your material which is present in your rock sample or the ore sample or the mineral sample. So, zinc carbonate we know which is known as calamine.

So, zinc carbonate if we heat that particular zinc carbonate if we allow to remove the carbon dioxide from there we will be remaining with zinc oxide. Zinc oxide is a very useful one along with your zinc carbonate which is the calamine one calamine main sources is it has a huge application for that. So, this particular zinc oxide since it is forming it in and we all know that this is basic in nature. So, either you use that this as

the corresponding salts. That means sodium salt or the potassium salt or the ammonium salt or you can use directly the corresponding acid because H is present already.

So, this is a sulfur based acid S minus H plus is there. So, we will get something where your life now is little bit complicated. Now what we are bringing? We are bringing zinc into the picture to make these additives the lubricating oil.

So, what will be getting here that this particular part as we all know that if we some donor groups from here, and if we had enough some donor groups from here they can function as a very good chelating agent like your free carboxylic acid or the carboxylates. So, when we have these carboxylates or the carboxylic acids like that of your free acid like acetic acid or formic acid or any other acid. So, how you get the corresponding one as from here your zinc oxide?

So, from zinc carbonate you have converted it to zinc oxide, now if I ask you how will you prepare zinc acetate from there. What will you do we will just simply react this zinc oxide or zinc carbonate with that of your acetic acid not your concentrated acetic acid.

But a little bit dilute one which can be your 1 is to 1 concentrated acetic acid and you put that particular carbonate or oxide. So, what will happen if you put powder sample of that your carbon dioxide effervescence you can see and the whole material will go into the solution as the corresponding zinc ions. And when you concentrate it on water bath in the laboratory if you concentrate it, and if you allow it for crystallization you will get the corresponding zinc as the corresponding zinc acetate in your hand.

So, like that if we have the acetate if we can recall the corresponding formula of acetate ion which is CH 3 COO minus similarly this is also P S S minus. So, like that of your carboxylate function that carboxylate function can bind a particular metal ion center at the point.

So, it is functioning as a bidentate ligand. So, this particular thing is also giving you the corresponding formation of a bidentate ligand. So, we will take this particular one; that means this sulfur and this sulfur. So, these two this sulfur and this sulfur will be your chelating part fine. So, we get this particular one is a very simple way similarly you have this and you have this, when you consider the charge in it because if you have this

removal of this H plus as the proton corresponding acid; if you make that corresponding salt also.

So, this H plus is going away remaining with this one minus charge on it. So, you have 1 charge over here for this part the whole part because, the negative charge the single negative charge will be delocalized over these two sulfur centers giving you a bidentate mono negative chelating ligand which can bind or which can hold the zinc center from its two positions.

So, if the zinc environment like that of our phosphorous environment what we are talking about earlier that this particular geometry the three dimensional geometry on this phosphorus is tetrahedral. Similarly this zinc will also be a tetrahedral one and the formula of the complex which we consider as the metal ion complex is nothing but your S 2 P OR whole 2 and 2 unit of these will be there and since hydrogen ions are going away taking this oxygen. So, you will have one molecule of H 2 O.

So, that is the formula of the complex now you get your additive for lubricating oils. So, this particular compound making of this particular compound for this is useful for your additive for making this lubricating oil. So, this compound; that means, this one along with this formation of the sodium and the potassium salt this can also be intermediate in manufacturing insecticides how? Because, this can be your intermediate your intermediate for making this.

So, how you consider it that that you have a insecticide. And if you want to make it definitely it will be phosphorous based compound and that phosphorous based compound along with that we are supplying sulfur. So, this particular function basically if we can have like your sulfate or the nitrate, you have the nitrogen along with our oxygen. Similarly that part of functional group. That means you have the phosphorous in your hand and you have the corresponding one as the corresponding sulfur in it and if you have a typical organic backbone.

So, that particular molecule can be useful for making these insecticides. So, what can be your starting material for this. So, definitely your P 2 S 5 will be the starting material for the inorganic chemical which will be useful for making your insecticide molecule.

So, stepwise what we are going we are going from one step to the further. So, the process is not so, difficult because when we go for the industrial processes you should know the corresponding one for your temperature, the raw materials and how we can utilize these things. But always we should keep in our mind that what reaction we are following. If we can have intention to make some phosphorous based compounds its fine then if we can go for oxidation based on oxygen or the sulfur we make the corresponding compound. And if we further allow it to some organic part because this is a very simple example where we are allowing to react this particular P 4 S 10 molecule with alcohol. So, any alcohol based molecules so, you can have a very long chain alcohol also.

So, that long chain alcohol can be modified with the introduction of this particular part; that means, if you can have two adjust and oxygen centers from the alcohol part you can clip it with that PH to minus unit. So, its basically clipping of this particular two part with that PH two unit giving some very useful molecule in your hand. So, that we will see also when we talk in terms of the corresponding sulfur compounds, how we can utilize the corresponding sulfate molecules or the sulfuric acid also putting the sulfate and at the long chain of the corresponding alcohols or any other organic molecule.

Thank you very much.