**Main Group Chemistry**
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Lecture – 34
Chemistry of Group 14 Elements

Welcome to MSB lecture series on main group chemistry. I had just initiated discussion on chemistry of group 14 elements, in my last lecture I started looking into the hydrides of group 14 elements. Let me continue from where I had stopped; methane having formula CH 4 is a odourless flammable gas and it is the simplest hydrocarbon and it is found in large natural underground deposits; from which it is extracted as natural gas and used as domestic and industrial fuel; how that happens? Essentially we burn methane.

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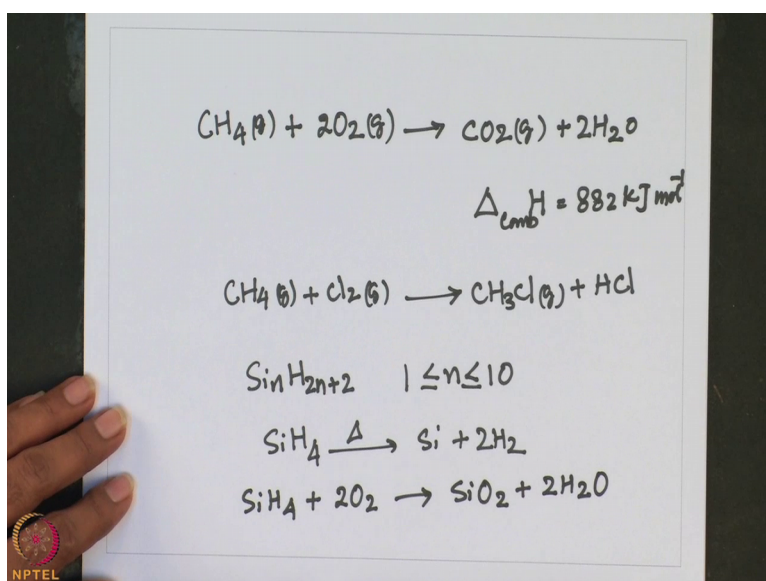
So, in this one if you look into combustion enthalpy that is equal to 882 kilo joules per mole. So, this indicates the exothermic nature of this reaction; apart from this combustion reaction methane is not very reactive. It is not hydrolysed by water and reacts with halogens only when exposed to ultraviolet radiation involving radical mechanism.

For example, if you take CH 4 gas and pass C l 2 gas under photochemical conditions or under ultraviolet radiation; it gives CH 3 C l with the formation of HCl. So, the alkanes up to butane for example, methane, ethane, propane, butane all are gasses and in fact,

butane has boiling point of 0.5 degree centigrade; are essentially gases those containing from 5 to 17 carbon atoms are liquid starting from pentane to 17 carbon atoms in a chain and the heavier hydrocarbons are essentially solids.

Silane in contrast S i; H 4 is formed when S i; C l 4 tetrachloro silane or tetrafluoro silane reacts with lithium aluminium hydride and is a source of pure silicon for semiconductor applications. Silanes having the composition n H 2; n plus 2 with straight or branched chains are known for 1. So; that means, and up to 10 silicon atoms in a chain are known similar to decane and compares the boiling points of the first five straight chain silanes with their hydrocarbon analogs.
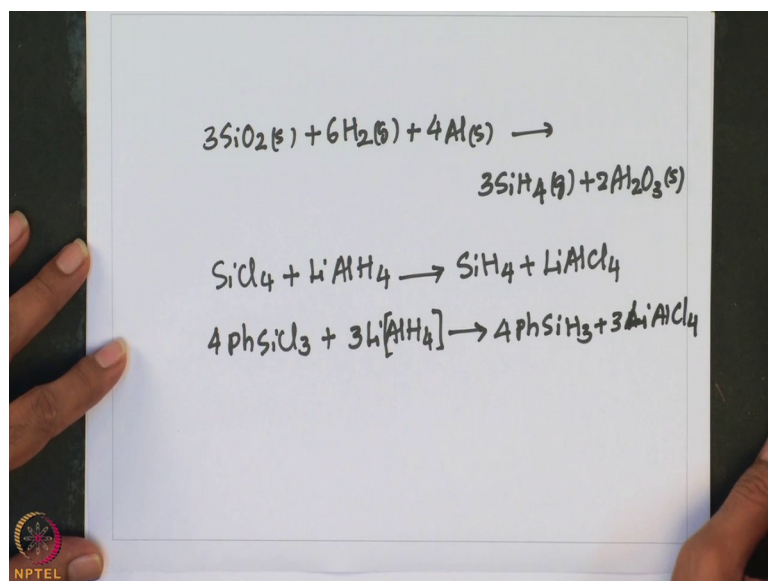
And silanes are exclusively inflammable in air; if we heat S i H 4, it gives S i plus 2 H 2 or if you take S i H 4 and if you pass oxygen gas. So, S i H 4 reacts with oxygen to form S i O 2 and formation of water will be there along with S i O 2. You can see a comparison of boiling points of silanes as well as hydrocarbons and it increases with increase in the number of atoms in the chain.

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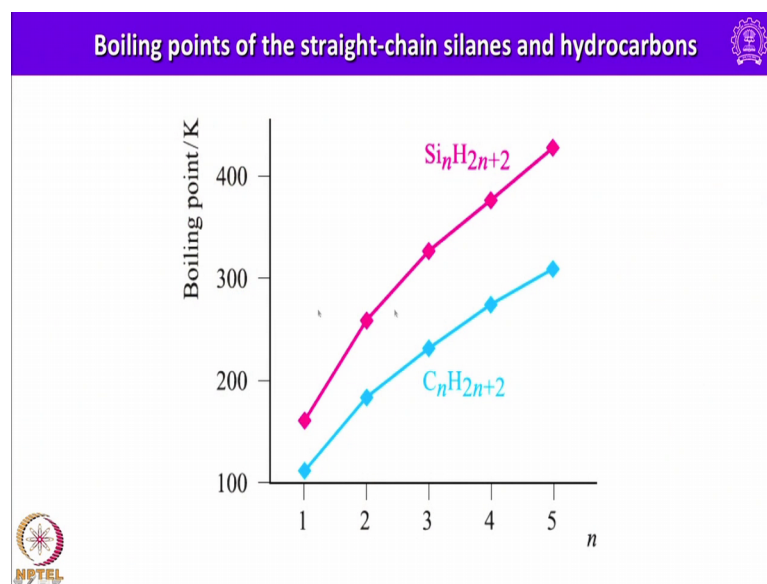
And same thing is to in case of silane as well and how to prepare silane; as I mentioned silane can be prepared started from tetrachloro silane or tetrafluoro silane. One can also start from silica or silicon dioxide; in that case you need high pressure of hydrogen in a molten salt mixture of sodium, chloride and aluminium chloride.

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$$3SiO_2(s) + 6H_2(g) + 4Al(s) \longrightarrow$$
$$3SiH_4(g) + 2Al_2O_3(s)$$

$$SiCl_4 + LiAlH_4 \longrightarrow SiH_4 + LiAlCl_4$$
$$4PhSiCl_3 + 3Li[AlH_4] \longrightarrow 4PhSiH_3 + 3LiAlCl_4$$

For example one can use S i O 2 it is solid; treat with high pressure of H 2, using a salt mixture of sodium chloride and aluminium chloride. So, this gives; so one can prepare this way; however, the general methods of preparation involves using chloro silanes. For example, S i C l 4 on treatment with lithium aluminium hydride; this lithium aluminium hydride is widely used to make a element to hydrogen bond in case of P block elements.

Or for example, one can take phenyl trichlorosilane; treat with lithium aluminium hydride. One can also write like this; this is how one can make the silance or organo silane compounds. The silence are much more reactive than alkanes and their stability decreases with increase in chain length. Silane it self for example, S i H 4 is spontaneously flammable in air; reacts violently with halogens and is hydrolysed on contact with water, very sensitive to moisture.

So, bonds between silicon and hydrogen are not readily hydrolysed in neutral water, but the reaction is very rapid in strong acid or in the presence of trace amount of base. Similarly alcoholysis is oxilerated by a catalytic amount of alcoxide for example S i H 4.

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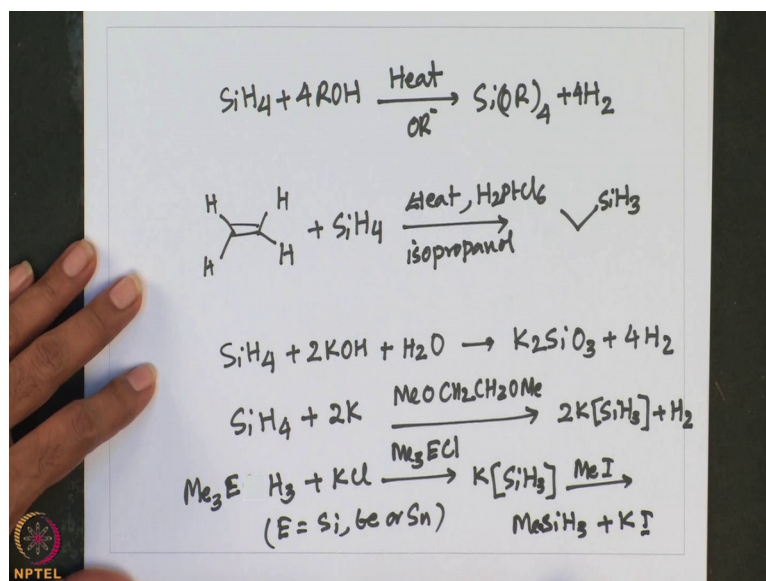
When it is treated with 4 equivalents of alcohol; on heating in presence of a small amount of alcoxide, so reaction gives alcoxy derivatives.

So, kinetic studies indicate that the reaction proceeds through a structure in which ore attacks the silicon atom while H 2 is being formed via a kind of H H hydrogen bond between hydretic and kotic H atoms. That means, essentially it is very similar to concentrate elimination process that we come across in the hydrogenation reactions using transmetal complexes.

Silicon analogue of hydroboration is called hydroselysation. So, the addition of S i H across multiple bonds of alkenes and alkynes is what hydroselysation means. This reaction is carried out at high temperature approximately around 300 degree centigrade under or one can carry out the same hydroselysation reaction and photochemical conditions.

In both industry and laboratory synthesis, radical path ways are essentially followed. In practice it is usually performed under for milder conditions, provided a metal complex is used as a catalyst. For example, let us consider a typical oliphene such as ethylene; when it is treated with S i H 4 in presence of a catalyst such as platonic acid and in isopropanal as a solvent it gives. So, this is essentially a hydroselylation reaction; addition across double bond.

Silane is a colourless gas which is insoluble in water, it can rapidly react with alkalis and form compounds of this type. Let me write here for example, it when it is treated with KOH plus H 2 O; it can give K 2 S i O 3 plus 4 H 2.

On the other hand, reaction of silane with alkali metal such as potassium; in ether, it gives it forms a compound of this type; a general reaction I am writing Me 3; E H 3; when it is treated with K C l in presence of Me 3 E C l; I will define what is E can be either silicon, germanium or tin.

Here also same thing; initially it gives this salt and this one on further treatment with methyl iodide; forms Me S i H 3 plus K I. So; that means, one can use conveniently this method to generate different types of alkyne silanes or alkyne germane or alkyle (Refer Time: 12:19) and S i H 3 C l is a very useful reagent; I will show you some reactions of S i H 3; C l chloro silane.

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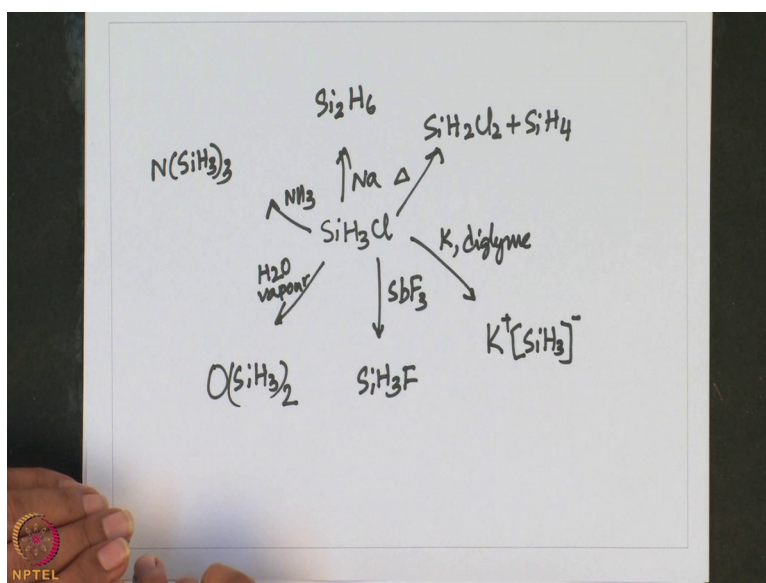
For example S i H 3 C l when it is simply heated; it gives S i H 2; C l 2 plus S i H 4. If it is treated with sodium, so then one can get S i 2; H 6 very similar; this compound is similar to ethane, if we take this one and treat with one equivalent of sodium; we get half equivalent of S i 2; H 6. If it is treated with ammonia it leads to the formation of S i H 3 three times.

And if it is treated with water vapour it gives; if it is treated with fluorinating agent such as S b F 3; it forms a fluorinated compound fluorosilane. Or as I mentioned earlier if it is treated with potassium in ether such as dyglime; it forms these are some of the important reactions of chlorosilane. And here we come across two important compounds here, let us look into the properties of these two compounds here.

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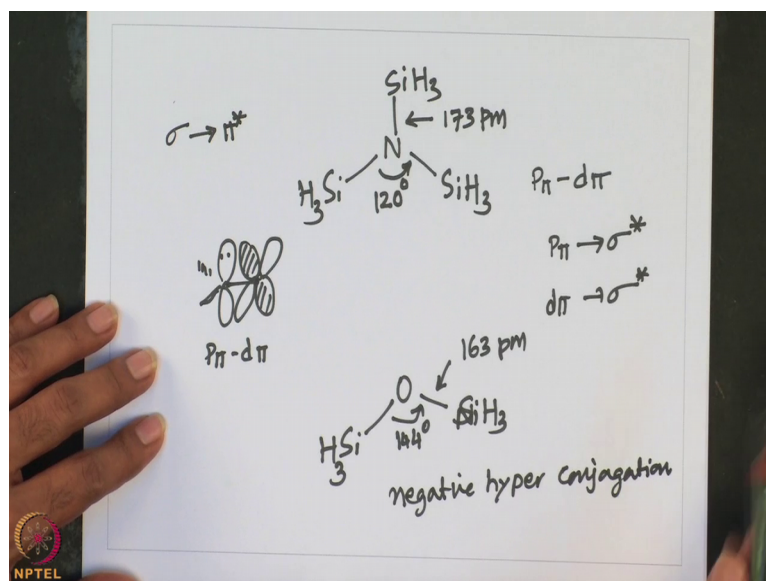
Let me write here the structure of these two compounds. So, if you just look into it here; please notice this one this angle is 120 degree and then this distance is N to silicon distance is 173 picometre. And here oxygen two silicon bond is little stronger; it is 163 picometre and whereas, this one is 144 degree.

So, what does it indicate? It indicates the geometry around nitrogen is not trigonal pyramidal as expected in case of amines like ammonia. Ammonia is trigonal pyramidal whereas, in case it is 120; that means, it indicates it does not have free lone pairs occupying one of the tetrahedral positions, to give a tetrahedral or pyramidal trigonal pyramidal shape. But here if it indicates it is planar; obviously, one can think that the lone pairs are nitrogen is delocalised over silicon atoms how that happens.

Whereas in this case; oxygen is tetrahedral and the angle is 144; so N S i 3 skeletal is planar and the N S i bond distance is 173 picometre. So, if you just look into some books they mentioned about the planarity using n pi d pi interaction; that means, silicon atom

has 3D orbitals; vacant 3D orbitals that are available for interaction with the 2 P orbital in which we have a lone pair on nitrogen.

So; that means, they talk about P pi d pi interaction and here this interaction they refer this way; if it is the P orbital and nitrogen and then we have something like this; silicon is there. So, silicon one of the d orbital it overlaps; so thus leading to the formation of a multiple bond. And this is where the lone pair of nitrogen is consumed; this what some book says, but this is not true.

So, the correct explanation for this one is; the lone pair of nitrogen is essentially given to the empty sigma star of S i H 3. This is very similar to what we come across in case of carbon monoxide or phosphene metal complexes; in case of carbon monoxide or metal carbonyls the metal t 2 g electrons are given to pi star of carbonyls through back bonding. Whereas, in case of phosphenes; this electrons from t 2 g orbitals are promoted to sigma star of P r 3 in the form of back bonding.

So, essentially if you just analyse this kind of electron transfer; it is very similar to P pi to sigma star in case of r d pi to sigma star. So, this is in contrast to what we come across in case of organic compounds where we come across the sigma 2 pi star. This we call it as hyper conjugation whereas, here it is opposite; so this is called negative hyper conjugation.

So, essentially lone pair of electrons from the nitrogen or donate it to the sigma star of silicon hydrate; that means, sigma star of S i H 3 and this is called negative hyper conjugation. And of course, this negative hyper conjugation is quite common in case of phosphorus nitrogen compounds, where nitrogen lone pair is essentially going to the phosphorus sigma star.

And that also denoted as negative hyper conjugation and the essentially strictly speaking the 3D orbits of silicon are very high in energy and they are not participating in any multiple bond formation between N and S i. So, because of this one the nitrogen lone pairs are consumed and it is a very weak Lewis base compared to ammonia; this compound here this is a very weak Lewis base compared to ammonia because its lone pair is now consumed, it is not available for performing it as a ligand.

Let us now look into hydrides of germane, stannane and plumbane germane is Ge H 4.

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Hydride of Germane, Stannane, and Plumbane

❑ Germane (GeH_4) and stannane (SnH_4) can be synthesized by the reaction of the appropriate tetrachloride with $LiAlH_4$ in tetrahydrofuran solution.

❑ Plumbane (PbH_4) has been synthesized in trace amounts by the protolysis of a magnesium/lead alloy but it is extremely unstable.

❑ The stability of the tertrahydrides varies in the order SiH_4 GeH_4 SnH_4 PbH_4, which is an example of the alternation effect.
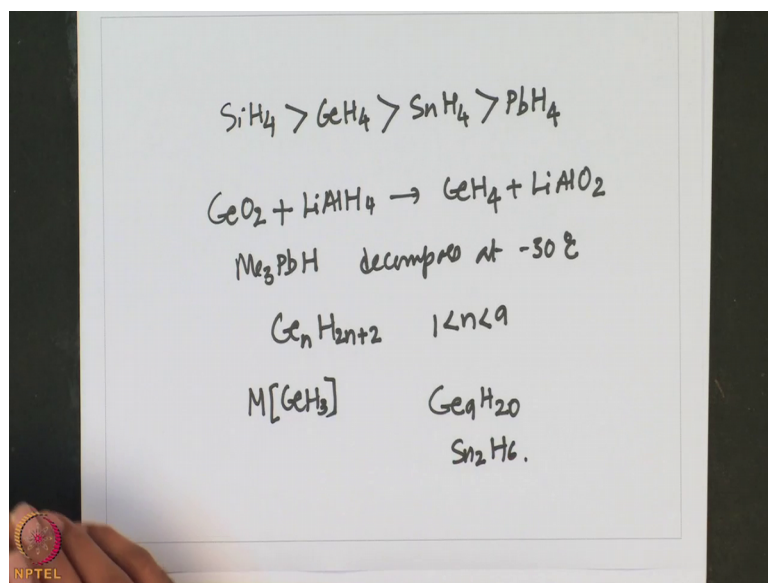
Stannane is S n H 4; they can be synthesized by the reaction of appropriate tetrachloride with lithium aluminium hydride; in tetrahydrofuran solution or in a typical ether solution. Plumbane PbH 4; has been synthesized in trace amounts by the protolysis of a magnesium lead alloy, but it is a extremely unstable.

The stability of the tetrahydrides varies is in order; that means, S i H 4 is more stable and then G e H 4; there is if you consider apart from CH 4; C H 4 is stable let us not bring CH 4 here. And if you compare the stability of hydrides of remaining 4 elements of group 14, they follow this order.

$$SiH_4 > GeH_4 > SnH_4 > PbH_4$$

$$GeO_2 + LiAlH_4 \rightarrow GeH_4 + LiAlO_2$$

$$Me_3PbH \quad decompos \ at \ -30°C$$

$$Ge_nH_{2n+2} \quad 1 < n < 9$$

$$M[GeH_3] \quad Ge_9H_{20}$$

$$Sn_2H_6.$$

More stable than germanium H 4 then; so, stability decreases down the group. And the general method of preparation of germane or germanium tetra hydride is starting from germanium oxide. When germanium oxide is treated with lithium aluminium hydride, it gives germane plus Li AlO2; the presence of alkyl or aryl group stabilizes the hydrides of all the 3 elements compared.

For example trimethyle plumbane; so, H; so this is a much more stable compared to P b H 4 and decomposes at minus 30 degree centigrade. But it can survive for several hours at room temperature and if you considered germanes; essentially they have the same formula. It can also form straight as well as branched chain isomers; here it is known up to 9 germanium atoms in a chain.

And germanium tetrahydride is less reactive than S i H 4; it is a colourless gas with boiling point 184 Kelvin and it decomposes 488 Kelvin and also this is insoluble in water. So, reactions between tetrahydride or germane and alkali metals also give similar to the; what I have described with silicon. So, they also form something like this with alkali metals and Ge 9 H 20 is known for germanium; in case of tin only S n 2 H 6 is known and S n 3 analog is not known for tin; this also very unstable.

So, let us look into a simple question here.
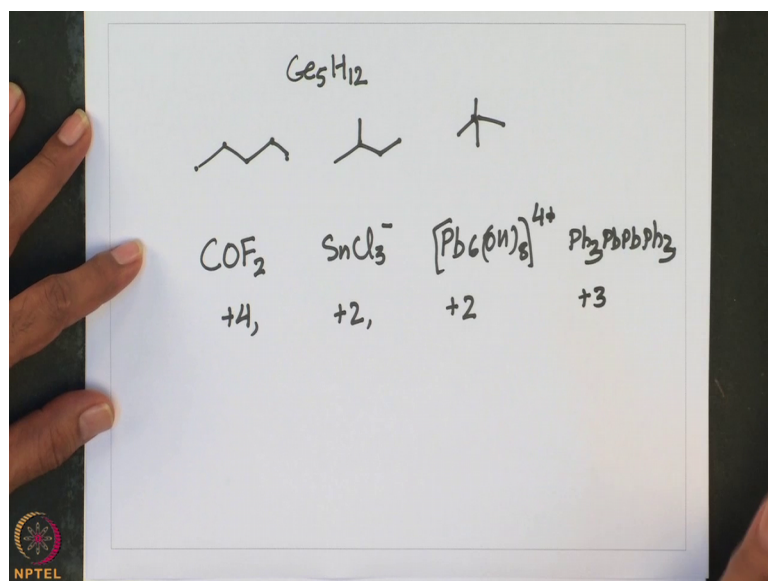
If we consider; a germanium 5 analogue germa pentane; so, how many isomers of germa pentane are possible? It is very similar to organic compound pentane. So, one can write here; 1, 2, 3, 4, 5; so, this is the one and of course, here we have 3 hydrogen atoms. So, this is one isomer; another isomer can be written like this and another can be written like this. So, essentially 3 isomers are possible; similarly if you take pentane one can write 3 isomers.

And now let us look into the oxide state of some of the group 14 elements in the following compounds. For example, COF 2 is there and S n C l 3 minus is there and P b 6 O H minus 8; 4 plus and P h 2; P b, P b, P h 2. So, let us look into it here of course, carbon is in plus 4 state and tin in this one is in plus 2 state. And here 4 plus charge is there; so this is in plus 2 state and in this one if any bond is there between two atoms; so, this one is a covalent bond.

So, we should not consider this one towards oxide state; so this is this one. So, P H 3 tri phenyl lead dimer; so in this case the oxide state of lead is plus 3 because this one is not considered.

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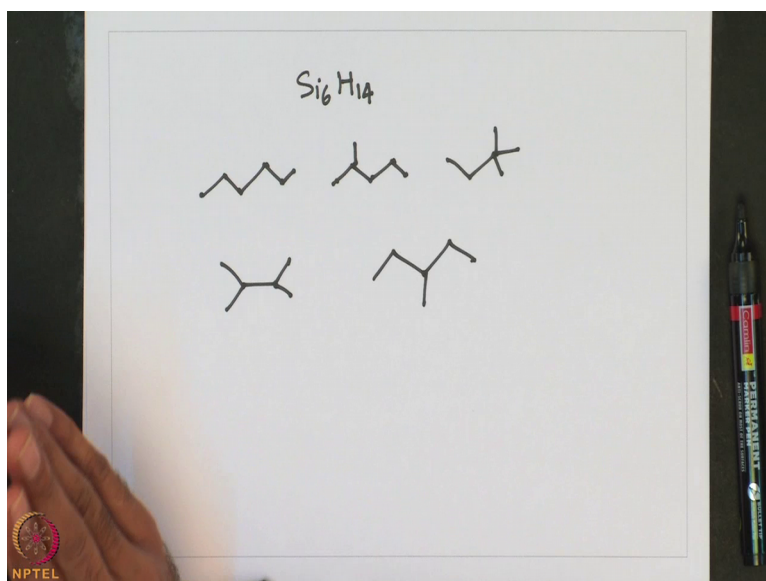
Similarly, one can write the possible isomers for a silane of this composition (Refer Time: 25:46) hexa silane. So, in this one also one can start writing 1, 2, 3, 4, 5, 6; 1, 2, 3, 4, 5. So, this one isomer and then this is the another isomer; so this is one more isomer 1, 2, 3, 4, 5, 6. So, totally you have five possible isomers for hexa silane; so very similar to the situation in case of hexane; organic molecule.

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So, with this let us move on to the oxides of group 14 elements; the oxides of carbon being gases are quite different from those of the other group 14 elements. It is very

interesting and to analyse the oxides of all group 14 elements; the structural differences results from the presence of strong P pi; P pi bonding between carbon and oxygen.

And carbon oxides if we take or discrete species whereas, in case of silicon this is exactly opposite; silicon does not form S i O double bond and it is unstable; with respect to 2 S i O single bonds and so silicon oxides and many oxyanions have infinite covalent network structures of S i O bonds. And heating the element in oxygen forms dioxide; that is S i O 2.

So unlike the heavier elements; carbon forms very stable monomeric oxide such as C O and also C O 2. So, analysis between C O 2 and S i O 2 can be made in the light of the thermochemical data. So, C O bond enthalpy is more than twice remember I repeat again C O bond enthalpy is more than twice that for the C O bond. While the S i O double bond enthalpy term is less than twice that of the S i O bond.

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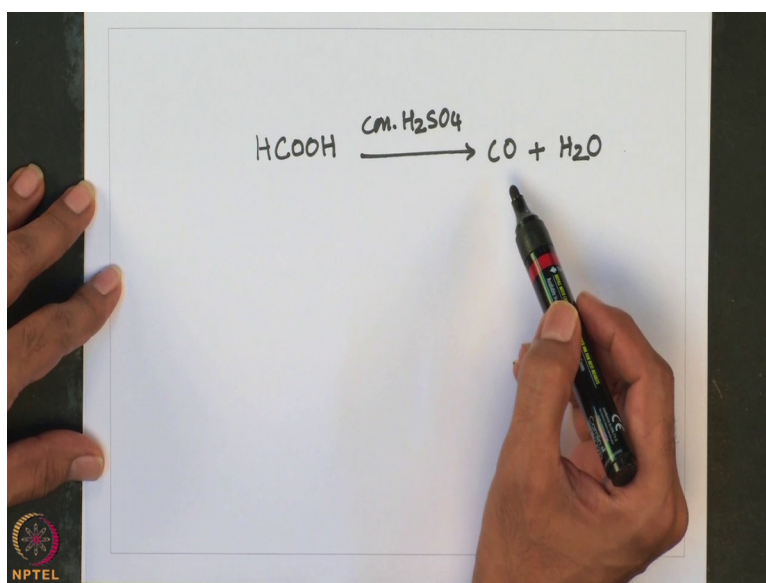
And here one can make carbon monoxide in the laboratory by treating fermic acid with concentrated sulphuric acid. This is the safest way of preparing in small quantities of carbon monoxide; for some carbonation reaction or making some organometallic compounds containing carbon monoxide. And essentially here water whatever is that is coming out will be taken by H 2 S O 4 and pure C O comes again it can be passed to some drying agents to get C O free from moisture and that can be used in organomettlic synthesis.

And if you just look into the C O; it is iso electronic with N 2 and has similar plysical properties. And carbon monoxide is a colourless gas formed when carbon burns in a restricted supply of oxygen. If more supply of oxygen is there; carbon dioxide is formed; in the restricted supply of oxygen C O is formed, small scale preparations essentially or preferably made using the method I have shown here; by treating methanoic acid or formic acid with concentrated sulphuric acid.

You can take formic acid in a round bottom flask and add concentrated sulphuric acid or you take concentrated sulphuric acid in a round bottom flask and formic acid in a dropping funnel. And if you add drop wise, the gas comes and if the round bottom flask has a side tube; you can take that one through drying agent and take it to the reaction for further utilisation of carbon monoxide. So, let me stop here; in my next lecture I will be giving more details on the oxides of group 14 elements.

Thank you very much.