

CIE Chemistry A Level

16 : Halogen Derivatives Notes



Halogenoalkanes

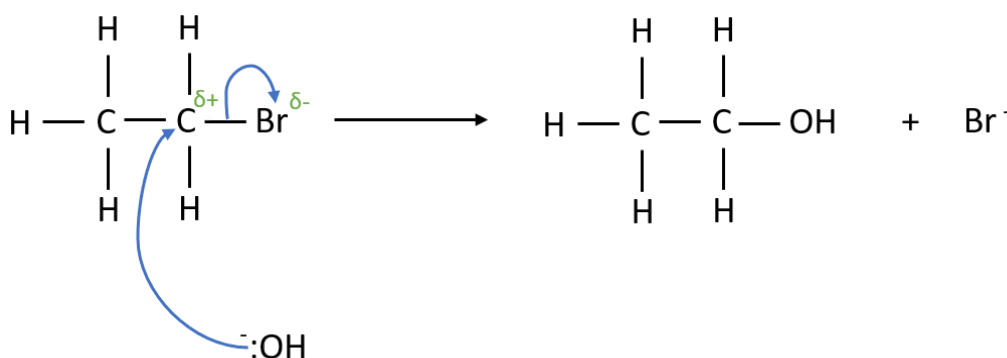
Halogenoalkanes are alkanes which contain a **halogen atom** covalently bonded to a carbon atom. When naming halogenoalkanes, the **prefix of the halogen** (fluoro-/chloro-/bromo-/iodo-) is put before the alkane name with a number to indicate which carbon the halogen is bonded to. For example 1-bromopropane, 3-chlorohexane and 2-iodopentane.

Nucleophilic substitution

The carbon-halogen bond in halogenoalkanes is **polar** because there is a large difference in **electronegativity** of these atoms. Halogens (particularly chlorine and fluorine) are much more electronegative than carbon meaning that the bonding pair of electrons is drawn towards the halogen. The polarity of this bond makes it **relatively easy to break**. When the bond breaks, a **positive carbocation intermediate** is formed which attracts nucleophiles. **Nucleophiles** are species that **donate electrons**. Common nucleophiles include: OH^- , CN^- and NH_3 .

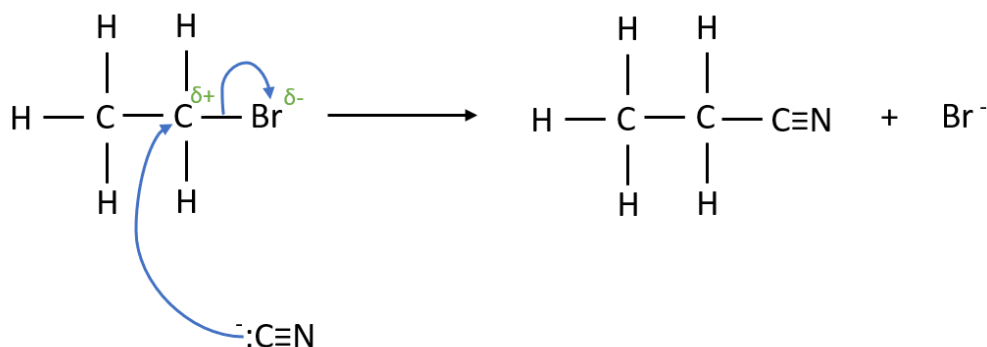
Hydrolysis

Hydrolysis occurs when a halogenoalkane undergoes nucleophilic substitution with a **hydroxide**. For example bromoethane reacts to form ethanol. **Warm aqueous sodium or potassium hydroxide** is required:



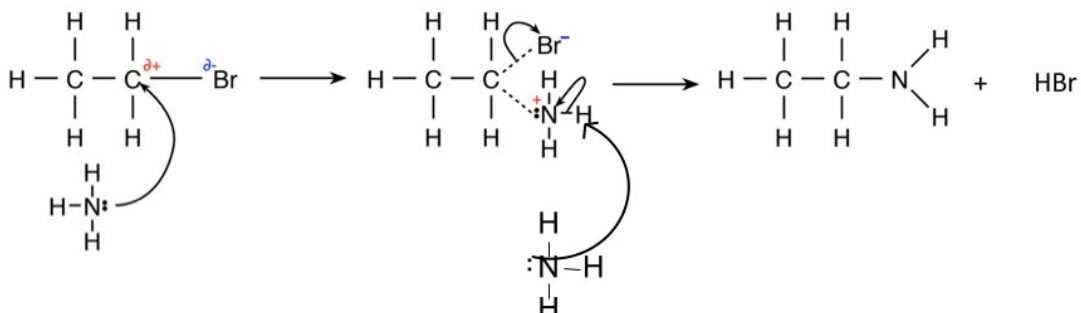
Formation of nitriles

Nitriles are formed when a halogenoalkane reacts with **cyanide**. The reaction requires **warm, ethanolic potassium cyanide** (ethanolic means dissolved in ethanol).



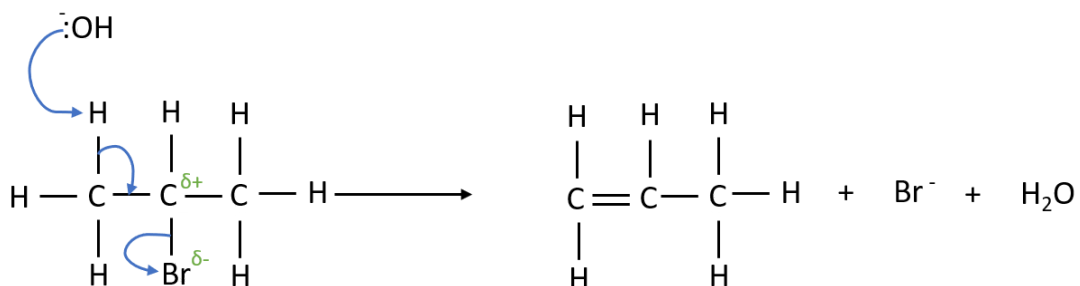
Formation of primary amines

Primary amines are formed when a halogenoalkane is **warmed with excess ethanolic ammonia**.



Elimination

Halogenoalkanes can also undergo an **elimination** reaction when they are **heated under reflux with ethanolic hydroxide ions**. The hydroxide ions can't be dissolved in water as this would cause hydrolysis to occur.



S_N1 and S_N2 mechanisms

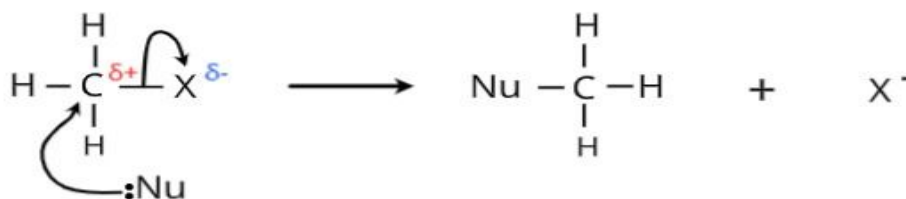
S_N1 and S_N2 reactions are both types of **nucleophilic substitution**. In these reactions, a nucleophile replaces a leaving group.

It is easier to understand if we look at S_N2 first:

S_N2

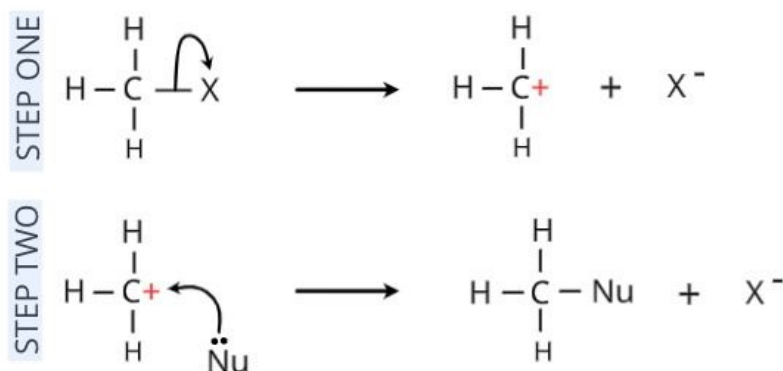
These reactions are a **one step mechanism**. The nucleophile attacks the substrate at the same time as the leaving group leaves the substrate. The **nucleophile attacks the carbon** atom from the **back side**, causing an **inversion** of the groups in the product. The nucleophile attacks from the backside because the large **halogen atom prevents the attack from the other direction**.

In the diagram below, :Nu is the nucleophile and X is a halogen:



S_N1

These reactions are **two step mechanisms**. This type of reaction takes place in **tertiary** and some **secondary** halogenoalkanes. If the nucleophile is unable to attack the back of the carbon atom (for example if it is blocked by larger atoms / groups such as -CH₃) a **carbocation intermediate** is formed. The first step in the process is generating the carbocation intermediate and the second step is the attack of the nucleophile on the carbocation to form the product.



Primary halogenoalkanes - S_N2 mechanism

Secondary halogenoalkanes - S_N1 and S_N2 mechanism

Tertiary halogenoalkanes - S_N1 mechanism



Effects of alkyl groups on reactivity

The halogenoalkane reactivity trend for S_N1 is: **tertiary > secondary > primary**.

This is because alkyl groups have a **positive inductive effect** which helps stabilise the carbocation. This makes the tertiary carbocation most stable and therefore the most likely to form.

The halogenoalkane reactivity trend for S_N2 is: **primary > secondary > tertiary**

This is due to **steric hindrance** which is caused by side chains on the molecule preventing a reaction occurring. Tertiary halogenoalkanes are less reactive because the alkyl groups prevent the nucleophile attacking the back side of the carbon so substitution doesn't occur.

Relative strength of C-Hal bond

Reactivities of halogenoalkanes

The **reactivity** of a halogenoalkane **depends on the strength of the carbon-halogen bond**. For a reaction to take place, the carbon-halogen bond needs to be broken. The **weaker the carbon-halogen bond** is, the **more reactive** the halogenoalkane.

C-F has the **highest bond enthalpy** and so is the strongest carbon-halogen bond. This makes fluoroalkanes the least reactive of halogenoalkanes so they **react slowest**.

C-I has the **lowest bond enthalpy** so is the weakest carbon-halogen bond. This makes iodoalkanes the most reactive of halogenoalkanes so they will **react fastest**.

Carbon-halogen bond enthalpy decreases down the group, so **reactivity increases**.

Fluoroalkanes and fluorohalogenoalkanes

Fluoroalkanes contain carbon and fluorine only. Fluorohalogenoalkanes contain carbon, fluorine and hydrogen only.

Fluoroalkanes and fluorohalogenoalkanes are **chemically inert**. The **C-F bond is very strong** and requires a lot of energy to break, making the compounds very unreactive.

Uses of fluoroalkanes and fluorohalogenoalkanes:

- Refrigerants
- Propellants for aerosols
- Solvents for dry cleaning
- Making expanded polystyrene



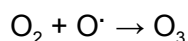
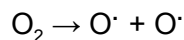
Chlorofluoroalkanes and the ozone layer

Chlorofluoroalkanes are compounds which contain chlorine, fluorine and carbon only.

Damage to the ozone layer:

Ozone (O_3) is a layer in the upper atmosphere which **absorbs a lot of UV radiation** from the sun, preventing it from reaching us. It is a crucial part of the atmosphere that prevents people getting too much **sun damage**.

Ozone is formed when an **oxygen molecule reacts with an oxygen free radical**. Oxygen free radicals are produced from another oxygen molecule in the presence of UV light.



Chlorine free radicals are formed in the upper atmosphere when CFCs are broken down by UV radiation:



Chlorine free radicals react with ozone and **break it down into oxygen**. This creates holes in the ozone layer.

