

hello everyone

so i am dr rameet ramapanikar an associate professor in the chemistry department at iit kanpur

so i would continue to talk to you about the reactions of halo alkenes and halo arrange the chemistry of halo alkenes and halo irenes

so these are topics that are covered in the unit 10 of ncert tech chemistry textbook for class 12 students

so in the previous class that i had i have already talked to you about various classifications of halo alkenes and halo arranes how their nomenclature is given how they are named and what are the common names of these compounds we also looked at certain examples of this class of compounds that are found naturally and also some of them synthetic and we discussed that these are highly important class of compounds that find a large number of applications in daily life then we proceeded on to say about the nature of chemic carbon halogen bond and which is the reason behind most of the chemistry that we would be discussing in the coming two classes or

so and then i also proceeded to discuss about the preparation of halo alkanes from simple starting materials and i have discussed only one of the points that was preparation of these compounds from alcohols

so i would start off by rewinding a little bit on the preparation of haloalkanes from alcohol

so that we get continuity with respect to what we have been discussing

so to start with i would talk about preparation of halo alkanes from alcohols

so as you can see in the screen here if you take an alcohol and treat it with a hydrohalic acid we would get a halo alkane plus water some of these reactions are catalyzed by zinc chloride a metal chloride

so the purpose of using zinc chloride is to facilitate the cleavage of the carbon oxygen bond and then the installation of the halogen bond onto the carbon atom from where the hydroxy group has left the order of reactivity for this class of compounds is generally tertiary alkyl halides reacting faster than secondary reacting faster than primary

so therefore the reaction of primary and secondary alcohols to be faster it is quite essential that we use the catalyst that we have already discussed

so synchloride in this case acts as a lewis acid that coordinates with oxygen and facilitates this reaction it is to be noted that this reaction is not possible for halloweens just for the fact that the bond between oxygen ah and carbon is quite strong in phenols

so we cannot prepare halo arrange using this particular method whereas this is only applicable for the synthesis of halo alkanes now the alcohol group the hydroxyl group can be replaced by a halogen atom in the presence of acid

so this is the essence of the reaction

so the acid that is used in this case can also be an acid different from hydrohalic acid provided that we also supply in the reaction mixture enough number of halide anions

so we can carry out this reaction with sodium iodide and or potassium added in such cases we will have to use another acid

so that water can be removed from the alcohol

so these are two examples of that kind and then i went ahead and said that phosphorus trihalides or even phosphorus penta halides can be used for making this reaction and some of the phosphorus trihalides like ah pbr3 and pi3 need not be added directly into the reaction instead they could be prepared in the reaction mixture by the reaction of red phosphorus with the corresponding halogen molecules

so this is something that we have already discussed and the most important

point when we were discussing the synthesis of halo alkenes from alcohols was the fact that when an alcohol is treated with thionyl chloride SOCl_2 that gives the halo alkene along with sulphur dioxide and HCl

so these two are the byproducts that are formed in the reaction and interestingly these are gases

so whenever we carry out the reaction of alcohol with thionyl chloride it is not only that the reaction is an effective one giving us the halo alkene it also produces byproducts which are gaseous that will escape from the reaction mixture allowing us to isolate the products in this case the halo alkenes quite easily

so so this for practical reasons is one of the easiest reactions

so now i will go further and i will talk to you about other methods for preparing halo alkanes

so the second method that i would like to talk to you is about the preparation of halo alkanes directly from hydrocarbons

so you would have to realize that by hydrocarbons we mean compounds that only have carbon carbon and carbon hydrogen bonds

so for this class of preparations we will have to break a carbon hydrogen bond and install a carbon halogen bond

so that is what we want to do

so this is normally done this is something that we can do

so this can be done by taking an alkane

so in this case i have represented the alkane as RCH_3

so let us assume that R is an alkyl group could be bigger attached to a CH_3 a methyl group in this case now if it is treated with chlorine or bromine it can be either chlorine or bromine in the presence of uv light or a lot of heat it can generate HCl that means the corresponding chloroalkane plus HCl

so when we look at this reaction as i have written here as the look at the equation it is quite evident that this is a very effective reaction because we are taking an alkane breaking a carbon hydrogen bond and installing a carbon chlorine bond

so nothing could be simpler however it isn't that easy

so in order to understand the reaction i will go into the mechanism of this particular reaction

so this whole reaction happens because halogen halogen bond as in chlorine molecule or bromine molecule or even I_2 is not very stable

so therefore if you provide enough energy either in the form of light or in the form of heat the halogen halogen bond breaks and once the halogen halogen bond breaks it doesn't break in an ionic fashion each of the halogen atom retains its electron

so they form free radicals which are normally represented by putting a dot over the halogen atom

so in this case i can show that Cl_2 which is chlorine molecule absorbs light energy and becomes two Cl^\cdot where the dot stands for that extra unpaired electron that is present in the radical

so now this is a chlorine atom

so there are two chlorine atoms that are formed from chlorine molecule now the chlorine atom then reacts with the alkane

so in this case RCH_3 and it abstracts a hydrogen

so because chlorine is extremely reactive once we have atomic chlorine or chlorine free radical it is extremely reactive

so it is able to abstract a hydrogen from the alkane thereby giving us RCH_2^\cdot with that dot indicating that it is another radical

so we create an alkyl radical plus HCl

so hcl comes out and an alkyl radical is created now this alkyl radical would then react with chlorine

so what do we have in the reaction mixture is chlorine molecules press alkane now we radiate with light

so the chlorine breaks first into two halogen atoms one of the halogen atom then abstracts a hydrogen that gives us an alkyl radical plus hcl now this alkyl radical that has formed would react with another chlorine molecule and in this case what it does is it breaks the chlorine molecule into chlorine atoms and bonds with one of the chlorine atoms and generates a chlorine radical

so you would find that in as a result of this reaction we have actually got an a halo alkene a alkyl chloride plus a chlorine radical which will go directly into this step and continue to do what it has been doing

so in effect what we are doing is in the second step we are regenerating a chlorine atom a chlorine radical that can continue the reaction further

so it just gets propagated

so this is how this whole reaction happens

so if you would like to see how what exactly is the mechanism of the reaction all we need to do is sum up these two reactions that i have written here these two equations

so it would amount to be $\text{rch} + \text{cl}_2$ giving you hcl plus the corresponding chloro alkene now

so this is the mechanism of the reaction i told you that although it looks simple it is not an easy reaction it has its own problem

so let us see what are the problems here

so once you have a chlorine radical the radical can pick up any any hydrogen from the alkane that is present

so normally alkenes would have multiple number of carbon hydrogen bonds

so radicals such as chlorine radical will not be able to distinguish between these various carbon hydrogen bonds

so therefore what happens is it starts to pick whichever hydrogen is immediately available

so therefore we end up getting mixtures of products not only that the product that has formed in this case which is rch_2cl also has additional carbon hydrogen bonds

so the chlorine radical can further react with the product that is already formed and lead to multiple halogenations or multiple chlorinations in this case

so this is one of the major disadvantages of this reaction

so their synthetic application although the reaction is in an equation looks simple is not much

so this is one of the limitation

so just to emphasize this point i have another example here

so i have butane which is being treated with chlorine and uv light

so i get two monochlorobutane products

so if i assume that only one of the hydrogens are picked even in that case i can get one chlorobutane and two chlorobutane these are monochlorobutane additionally i can also have polychlorobutanes where there can be more than one that is two three four or five hydrogen atoms replaced with chlorine

so what we get at the end of the reaction is a mixture of products where there are these various isomers of monochloro dichloro trichloro and

so on ah compounds present which cannot be isolated that easily

so therefore this looks like a good reaction but it is not very useful in terms of its synthetic applications now the third reaction that i would talk to you about the preparation of halo alkynes is the reaction of alkenes with hydrogen halides h x

so this is probably a reaction that you studied when you have studied the reaction of alkenes

so alkenes add on to HX

so in this case H plus and X minus one as one would add across this molecule too

so it reacts with alkenes to give haloalkanes that have a hydrogen and a halogen added across the double bond

so this reaction then gives a new carbon halogen bond

so therefore haloalkanes

so I have an example here which is propene when propene is treated with HX we get the corresponding haloalkane with H attached to the first carbon atom that is one haloalkane or two haloalkanes you would find that two haloalkanes is the major product in this case and this is something that you already studied because reaction of unsymmetrical alkenes such as this that means when you have a double bond that are differentially substituted on the two carbon atoms that are involved in the double bond then the addition reactions of such molecules happens in such a way that the halogen atom gets itself attached to the most substituted carbon atom that is there is a preferential formation of more substituted haloalkanes this rule is Markovnikov's rule which you have studied already

so it simply tells you that the products of such reactions usually result from the most stable carbocation that one can imagine

so in these cases the you would already know that the most stable carbocation is a tertiary one followed by a secondary and a primary

so in the case of the reaction of propene the carbocation intermediate formed would be the one that is having positive charge on the secondary carbon atom that is a carbon atom in the middle therefore H gets attached to the second carbon atom giving this as the major product in this particular reaction

so so this is

so the addition of hydrogen halides to alkenes is something that can give us mixture of products but in these cases the mixtures that we are going to get are predictable and not too many because the addition is only going to happen to two of the carbon atoms which are involved in the double bond and there will be one major product and one minor product which normally can be separated

so this is a useful reaction and in case we are looking at adding multiple number of halogen atoms

so let us say two halogen atoms we can also add a halogen molecule instead of hydrogen halide we can add a halogen molecule such as bromine across a double bond in this case there are no issues a bromine atom each gets added on to both the carbon atoms that are involved in the double bond

so therefore we get one two dibromo compounds we already discussed while discussing the classification of these compounds that if there are substitutions on carbon number one and carbon number two that those are adjacent carbon atoms we call them as vicinal dihalide substitutions or vicinal halogen halides in this case

so this is

so this particular reaction gives you vicinal dibromide from this

so this again is an efficient reaction because we break bromine into two bromine atoms and add them across a double bond to get these compounds

so this is an effective reaction if you are looking for one two disubstituted compounds now there is a simple application of this reaction which is normally done in smaller analytical labs probably in the lab that you have in your schools or colleges

so what is done here if you take bromine in water it dissolves a little bit in water

so you get a brown solution of bromine water now if you want to know whether a compound that you have is an alkene whether it has a double bond we can add bromine water to that and what happens is if it has the compound that you are trying to analyze as double bonds then bromine gets consumed because it adds across the double bonds and as a result the reddish brown color of bromine disappears

so if you take bromine water which is colored and add into an alkene the color of the bromine water disappears

so this can be used as a test for alkenes

so provided you do not have any other methods to detect the presence of alkenes this can be used as a method

so this is normally used in your school labs and

so on

so that you understand the chemistry and appreciate this particular reaction ok

so now ah in most of the methods that we have discussed

so far you would have seen that we were only talking mostly about the reactions of chlorines and iodine and bromine because we were it is rather easy to prepare chloroalkanes and bromo alkanes but once it comes to iodo alkanes and fluoroalkanes the reactions are problem normally for example the reaction that we did in the presence of light the reaction of chlorine and bromine works well iodine does not react normally under those conditions and fluorine reacts violently

so if the effort is to make fluoro alkynes or iodo alkynes the number of possibilities are limited whereas for chloro alkenes and bromo alkanes we have multiple number of methods and most of the reactions work well because their reactivity falls in the range that is controllable by a chemist under the conditions that we can produce now

so therefore if you are interested in preparing an iodo alkane there is a simple way we can easily prepare them from other halogenated organic compounds

so for example if you take a chloroalkene or a bromoalkane and treat it with sodium iodide as it is shown in this particular reaction

so if you take an RX where X is chlorine or bromine and treated with sodium iodide in acetone as the solvent we would get the corresponding iodoalkane plus the sodium halide now the whole reaction works better because sodium iodide is more soluble in acetone than sodium bromide or sodium chloride

so therefore once you take this reaction we would have considerable amount of sodium iodide dissolved in acetone

so if you add an alkyl bromide or an alkyl chloride into the solution the reaction happens and the sodium chloride or sodium bromide that comes out would start to precipitate

so the reaction is always running in the forward direction are suggested by Lehardler's principle and therefore we can easily prepare iodo alkynes using this method this reaction has a name for those who are interested in names this is called Finkelstein reaction

so Finkelstein reaction is nothing but an easy preparation of iodo alkenes from chloroalkanes or bromo alkenes using acetone as a solvent using a similar method using a rather parallel method we could also make fluoroalkyne starting from high chloroalkanes or bromo alkanes

so in this case what we use is certain metals certain metal salts of fluorine where the metal has a better affinity for chlorine and bromine

so such examples include silver of course then it has mercury cobalt or antimony

so if in the case of these metals what actually happens is the corresponding bromides and chlorides are more stable

so once we treat them with the with an alkyl halide or an alkyl chloride or an alkyl bromide the reaction proceeds by the formation of corresponding methyl bromide or metal chlorides i have written metal bromide here assuming that what i take is a bromide or a metal chloride plus the corresponding fluoroalkane

so this again is an exchange reaction

so these two reactions that i have discussed now on this particular section are halogen exchange reaction one where a chlorine or bromine is exchanged with sodium iodide and another one is a chlorine or bromine exchanged with a fluoride of certain metals that have higher affinity for ah bromides and chlorides

so that reaction again has a name it is called swarts reaction for those who would like to remember these reactions by their name ok

so this

so much about the reactions of halo alkynes now we would go ahead and start discussing about the reactions of halo arrays

so i have already mentioned that the synthesis of halo arrhenes are slightly different from the synthesis of haloalkanes even their reactivity patterns are different this is largely because in a halo arrane the carbon halogen bond is true and sp to hybridized carbon atom not only that this speed to hybridized carbon atom forms a ring

so it has its geometrical constraints

so that it cannot give a lot of other reactions that alkyl halides can give so therefore there are difference in the reactivity and therefore the preparation methods also have to be slightly different

so one of the simplest methods that one can think about when we talk about aromatic compounds is uh their synthesis through electrophilic substitution reactions

so i have a simple example here

so i have taken an alkyl substituted benzene

so when an alkyl substituted benzene is treated with x two

so x two you will find that again in this case is chlorine or bromine ah most likely

so when it is treated with the halogen in the presence of f e

so in the presence of iron ah under dark conditions because you do not want any photochemical reactions to happen

so when it is done under dark conditions with no light involved what iron does in this case what if it does is it first reacts with x2 to give you fe x3 the corresponding trihalide now this fe x3 acts as a lewis acid and it breaks additional number of halogen atoms

so so what exactly happens i might be able to draw it for you

so what happens here is you get an f e x 3 which then reacts with x 2 further to give you ideally an f e x 3 bonded to an x through f e with a negative charge plus an x positive

so the x positive

so you are effectively creating a halogen positively charged halogen atom in this case this is formed because f e x 3 that is formed from x 2 and f e can act as a lewis acid now this x plus is an electrophile

so electrophile is something that has a liking for negatively charged species something that has a liking for electrons

so this x plus can then react with the aromatic compound and form a positively charged ah aromatic species here

so the aromatic ring breaks down and is no more aromatic it forms a positively charged species cation and from this we lose an h plus and a double bond is

reinstated to give us the corresponding halo arrange

so this reaction as you would see works through the formation of a cation and the cation is formed when an electrophilic halogen ion and halogen cation is reacting with the aromatic ring forming a cation and then it removes a proton giving us finally the halo array and this reaction again works well with bromine and chlorine

so you would find that when there is an r group already present on the aromatic ring the x can be on any of this carbon atoms it can be here as i have shown here or on any of the other carbon atoms too but ah the position of the newly formed bond actually depends on the nature of the substituent that is already present

so for simple alkyl substituted aromatic compounds the preferential formation would be on either on the para position or on the ortho position to the alkyl group

so you already know that alkyl groups are ortho para directing

so that results in substitutions on ortho or para position it does not matter even if you get mixtures because these mixtures have different physical properties

so they can be separated by various methods that are available to a chemist to separate mixtures of organic compounds now ah again once again i will come back to the point that chlorine and bromine reacts better for this class of reactions and gives us bromo arrange and bro ah chloroarynes better what happens with iodine is the byproduct of this particular reaction you would see is

so if i have to write the byproduct of this reaction the by product is the corresponding hydrogen halide

so you get h x as a byproduct

so when the reaction is done with iodine the byproduct is h i

so h a is not a stable compound

so it is always in equilibrium with hydrogen and iodine

so what happens is the reaction could go backwards

so therefore whenever if we do this reaction with iodine we would not be able to control the reaction and get an iodo arrange as the final product because the product might undergo a reversible reaction giving us back the aromatic compound plus i₂

so therefore what has to be done is if an iodo arrange has to be prepared we make sure that the hci that is formed is somehow consumed there are various methods to do that one of them is to oxidize h i to a hypervalent iodine species

so that the reaction does not go back or the other thing is to do is hi is an acid as you know

so if you use a base then h a gets neutralized and then we form the corresponding corresponding metal iodide which would also make sure that the reaction does not go backwards however the reaction cannot be done for fluorine because we would have absolutely not controlled fluorine reacts extremely fast and extremely violently

so we will end up having mixtures of aromatic compounds having multiple number of fluorine atoms and then their purification or isolation becomes difficult

so the preparation of fluorides are no is not possible using this particular method okay now i will talk to one of ah the more controlled reaction for the preparation of these compounds where we would have an absolute control over where exactly the halogen atom is going to be formed and this method can also be used for the preparation of not only chloro and bromo arrange but also for the preparation of fluoro and iodo arrange as well ok

so the reaction starts from a primary amine

so when a primary amino group nh₂ is attached to benzene it is called aniline

it is a primary amine as you know because nitrogen is attached only to one group one aryl or alkyl group those are primary amines

so i take a primary aromatic amine and treat it with sodium nitrite and HX where HX is an acid

so this generally is hydrochloric or hydrobromic acid as one would assume it can also be H_2SO_4 or any of the acids that can give H^+

so what happens under these conditions when sodium nitrite is treated with a hydrohalic acid or sulfuric acid it generates an HNO_2 which is nitrous acid

so $NaNO_2$ gets changed into HNO_2

so we do not normally start with the solution of HNO_2 instead we prepare HNO_2 starting from $NaNO_2$ and an acid

so now once you have access to nitrous acid what happens is nitrous acid would react with the primary amine and give us something called as the diazonium halides

so in this case because we started with aniline we get benzene diazonium halide where X corresponds to the anion that was present in the acid that is used

so if you use HCl it would be benzene diazonium chloride if you use HBr it would be benzene diazonium bromide and if it is sulfuric acid we get benzene diazonium hydrogen sulfate and

so on

so we get a benzene diazonium salt where there is an aromatic ring that is attached to a nitrogen molecule with the positive charge is not just one nitrogen there are two nitrogen atoms

so what it does is this particular bond here can be cleaved quite easily

so the carbon nitrogen bond can cleave and then into molecule you know nitrogen molecule is a very stable molecule that is why we have it in the atmosphere

so much because nitrogen molecule can easily leave out from various organic compounds because it forms a very stable species

so in this case the benzene diazonium halide that is formed would break down and give us an end to plus the corresponding cationic aromatic species now this can be trapped with various number of nucleophiles or some of these reactions also follow radical mechanisms

so one particular application is when you take this benzene diazonium halide and treat it with a cuprous salt such as Cu_2X_2

so this can also be written as CuX there is no problem where X is normally chlorine or bromine then we get the corresponding halo arranged plus nitrogen

so the reaction proceeds this way we already have an aryl diazonium highlight you can see an X^- form there

so when it is treated with Cu_2X_2 or CuX in short it gives us the corresponding halo arranged plus nitrogen now the interesting point here is this X^- that is replacing here can be either one that is attached to copper or the one that is present as the anion along with diazonium salt

so normally if you want a chloride it is better to start with an aromatic diazonium chloride if you want a bromide it is better to start with an aromatic diazonium bromide and

so on now the reaction with Cu_2X_2 normally proceeds to a radical mechanism the mechanism is quite complex copper the presence of copper one metal ion in this case is to make sure that this reaction happens quite feasibly these two reactions which can give us chloro or bromo arranged are called sandmeyer reaction

so sandmeyer's reaction is the preparation of chlorobenzene or bromobenzene or chloroarene or bromoarene starting from the corresponding primary amines through their benzene diazonium salts using a cuprous halide as the reagent for doing this conversion okay now i said that this method can also be used for the preparation

of iodo arrange as well as fluoro arrange but in these cases we do not need the intermediacy of a cupra salt we can directly take a benzene diazonium salt benzene diazonium halide and treat it with potassium iodide

so in this case we would get the corresp the potassium halide where x being the one that was associated with the diazonium salt as an anion

so that comes out along with the nitrogen molecule and we get the corresponding iodo benzene as the product

so in this case because i have used benzene i get iodo benzene as the product

so this reaction does not require copper it is directly treating an i minus with the diazonium salt to get this reaction interestingly this reaction also proceeds through a radical mechanism if you look carefully into the mechanism but it can also be treated as a simple reaction where an n2 molecule goes out generating an aryl cation that reacts with i minus to give you an iodo array now the preparation of the corresponding fluoro arranged from dysonium salts is more straight forward but it would require that we use certain anionic species such as tetrafluoroborate or hexafluorophosphate

so these are boron and phosphorus salt where one extra fluorine is attached to both boron both boron and phosphorus giving us this anionic species b of 4 minus which is called as tetrafluoroborate or pf6 minus which is hexafluorophosphate

so when the dysonium salt has these anions as the counter anions once we heat them what happens is nitrogen molecule is liberated from the species and while that happens this extra fluorine atom that is attached to boron or phosphorus gets added on to the aryl cation giving us fluoro arrange and the by-products that are formed will be nitrogen molecule plus bf3 or pfi depending on which salt we have started with

so this method as you can see is quite efficient and the fact that this can be used for the preparation of both iodo and fluoro arranged unlike some of the other methods which are limited to the synthesis of chloro or bromo compounds ok

so now with this we have a fairly good idea about how some of this halo alkenes or halo arrange can be prepared

so once we know how to classify them you know how to name them you know how to prepare them now it is time that we look at what are their properties and how they can be used

so now going through the physical properties of organo halogen compounds you start off with alkyl halides

so most of the alkyl halides are colorless

so they do not have anything that can absorb light

so as a result alkyl simple alkyl halides if you take they are colorless however bromides and iodides if you keep them for long time carbon bromine and carbon iodine bonds are not very strong we have already seen that in the previous class that carbon bromine and carbon iodine bonds are weak they do not have a very high bond energy

so therefore once they are exposed to light or once they are kept under a condition where they are being heated over a period of time those bonds can break resulting in the formation of bromine or iodine

so these colorless compounds would slowly start to ten start to get this brown darker colors

so effectively they are colorless but they could get color if they start to decompose now most of the alkyl halides that are gaseous or that has a high vapor pressure they have a sweet smell

so if you smell them you would feel that they are good to smell even chloroform which is known to be not a good thing to smell has a pleasantly sweet smell once you inhale them in smaller amounts and in comparison with the corresponding hydro not even the corresponding hydrocarbons

so if you take a hydrocarbon with a particular molecular weight let us say hundred and if you compare it with a halo alkene which also has a molecular weight of roughly around hundred you would always find that the halo alkane has a higher boiling point boiling point than the corresponding hydrocarbon it is because we saw that the carbon halogen bond is polarized and because of polarization they do have better inter molecular interaction

so even if even if they are in solutions even if they are in by themselves as a liquid you would find that they have better intermolecular interactions through dipolar interactions or wonder well interactions and

so on

so they have higher boiling points than the hydrocarbons of exactly the same molecular weight or nearly the same molecular weight now boiling points of alkaline halides of course increases in the order um from fluorine to fluorocommons to idol converts or they decrease in the order ri as i have given here are a greater than rbr greater than rcl greater than rf

so these are this is the order in which their boiling points vary of course when you have these larger atoms present in them their dipole moments and their van der waals interaction which is also associated with the surface area of these molecules are higher

so they have better intermolecular interactions

so normally iodides would have a higher boiling point than bromides chlorides or fluorides now if we take isomers of this compound

so let us say we take a linear isomer and a highly branched isomer

so the linear isomers have better intermolecular interaction and that results in higher boiling points for them

so here i have an example of bromobutane

so if you take normal bromobutane or that is one bromobutane it has a boiling point of 375 kelvin whereas if i take distributing bromide it has a boiling point of 346

so you can see that there is a variation and the variation is in and the highest values are in favor of the linear chains which do have better intermolecular interactions holding them together

so boiling points are also reflected in that particular thing now if you talk about halo arrange not much general information that we can take home and keep in our memory and use but it is ok to say that isomeric halo arrange have similar boiling points other boiling points are normally similar but if you take ah disubstituted compounds that if you assume that there are two substitutions present in them then normally the para isomers can be stacked better in crystals so therefore they do have higher melting point but their boiling points are still comparable with that of the other isomers

so here is an example of dichloro benzene

so if you look at various dichlorobenzenes you would find that for ortho methane para the boiling points are nearly the same

so there is nothing that distinguishes them too much

so although there is minor differences it is not something that we can that is worth remembering

so it is just that they are all in the same range however once we talk about the melting points while ortho and meta isomers have similar melting point the para has a very high melting point it is because the para as you know is very symmetric

so they can stag well in crystal structures

so the they can be ordered well once you want to stack them in a crystal and therefore as a result they do have better interactions in crystal structures and their melting points are normally higher then coming to the density of these

molecules bromo and iodo compounds are extremely dense chloro compounds are denser but not

so much if there is only one chlorine atom present but poly chloro compounds even if we have just two chlorine atoms attached to a methyl group

so that is dichloromethane you will find that it is more dense than water

so if you take water and these halogenated solvents that have either bromine or iodine or more than one chlorine atoms they are more than

so they would go under water

so if you take them in a bowl and make a mixture you will find that water floats on top and these halogenated solvents are at the bottom they are not necessarily soluble in water

so that is why they form two levels

so if you compare the amount of a halogenated compound dissolved in water it is not normally very high

so the solubility of halogenated compounds in water are not

so much

so they are not soluble but they are soluble in most of the organic solvents because these are organic compounds and they can have very good interaction with organic molecules in general

so they dissolve well in organic solvents what happens when we put them in water is water is held together by hydrogen bonding and in an organo halogen compound or a halo alkene or a halo alkane you will find that there is nothing to do a hydrogen bonding with

so effectively we will have to break the hydrogen bondings that are formed in water molecules to dissolve these molecules in them

so that does not normally happen

so therefore they stay insoluble okay

so with this I would go into the chemical properties rather reactions of halo alkanes

so here again I am not going to the reactions of halo alkenes and halo alkanes in one go instead what I am going to do is discuss their reactions separately

so first I will discuss the reaction of halo alkenes then I will go on to discuss the reaction of halo alkanes they do have different patterns of reaction

so starting with the reactions of halo alkanes you will find that the most discussed reaction of a halo alkane the one that is of most synthetic value to an organic chemist is nucleophilic substitution reactions

so as the name suggests these are reactions that means we have a compound we substitute a part of this compound with something else and because we are talking about halo alkanes here the halogen atom is the one that is being substituted with something else and what is it that is used for substituting the halogen atom is a nucleophile

so these are therefore called nucleophilic substitution reactions as I have shown here

so nucleophile is a species that is normally negatively charged that means they are anions or they could also be neutral compounds with a high density of electrons present in them

so for example if you take ammonia which is a neutral molecule but you know that there are lone pairs of electrons on nitrogen

so therefore ammonia is a nucleophile it has those electrons that are ready to react with positively charged compounds

so nucleophile simply means something that likes nucleus and nucleus is positively charged

so any species that likes to interact with positively charged nuclei are called as nucleophiles

so nucleophilic substitution reactions are substitution reactions where a nucleophile is used to replace a particular compound a particular moiety from a react from an organic molecule

so in this case we are talking about the reaction of haloalkanes

so have a look at the reaction that i have on the screen here

so you can see that there is a carbon x bond and this bond we have already discussed while discussing the nature of carbon halogen bonds that the carbon has a positive charge and the halogen has a negative charge

so this bond is polarized now the nucleophile with is negatively charged with its electrons would come and react with the positively charged carbon atom that is shown in blue here

so it would react with the carbon atom giving us a new compound where they have a carbon nucleophile bond

so the nuclear foil could be anything we will look at example soon

so it would form a new carbon nucleophile and the halogen atom now completely takes the electrons that it was sharing with carbon and goes out as an x minus

so we have one negatively charged species to start with that is a nucleophile and in the product mixture we have a halide ion that has come out

so as i have said nucleophiles can be anions or they can be neutral electron rich molecules

so they have to if they are neutral they have to be electron rich if the molecule is not electron rich then they cannot be a nucleophile ok

so now i told you that these are some of the most useful synthetic reactions

so to emphasize on that point to demonstrate those points better i have some examples here

so a general reaction general nucleophilic substitution reaction can be given as $R-X$ where x is the halogen atom r is the alkyl group when you treat with the nucleophilic reagent we get $R-Nu$ and x comes out

so this is the reaction RX can give you RNu

so now let us have a look at various nucleophilic reagents and the products that can be formed

so if you use sodium hydroxide or potassium hydroxide

so these are anionic nucleophiles where sodium is positively charged and hydroxide is the negatively charged nucleophile

so when we treat an alkyl halide with sodium hydroxide or potassium hydroxide we would get the corresponding alcohol

so the OH^- replaces the halogen atom we can also do the same reaction with water water in this case is a nucleophile but it is not an anionic nucleophile it is a neutral molecule but because of the presence of lone pairs on oxygen it is a nucleophile

so water can also do the same reaction and in that case two we get alcohols as the product we could also use a sodium alkoxide

so that means you take methanol replace the h from methanol and put a sodium there then we get $CH_3O^- Na^+$

so these class of compounds are called alkoxides which are all the metal salts of alcohols

so if you treat an metal alkoxide with an alkyl halide there again sodium chloride sodium bromide would come out the corresponding sodium halide would come out and we would get an OR attached to the alkyl group and these are ether

so you would learn about these molecules in a different unit in your textbook so we would get ethers as the product similarly i started off by telling about ammonia which is a nucleophile

so if you treat ammonia with an alkyl halide we get the corresponding amine

so $H-X$ comes out in these cases ammonia is a neutral molecule

so we get RNH_2 and amine is the product now in the second part of this table in the second set of columns that I have here I have rather interesting nucleophiles

so first of them is potassium cyanide KCN

so potassium cyanide you have already had of that particular molecule I'm sure

so when you treat potassium cyanide with the haloalkane the product is an alkyl cyanide it's also called nitriles

so you get a nitrile as the product

so an alkyl halide reacting with cyanide C^- and N^- gives you the corresponding alkyl cyanide or nitrile alkyl nitrile

so now ah the same reaction instead of potassium cyanide if I do with silver cyanide AgCN

so you can see that the difference is only in the metal that is used

so potassium cyanide or silver cyanide but in this case the product is not a cyanide it is an isocyanate and you would also see that I have drawn it with an RNC I draw it as RNC not as RCN and cyanide is CN^-

so if I have to draw how these nucleophiles look I would be able to say that a cyanide anion is C^- and N^- now the negative charge here is centered on the carbon atom

so if I have to draw the cyanide anion I will be able to draw this with the triple bond between carbon and nitrogen and a negative charge on the carbon atom

so this normally is in it has another resonance structure that can be written like this with the negative charge on nitrogen and the carbon having a lone pair

so cyanide anion has these two particular forms in which they can be written

so this is to say that the negative charge is centered either on carbon or on nitrogen

so once we have cyanide anion reacting with an alkyl halide as a nucleophile

so the nucleophilicity of cyanide ion is in such a way that the most stable bond forms

so generally a carbon carbon bond is more more stable to form

so if you take cyanide anion and react with alkyl halide will always get the cyanide but if silver cyanide is used the silver cyanide bond the carbon silver bond is not ionic

so therefore what happens is when we put in silver cyanide in a solution the Ag^+ and CN^- doesn't come off instead there is always this covalent bond between silver and carbon

so it is partly partially covalent

so silver always remains associated with the carbon atom therefore ah the negative charge on the nitrogen atom at the other end of the cyanide anion would be able to react as a nucleophile nitrogen always has its lone pair

so we can see that in this structure I have put this lone pairs on this one

so let me just highlight those

so you would find that I have these lone pairs on sign on the nitrogen atom

so if the silver atom is attached to the carbon atom strongly then the lone pair on nitrogen will start to react as the nucleophile and as a result we get a product where the alkyl group is attached to the cyanide through nitrogen and that is called an isocyanate or an isonitrile

so with the same nucleophile literal means for practical concepts you can assume that it is the same nucleophile but it has two different centers of reaction and these kind of nucleophiles are called ambident nucleophiles

so an ambident nucleophile is something that has a negative charge that is shared between two atoms of different kind

so in this case a carbon and nitrogen

so the reaction can be through the carbon atom or through the nitrogen atom depending on the reagents that are being used or sometimes depending on the conditions that are being used another of that class is the nitrite anion

so if i take potassium nitrate which can be written as again i will try to write that a nitrate anion is o minus attached to nitrogen and an n plus o

so this nitrogen has lone pairs

so this potassium nitrate would be like this with k plus at uh associated with the negatively charged oxygen and then the nitro group now if you use KNO_2 as a nucleophile then it is always the minus charge on the oxygen that is acting as the nucleophilic atom and it goes and forms a carbon oxygen bond if i use silver nitrate in that case the c-o bond remains strong

so therefore the reaction again just like in the case of isocyanate happens through the lone pairs that are present on nitrogen atom and as a result the reaction would be happening from here

so then we get a carbon nitrogen bond in the product and those compounds are called nitro alkynes

so if a carbon nitrogen bond is present in a compound that is NO_2 as the substitution then we call them as nitro alkanes another case they are alkyl nitrate

so this table as i have shown just tells you how useful are nucleophilic substitution reactions are because we can use not only that we can put various groups onto an alkyl group by doing nucleophilic substitution reactions sometime we can use the same class of nucleophiles but react them through different atoms and get different products

so this is a very synthetically useful reaction

so therefore it is also important that we study this reaction in more detail

so nucleophilic substitution reactions are very useful

so let us have a closer look at them

so there are two kinds of nucleophilic substitution reactions that we can do on a halo alkane the first of its class is shown here is a substitution nucleophilic bimolecular

so this reaction is normally shown as $\text{S}_{\text{N}}2$ reaction

so $\text{S}_{\text{N}}2$ means s stands for substitution n stands for nucleophilic and two stands for bimolecular

so i have an equation here a reaction sequence that is written here with structures

so this pretty much sums up what exactly this reaction is

so in the example that i have chosen i have taken a hydroxide anion which is the nucleophile reacting with chloro methane

so it is the carbon atom that is attached to three hydrogen atoms and a chlorine atom and now the reaction proceeds in such a way that the hydroxide anion reacts with the carbon forming an intermediate forming a transition state that is not an intermediate in one step

so the whole reaction happens in one step where initially the carbon chlorine bond starts to weaken and a carbon oxygen bond starts to form and we get a transition state like this which then collapses into products where a new carbon oxygen bond is formed and Cl^- comes out now why do we call this as an $\text{S}_{\text{N}}2$ reaction is the react

so this whole mechanism can be summarized into a few points

so i would read out those points for you

so the reaction follows second order kinetics

so if a nucleophilic substitution reaction follows second order kinetics that means if the order of the reaction depends on the concentration of the halo

alkene as well as on the concentration of the nucleophile then that is a bimolecular reaction that is an $\text{S}_{\text{N}}2$ reaction otherwise in an $\text{S}_{\text{N}}2$ reaction the rate of the reaction depends on the concentration of the nucleophile as well as the concentration of the haloalkane it is a single step reaction there are no intermediates formed there is only a transition state and the transition state the carbon atom is bonded to the nucleophile and the halogen atom

so in this case the halogen atom is called as a leaving group because this is the group that leaves

so the nucleophile the carbon atom is bound equally to the nucleophile as well as the leaving group in the transition state of the reaction and in the transition state we can assume that the carbon atom is penta coordinate that means it has five atoms attached to it three hydrogen atoms that we started with which are present in the methyl group then the chlorine atom and the nucleophile all of them are bonded to carbon giving a penta coordinate carbon atom and also this reaction happens with inversion of configuration

so just to tell you what exactly do i mean by inversion of configuration i would use some models to show you how this reaction works

so you can assume a halo alkene to be like this

so this is let us assume that this is chloro methane and imagine that the blue colored atom here

so this blue colored atom here that i have shown in this model is chloride then the black one is carbon and it is attached to three hydrogen atoms

so this is chloro methane for you

so you can see that this is tetrahedral

so if you look at the model i can rotate it for you

so you feel that this is a tetrahedral carbon atom all the bond angles are 109.5° degrees

so now how does a nucleophilic substitution reaction happen is you would have this halo alkene chloromethane in this case then the hydroxide anion which is red in color starts to approach from the back side of the carbon chlorine bond

so always this attack in an $\text{S}_{\text{N}}2$ reaction the approach of the nucleophile is from the back side of the carbon halogen bond

so once it starts to approach from this direction you would start to see that this particular bond between the halogen and the carbon atom starts to weaken

so this nucleophile approaches it starts to form a bond

so as there is a new bond starting to form this bond starts to weaken and when this bond starts to weaken what also happens is these two three hydrogen atoms which are slightly pointed in this direction starts to flatten out

so we would reach a stage where the carbon atom is equally bonded to the blue atom that is halogen and the red atom with all these three hydrogens being in one plane

so this is the penta coordinate structure that i was talking about

so if you look at the screen again where i have this molecule you will see that in this particular part what i have is a planar species where there is one carbon atom and three hydrogen atoms attached

so you could also assume that in this particular carbon atom is sp^2 hybridized with three hydrogen atoms in one plane and there is a p orbital now let us assume that the nucleophile and the halogen atom are bonded to the two lobes of the p orbital

so that is how this transition state has to be viewed and now

so this was our starting material

so what happens is the nucleophile comes from the back side reacts with it forms a new bond and then we get a product that looks like this

so this was the starting material we had chlorine on one side and now the

nucleophile has come and it almost comes from the back side

so if the starting material look like this if the halo alkene look like this the product looks like this with the new carbon oxygen bond being exactly in the opposite direction

so what you can imagine is if you assume this to be an umbrella where i hold here and this if you assume today the part of the umbrella after the reaction i get a product that looks like this

so this is as if your umbrella has undergone an inversion in wind

so this therefore we normally say that a substitution nucleophilic bimolecular reaction happens with an inversion of configuration this is as if an umbrella has inverted during the course of the reaction

so these are the main features of a nucleophilic substitution reaction now let us look at this reaction a little more closely

so what i have in this particular screen here a methyl group a halomethane a halo ethane an isopropyl halide and a tertiary halide undergoing a reaction

so the point i want to stress here is because substitution nucleophilic reaction has this very strange transition state where a carbon is attached to five different atoms

so in this transition state the bulk around a carbon atom plays a lot of role and also the approach of the nucleophile towards the carbon atom also is limited by what is present on the carbon atom

so we look at a methyl group that i have in the first structure here you see that a methyl has three hydrogen atoms and when the nucleophile is approaching this it only feels these three hydrogen atoms hydrogen atoms are extremely small

so the nucleophile has no problem in approaching this carbon atom and starting to form the new bond once they go into an ethyl group the nucleophile almost approaches the same way but one of the hydrogen atom is now replaced with the methyl group with an alkyl group

so therefore the repulsion between the nitrogen and the alkyl group the steric crowd that the nucleophile is starting to feel is quite higher

so therefore the nucleophile will not be able to reach closely enough onto the carbon atom to form this bond very effectively

so as a result this reaction is slower and once they have an isopropyl group there are two alkyl groups

so the reaction is even slower and if i have tertiary butyl group then there are three alkyl groups

so therefore the nucleophile cannot even approach the carbon atom

so these numbers that i have written here

so i have 30 written here i have 1 here i have 0.

02 and a 0 written here

so these numbers actually represent the relative rates of this reaction

so if you assume that a methyl halide undergoes nucleophilic substitution with the rate of 30 the corresponding rate of an ethyl halide would be only one and that of an isopropyl halide is 0.

02 and that of a tertiary butyl halide is just 0.

so this tells you that the rate of these reactions are largely dependent on the bulkiness of the carbon atom the bulkiness of the groups that are around a carbon atom and the least substituted a carbon atom and the rate of an S_N2 reaction is faster and as we keep on adding substitutions on this the reaction becomes slower

so there are very many things that is associated with this S_N2 reaction it is a bimolecular reaction it depends on the concentration of the nucleophile and also on the concentration of the alkyl halide that is being used it depends on

the structural features of the alkyl halide because the bulkier alkyl halide will not be able to have an initial bond starting to form between the carbon and nucleophile

so therefore primary alkyl halides react faster than secondary which react faster than tertiary and a methyl halide or a halomethane reacts the fastest because it does not have any sorts of steric crowding around the carbon atom so it reacts the fastest

so these are the representative reactions now if you would also like to think about what kind of solvents can be used for this reaction remember this particular point that anything that can dissolve an anion can be a good solvent

so what we would need we would need a solvent that can dissolve these anions so normally polar solvents are required then we also do not want these anions to be highly solvated

so we do not want solvents that have hydrogens present in them like alcohols for example

so normally polar aprotic solvents are the ones that are used for nucleophilic substitution reactions

so these are solvents that are polar but do not have a proton attached to an electronegative atom

so that the anion can be solvated

so we want solvents in which the nucleophile is rather bare and not at all solvated

so with this i would stop today and we would continue to discuss the second class of nucleophilic substitution and the coming class and their stereochemical features as well

so thank you very much you