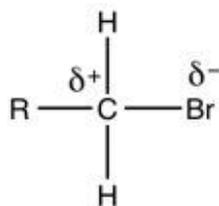


Nucleophilic Substitution

[Click here for elimination](#)

Halogenoalkanes

A halogenoalkane has a **polar** carbon-halogen bond as shown below due to differences in electronegativity. The carbon atom with the δ^+ is open to attack by nucleophiles.



the main reaction of halogenoalkanes is **nucleophilic substitution**

What is a nucleophile?

*an **electron pair donor** that is attracted to areas of low electron density*

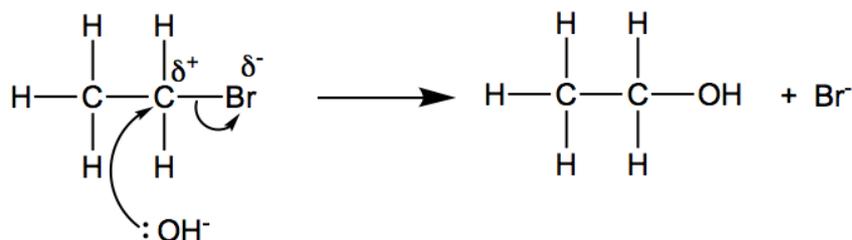
A nucleophile has either a full negative charge such as CN^- or a lone pair as in water or ammonia.

The main nucleophiles for AS are: CN^- , OH^- , NH_3

- ✓ for the negatively charged nucleophiles, the reagent (the thing you start with) for CN^- is usually KCN and for OH^- , something like NaOH. With H_2O and NH_3 , both are the nucleophile and the reagent.

Nucleophilic Substitution Mechanism

The reaction mechanism for nucleophilic substitution is much easier than for [electrophilic addition](#). It's just one easy step:



The lone pair on the OH^- is attracted to the positive charge on the carbon atom (remember negative goes towards positive).

- ✓ Note that the lone pair is on the O, even though the minus is on the H. It's just more convenient to write the minus on the H but make sure the lone pair and arrow come from the O.

A second arrow is then required to remove the Br as Br⁻ by breaking the C-Br bond. Just remember that the halogen atoms 'like' to leave as the halide ion; they 'want' to have the minus charge as they are quite electronegative elements.

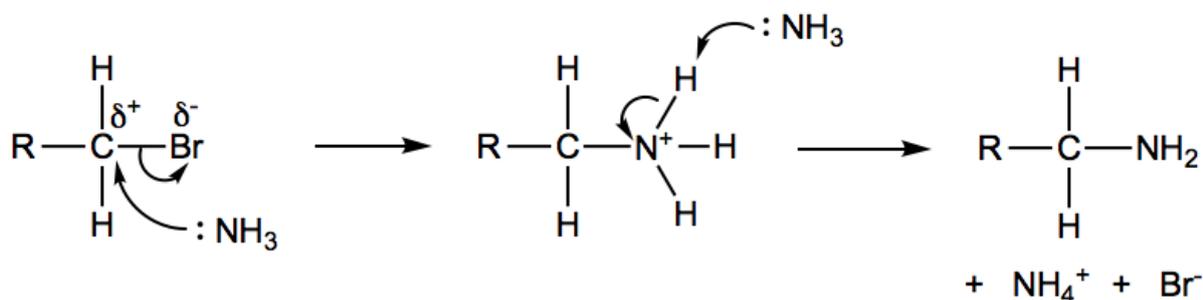
- ✓ Beware that when using CN⁻, it is a **carbon** nucleophile (lone pair on the C) and a **new carbon-carbon bond** is formed (increases the chain length by 1 carbon). Sometimes students get confused as the minus sign appears to be on the nitrogen but it's just written that way for convenience.
- ✓ OH⁻ in water is a favourite nucleophile, which does the same mechanism as CN⁻ above. Compare it to the elimination reaction in the [elimination](#) tutorial.

NH₃ (or H₂O) Nucleophiles

If you did the same reaction with water or ammonia, then an **extra** step is involved.

As we are starting with a **neutral molecule**, we need to put a positive charge on the N or O to show that we have used the lone pair (see the 2nd structure below).

We have to then lose a hydrogen atom attached to the N to neutralise the charge. Usually another NH₃ molecule will swoop in to do this:

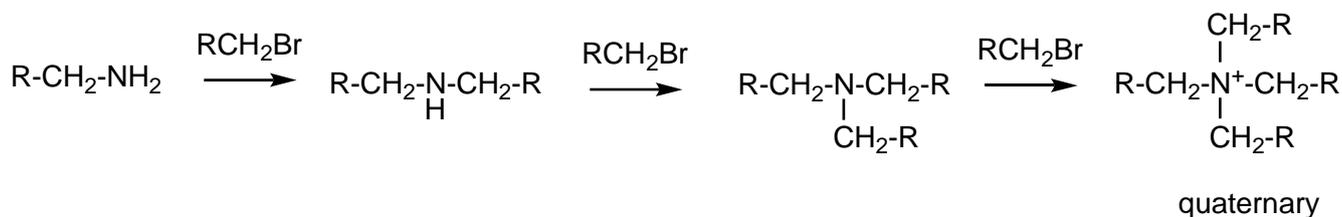


- ✓ This is the same sort of discussion as in the [electrophilic](#) tutorial. To see what is going on you need to draw dot and cross diagrams. Remember the + means N has **lost one electron** in comparison to how many it usually has. It's in group 5 so it should have 5 involved in bonding. It is using its lone pair (2 electrons) but the electrons are being shared with the C, so think of one of those electrons now belonging to the C; therefore technically N has only lost one electron. I know it's a bit confusing.

Further Substitution

After adding NH₃, as in the example above, an amine is formed which still has a lone pair of electrons. This means that the amine formed can react again with another halogenoalkane. This can continue until the N has no lone pairs left.

The final product is a **quaternary ammonium salt** where the N has a + charge on it.



Just losing an H from the N and adding on the R-CH₂ group until we get to the quaternary structure.

Rate of hydrolysis

Hydrolysis: *the breaking of a bond by the addition of a small molecule.*

In the example above, the **breaking of the C-Br** bond is an example hydrolysis.

This type of bond breaking is known as heterolytic fission i.e. two different fragments are produced.

A favourite question is to change the halogen and to ask which bond would break the fastest or which reaction has the fastest rate or which has the fastest rate of hydrolysis (they all mean the same thing).

The order from fastest to slowest:



This is simply because the **C-I bond is weakest** and is therefore the easiest to break.

They might give you a table with the bond enthalpies but you are just talking about the same things. It shows that the C-I bond is weakest and therefore breaks first, therefore the reaction is fastest.

	C-I	C-Br	C-Cl	C-F
Bond enthalpy (kJ mol ⁻¹)	+238	+276	+338	+484

The bond strength is just down to the **size of the halogen**. Iodine is biggest and therefore the electrons in the bond are further from the nucleus → less attraction.

Polarity

The other factor that affects the reactivity is the polarity of the carbon-halogen bond. As C-F is the most polar, the carbon will have a strong δ⁺ charge and will attract the nucleophile more than the other halogens would, which should increase the rate of hydrolysis. This contradicts our theory above.

But, the **bond strength** is the **more important factor** when explaining why C-I is hydrolysed fastest. I wouldn't talk about polarity here unless they ask about it.

Monitoring the reaction

There have been several questions on experiments to do with the rate of hydrolysis of halogenoalkanes.

It is quite simple. To monitor the rate of hydrolysis you have to measure something. This is done in two steps:

1. The halide ion must firstly be substituted from the haloalkane to get the halide ion free in solution. This is just a normal nucleophilic substitution reaction. The halogenoalkanes are insoluble in water so **ethanol** is added as the solvent (to dissolve them). Water acts as a nucleophile to do the substitution.
 2. Add **AgNO₃** to react with the displaced halide ion. This is now the usual [halide ion test](#) as done in the Group 7 topic. AgNO₃ reacts with the halide ion to give precipitates: AgCl (white), AgBr (cream) and AgI (yellow). You are looking to time how long it takes for the precipitates to form and therefore which forms quickest is the fastest rate i.e. from the iodide.
- ✓ OH⁻ is not used as a nucleophile in this experiment. It is a powerful nucleophile and the reaction happens too quickly to give meaningful results. **Water** is used as it is a much weaker nucleophile and the reaction occurs more slowly giving us a chance to distinguish between the precipitates.

[Click here for elimination](#)