

Industrial Inorganic Chemistry
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Lecture – 04
Fine and Specialty Chemicals

Welcome back to this class.

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Named Inorganic Compound

CrO_2Cl_2 oxidizes terminal alkenes to aldehydes

Étard's reagent (CrO_2Cl_2)

Internal alkenes give α -chloroketones or related derivatives. Also attacks benzylic methyl groups to give aldehydes *via* the Étard reaction.

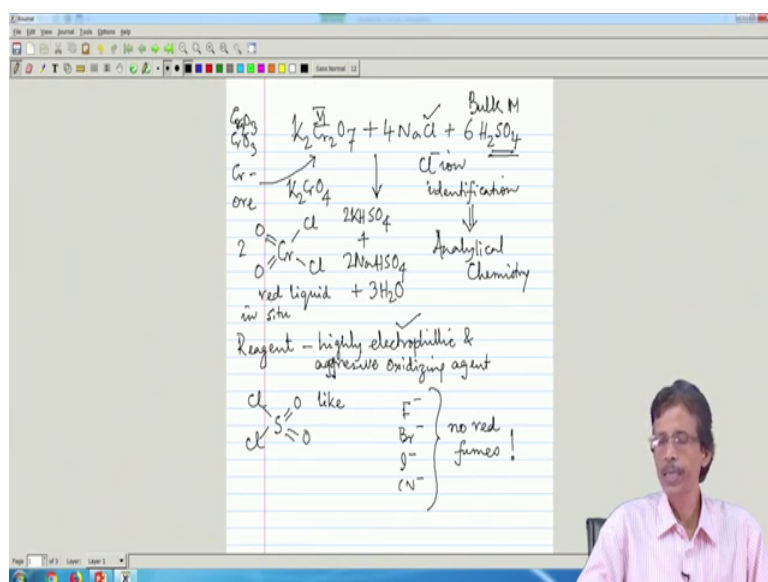
Where we are talking about the usefulness of some named inorganic compounds. And, we have taken the example of chromyl chloride. What is that CrO_2Cl_2 ? CrO_2Cl_2 is our chromyl chloride? And, that chromyl chloride is a very useful compound from analytical chemistry point of view also, but if we talk in terms of industrial chemistry. How, we can make it if it is a speciality chemicals for some kind of conversion?

And, if it is prepared in a bottle we can produce it and we can sell in to the market, but sometimes we find that these compounds are not so, easy to preserve it because this is a highly oxidizing compound, because if you just look at the corresponding oxidation state of the chromium. It is chromium hexavalent compound which should be highly oxidizing. Like your potassium chromate like your potassium dichromate, it has also a plus 6 oxidation state. Because, your 2O^{2-} is giving you 2O^{2-} minus charges of 4 negative charges along with the 2 chloride charges making 6 negative charges in it; so this chromyl chloride species, if we can form it very easily in the laboratory.

So, this is the bottle which has been giving you some red liquid and this red liquid is nothing, but our chromyl chloride molecule. And that chromyl chloride molecule is formed from a reaction of a compound, which is nothing but your compound in the hexavalent state. And, we have to use for it is corresponding chloride concentration; that means, the chloride should also be available in that particular reaction.

So, what we will see that, what that particular type of reaction we can get for the production of chromyl chloride, that we will see now is from that of the reaction of $K_2Cr_2O_7$.

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So, if we can have. So, this is our $K_2Cr_2O_7$ and that $K_2Cr_2O_7$, if we use it to react with NaCl along with sulphuric acid. So, this is a typical example, because we will not be able to give you all the different types of reactions what we can use?

So, this is also a hexavalent chromium and you can have the corresponding availability of the chloride, because we will be talking in terms of the corresponding formation of CrO_2Cl_2 . This is our chromyl chloride, which is our red liquid liquid. So, we have 2 chromium. So, definitely we will be able to produce 2 of this chromyl chloride, which is a red in liquid and we should produce it in CrO_2Cl_2 ; that means, within the reaction medium.

So, N C 2 preparation is will take place from the reaction of potassium di chromate with sodium chloride. Because this is the source of this chloride, which is attached to this particular chromium centre, because these particular re agent is a very good reagent. What sort of re agent it would be highly electrophilic, as well as aggressive oxidizing agent. So, if we consider in terms of organic chemistry, that we can go for some electrophilic substitution reactions or electrophilic other types of reactions, we can use this particular re agent. So, this we have seen that, this potassium dichromate preparation from any chromium ore.

If we consider that will be able to make it form a chromium ore; that would be an interesting thing; that means, it can give you the value addition. Because, the chromium ore what is the available to us will be the bulk material, bulk in organic material, which can be purified for these chromium dichromate preparation and sometime we can go it through K_2CrO_4 ; that means, potassium chromite form.

So, once we make through the direct oxidation; that means, sometimes in the laboratory we do it through alkali fusion reaction. And, that, alkali fusion reaction convert this chromium ore, which can be a simple chromium oxide. Cr O_3 or Cr_2O_3 ; chromium in the trivalent state the corresponding oxide in the trivalent state or chromium in the hexavalent state can be our ore material.

So, that as we all know that the different metal ions available on the earth crust or the earth mantle just we have seen in our previous class, that those materials are available as the typical oxides and how we convert it to some useful organic compounds? So, our this potassium chromate and the potassium dichromate will be your useful material. So, it has some amount of speciality material from the bulk material which is our own material. And, this can be useful for identifying your sodium chloride. So, it can give us some the identification of chloride ion; so, chloride ion identification.

So, is a part of this particular one is a typical analytical chemistry. And, as we all know from our laboratory analysis that this is a part of your qualitative analysis. So, qualitative analysis if, we want to identify the chloride ion we can go for this particular reaction again through the use of our bulk in a organic material. So, bulk inorganic I m inorganic material, bulk inorganic material sulphuric acid. So, we have to use the sulphuric acid. So, you see that how we consume sulphuric acid from simple laboratory to the industry.

So, if we are able to produce some of these compounds where sulphuric acid because the maintaining acidity of this particular reaction is also important. And, maintenance of that acidity for that particular one is only from sulphuric acid not from hydrochloric acid or not from nitric acid. So, because these sulphate ions can some have some important role and interesting role because, when we talk in terms of the corresponding chromium in the hexavalent state we always be try to understand that it is a hexavalent state it is highly oxidising. And, when we are levelling this molecule is highly electrophilic as well as aggressive oxidizing one. So, we should not use any other inorganic acid or mineral acid like hydrochloric acid why not? Because, we know that hydrochloric acid will have the corresponding chloride ion.

So, that chloride ion from the acid source if it is available for this particular one is going for it is oxidation part. At the same time we should also remember that we have plenty of these chloride ions, but it can go very nicely with the sulphuric acid because of the presence of this sulphate an ion. Though the sulphate ion is not taking part in this particular reaction, it is the chloride ion which is available from the other solid salt inorganic salt like sodium chloride to giving us this particular one. And, this chromite chloride is forming along with what other thing it can form because it can have the corresponding one as 2 molecules of potassium bisulphate.

So, when we make these as a red liquid we have to go for it is corresponding potassium bisulphate formation. So, if we take hydrochloric or nitric acid we will be ending up with potassium chloride or potassium nitrate, but the separation of these from the material cannot be some time so easy. So, we will end up with some other problem. So, this potassium bisulphate again this sodium will be consumed as your sodium bisulphate. So, this can be used as twice NaHSO_4 . So, this sodium can go for like this and plus $3 \text{H}_2\text{O}$.

So, these are the some reaction balance type of thing. So, what we get is that your red liquid which is forming in C 2 is our chromyl chloride. And, which is very much similar to the corresponding analogue of sulphuric chloride as we all know thus this is the corresponding one. So, is reactivity pattern; that means, there is a electrophilicity and is typical oxidizing agents. So, it has some behaviour which is similar to that of our sulphuric chloride. And is a typical one for the identification of the chloride ion.

Then, it can be distinguished for some other salt or some problem is there for industrial problem that, if we can have the typical identification of the chloride ion in presence of other alludes which are fluoride, bromide, iodide, and cyanide, but presence of these 4. That means, instead of sodium chloride if we can have sodium fluoride, sodium bromide, sodium iodide, or sodium cyanide, weather will be able to get the corresponding type of compound where the chrome the chromium centre is attached to fluoride or attached to cyanide, but this is not happening because the same reaction the laboratory reaction is not forming any red fume.

So, no red fumes are form. So, that is very interesting. So, the attachment of this fluoride bromide iodide as cyanide to this particular chromium centre as through the adjacent CrCl bond is not possible, because the fluoride bromide iodide this can be oxidized or this can be converted to some other form. So, this particular reaction; that means, the corresponding chromyl chloride formation from any other chromium source is only useful for making this chromyl chloride re agent. And, which can also show us that how we can go for a particular type of speciality molecule for our useful purpose. So, what is that purpose red fumes as your chromyl chloride formation?

So, this chromyl chloride formation which should be prepared it in C 2 and then we can use this particular red liquid for other purpose. So, the person who first utilise this for some useful purpose like that of oxidation of terminal alkene to aldehyde was the person the scientist Etard. So, scientist Etard when see he use this particular one for some useful purpose is known as the corresponding Etard reagents.

But, naming this thing is also remembering that particular person, but we should not forget the corresponding composition of this particular material is a very simple one, which is a test for chloride ion, the chromyl chloride formation the red fume formation and we should also know the corresponding molecule very nicely. So, the understanding of basic inorganic chemistry is a base for understanding this particular re agent, which we can produce in the industry as a typical inorganic compound in organic material. Because, this particular reagent can be useful for the oxidation of terminal one, as well as the internal alkynes also, because in case of internal alkene it gives alpha chloro ketones or related olefins so, what we see now that?

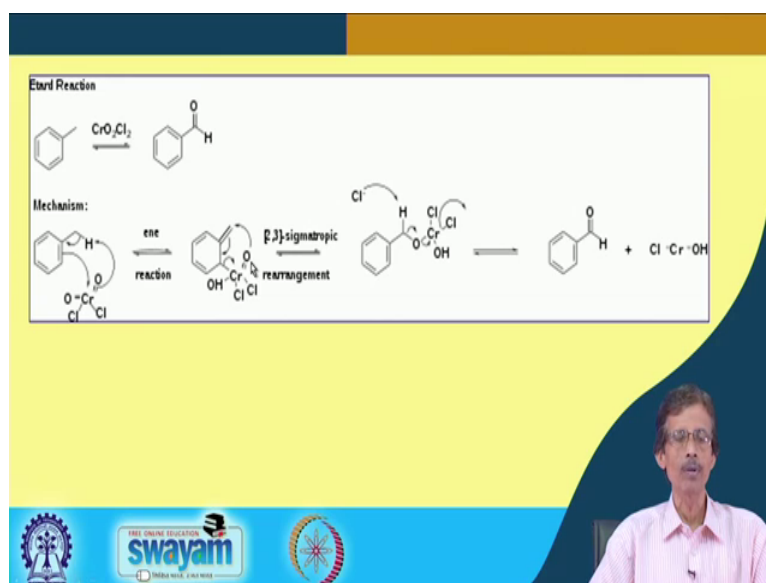
Previously we are talking about the oxidation of terminal alkynes to aldehydes. So, if we can have terminal alkyne or if we are able to make it some amount of terminal alkyne from some alkane also. That can be converted to the aldehyde because the conversion of the typical alkane type of thing to aldehyde is not always easy. And, always we try to go for this particular reaction that, how easily, how quickly, and the process should be a cheaper one also; in terms of our man hour investment, our labour investment, our material investment, our time investment.

So, if very easily we can convert it to aldehyde through this particular process we should utilise this particular process for these oxidation. But now, if our substrate for that oxidation reaction is changing from terminal alkyne to internal alkyne, what we see now we get alpha chloro ketones. That means, whatever we are getting similar to that of ketone molecule; that means, instead of aldehyde we are getting now ketones.

But, it is also supplying the chloride ion that is why we are saying that how useful is the attachment of that particular chloride ion. That means, the involvement of that particular oxidation state of chromium as the highest possible oxidation state is not only the only thing, which can be useful for this purpose. Otherwise, we could have used chromate salt or the potassium dichromate salt these are also oxidising and these are all having chromium with oxygen double bonded oxygen.

But, attachment of these 2 chloride ions through the chromium centre gives us something very different. So, alpha chloro ketone or any other related derivatives or the compounds we can make through this reagent. And, also it can attack benzylic methyl groups. If, you can have the corresponding benzylic methyl groups to give aldehydes like if you can have only C h_3 function attached to the (Refer Time: 15:31), we can have the corresponding reactions, since the reagent is used by his name. So, the reaction can also be considered as the Etard reaction.

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So, what is that reaction let us see that reaction from a typical organic chemistry point of view, because small small organic reactions we should also know when we are utilising this particular chromyl chloride. So, what is Etard reaction Etard reaction is nothing, but if you have methyl substitution on the phenyl ring. So, if you can have only that corresponding one as the methyl function attached to the phenyl ring you can get this corresponding oxidation to the benzaldehyde formation.

So, how we can make or how we can convert the bulk amount of this hydrocarbon to the benzaldehyde. So, if the easiest or the simplest process is through the use of chromyl chloride, we can go for this. And, since we are talking about something which we considered is as the corresponding formation of the terminal in. So, we can considered it when the reaction is taking place through this is that corresponding in formation in molecule formation.

So, we considered is as the in reaction. And, this can happen only because this was C H_3 and this can be converted to C H_2 , because this particular hydrogen. The hydrogen from the methyl group can be taken up by the corresponding chromium oxygen bond; that means, this oxide ion which is attached to the chromium centre converting it to $\text{O}_2\text{O H}$.

So, the abstraction of this particular hydrogen ion is very easy by this particular group and still the chromium if it is attached to that particular carbon centre, which can considered as the carbon chromium bond. Which is the typical process or procedure

which is going through some organometallic pathway, because it is sometimes difficult to identify that at least you are getting that particular chromium carbon bond formation; instead what we can propose that as an intermediate and a very unstable intermediate. It can form this particular species through the abstraction of these hydrogen one of the CrO bond is converted to CrO H.

Other is remaining as the double bond in the second step this particular one can attack again the corresponding in function and the attack of this particular in function through the other double bonded oxygen will give you some carbon oxygen bond formation. Which is the basic requirement for our conversion to benzaldehyde, because what we are looking for we are simply looking for a carbon oxygen bond that mean the carbon oxygen double bond formation for aldehyde formation. And, sometime we can go for the ketone formation; that means, wherever we go for the aldehyde or the ketone formation we should go for the corresponding carbon oxygen double bond.

So, initially when this is present it is like that of our formation; that means, it is there you have the corresponding one as the CH₂; so CH₂ O which is attached to the oxygen of the chromium centre of chromyl chloride. So, then this hydrogen can be abstracted back by the Cl minus which is present over the chromyl chloride forming our HCl in the medium. So, this HCl formation from that particular medium is useful then, and that is also one it is abstracted then it is going back to give you the corresponding aldehyde so, you get that.

So, once you get it that as because this particular interaction will give you that transfer of this oxygen. So, chromyl chloride is basically transferring this oxygen from it is reagent form to the substrate molecule giving you the corresponding benzyl dehyde formation. And, the remaining part is taste like that of your chromium salt, because the chromium if it is reduced you will get the corresponding chromium compound in it is lower oxidation state.

So, that gives us a very useful example of utilisation of a chromium compound, and that utilisation of chromium compounds from making some useful molecule and some useful organic transformation and that gives us some good idea. How, we can have a bulk or commodity material like our chromium oxide as a ore material can be converted to some

simple sophisticated material which can be convert called as a speciality chemicals, like that of our chromyl chloride.

Now, we will move on to the species part will be talking now is the different bulk material, which is available in a large amount from different sources like water. We have already discussed little bit about the usefulness of water molecule, which can be the very useful molecule for inorganic industrial chemistry. So, not mat making the portable water molecule or not man making the drinking water molecule; this is another aspect, but how we can utilise the different types of water is in the recycling of water, rainwater, to ocean water, how we can utilise for different or useful purposes?

Because, this simple water molecule can function as a very useful solvent. As, we have just seen all other reactions what we do in water media, because most of the inorganic compounds and inorganic chemicals like that of our sodium chloride, which we use every day from our kitchen to laboratory, which is the highly soluble in water to any organic molecule like our dextrose the sugar, which is soluble in also in water.

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Water

Vital in many processes, a wide array of purification techniques has been developed.

It is required as a reactant in an industrial process

- Sulfuric acid production
- Phosphoric acid production
- Sodium hydroxymethylsulfinate production
- Chlor-alkali process
- Ostwald process
- Solvay process
- Ilmenite process
- Gold cyanide refining

swayam

So, if we consider we can make some saturated solution of sodium chloride in one hand and scraggy in the other hand will be utilizing with the water molecule. So, what type of water molecule we can use this as the solvent. So, different types of inorganic reactions or organic reactions, which we can utilised for making some useful compound. So, from industrial point of view how good is the water as the solvent. Because for making all

these molecules in the greener way, because we all know we will be very much concerned about the environment, which is not contaminated or destroy the environment by making some hard solvents for doing some reaction.

So, sometime we call a reaction which is solvent free reaction. So, if we consider this as the solvent free reaction. Means that, we are not using any organic solvent; like chloroform, like, dichloromethane, like acetonitrile. So, we will be trying to utilise these only on alcohol like solvent, which is more friendly environment friendly or water or sometimes without solvent; that means, the solvent free reactions. So, those are the things. So, making water studying water and doing some reactions on water always will be treating water as the solvent. Next thing is that how we utilise this as the reactant.

So, this reactant what we can use this as a particular reaction; that means, what we have give you give you the example of reaction of sulphur trioxide with water for giving you, the formation of sulphuric acid. So, the formation of this particular sulphuric acid will be useful for giving this water as the reactant molecule. So, starting from solvent to reactants so, production of sulphuric acid will be dependent again on the quality of the water which can be utilised as the reactant for that particular reaction.

Then, we can have water as the solute also because sometimes if it is used as a very small amount water can also be useful for as a solute. And finally, water can be utilised as a catalyst, because some of these organic reactions or the pharmaceutical reactions can be governed by catalytic amount of water. So, if one drop or less than one drop or one micro litre of water can be useful for giving you some useful conversion. In that particular case this water can will be useful as a catalyst.

So, what we see now that water which is forming in many vital processes. A wide array of purification technique has been developed how we utilise or how we can purify the water? That means, the quality of the water as I told you the extreme purification what we can have in our hand is the distilled water, where we can have only H₂O not even D₂O. That we will consider that how we can get that D₂O also, when we talk in terms of the production of water, because following these will be considering the production of hydrogen, then hydrogen peroxide and then the other peroxide compounds. So, these are the few things for all these classes what will be talking in terms of the hydrogen only.

Because, the availability of the hydrogen unlike your nitrogen or oxygen is not much in the environment, but that is available as at the compound only like water. So, how we get a good quality of water? And, how we can produce hydrogen from that particular water that is our ultimate goal that is why we should study little bit about the water molecule. So, this purification technique has been widely developed and people are trying for development of all these things for getting good quality of water. So, this water can be your typical starting material for as a raw material for different types of industrial processes.

So, this different types of industrial processes what we can have as I already gave you the typical example, which is sulphuric acid production. So, if I now say you tell me that which particular material can be useful for sulphuric acid production. So, already we know the brief outline of the sulphuric acid production starting from your raw sulphur material, starting from the raw sulphur what we get from the ore, which can be utilised for useful sulphuric acid production, because the quality of water molecule is very important for the production of this sulphuric acid. Because, when we produce sulphur trioxide that sulphur trioxide can be trapping your water molecule giving you H_2SO_4 .

What does it mean there for that your H_2O from water H_2 from water? And, the whole H_2O molecule itself is going to your sulphuric acid. So, directly the amount of water what we are getting the purified water molecule in your hand is directly converted to your sulphuric acid. And, that sulphuric acid will be utilising for different purposes. As well as for supplying the sulphate ions, also because we will be producing, other species based on sulphuric acids such that if we want to make sodium sulphate or sodium bisulphate.

So, that also utilising the same sulphuric acid, so the sulphate and ion and ultimately if we are trying to make barium sulphate. So, that sulphate molecule what we are in our hand, one of the oxygen of that sulphate ion is still coming from that water molecule. Because, we have use sulphur trioxide and the other oxygen is given from your water molecule. So, the water molecule is being fixed as the typical sulphate ion and that can be utilised for all other different purposes. Starting from getting sulphate for barium sulphate formation and is a standard material for the water turbidity measurements also.

Similarly, we can have the phosphoric acid production, because it is also H_3PO_4 . So, if we consider that again we are having something which is coming directly from the water molecule. So, we will be utilizing it for the phosphoric acid production as well as. So, these are the industrial areas basically, where we can produce sulphuric acid in a large amount, we can produce phosphoric acid, then sodium hydroxide methyl sulphinate production. These are little bit high and sophisticated molecules that we will also see from one after another then we can have the chlor alkali process.

The chlor alkali process is nothing, but the electrolysis of sodium chloride, because the sodium chloride. We get in a large amount from seawater from all other sources like that of our chilli saltpetre what we know from our school days, that electrolysis of sodium chloride will give you some useful molecules and that is being done in presence of water only. Then, we will just see because these are only some collection of the name reactions or some name processes, which will be utilised for our journey for studying this industrial inorganic chemistry.

We will be studying of Ostwald process also, we will be studying the Solvay process we will be ilmenite process and ultimately, the gold cyanide refining. So, all these processes if we say consider 1 2 3 4 5 6 7 8 processes and all this process are dependent on water. So, if we consider we are dealing with some water industry. So, it is also in some way it is also true, because we should also be very much concerned about the quality of the water what will be utilizing and the amount of water.

So, what quality of water weather we will be utilising the distilled water or simple ocean water or simple revolve water is sufficient, because we all know that anything where you produce electricity there also we require water. Anything with we get the corresponding furnace the cooling down of the furnace is also because of water has large number of utilisation. That means, as a reagent, as a solvent, or some other as a heat sink also in other cases which can train out the excess temperature from the industrial processes. So, that can also be seen in a stepwise manner from one after another for different things as we proceed for this particular type of course.

Thank you very much.