

CAIE Chemistry A-level

15: Halogen Compounds Notes

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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.

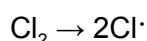
Formation of Halogenoalkanes

Free radical substitution

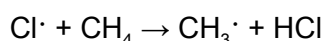
This mechanism requires a **free radical** (a particle with an **unpaired electron**). A free radical is denoted by having a dot next to the chemical symbol, e.g. $\text{Cl}\cdot$. There are three stages to free radical substitution: initiation, propagation and termination.

Example: The reaction of methane with chlorine

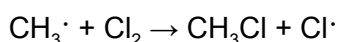
Initiation - Free radicals are produced. UV light is required to split the covalent bond in Cl_2 and form two chlorine atoms each with an unpaired electron (free radicals):



Propagation - The free radicals are used up and recreated in chain reactions:

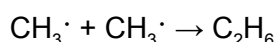
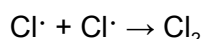
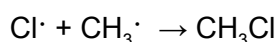


A methyl radical, $\text{CH}_3\cdot$, is produced which reacts with Cl_2 to produce more radicals.



These reactions continually occur in a chain until the termination stage.

Termination - All the free radicals are completely used up. When two radicals react, they form a covalent bond. Several termination reactions can take place:



Electrophilic addition

The electron dense double bond in an alkene is susceptible to attack from electrophiles. This leads to electrophilic addition reactions which can lead to the formation of halogenoalkanes.

Addition with halogens:

When alkenes react with halogens, covalent bonds form between the halogen atoms and the carbons on either side of the double bond, producing a di-halogenoalkane. The mechanism is called electrophilic addition and can be seen in 'Electrophilic addition' on the following page.

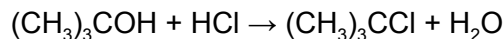
Addition with hydrogen halides:

A hydrogen halide is polar due to the difference in electronegativity between hydrogen and the much more electronegative halogen atom. This polarity means both the hydrogen and the halide bond to carbon atoms in the alkene, forming a halogenoalkane.

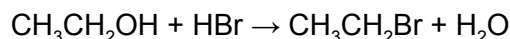


Substitution of alcohol with hydrogen halide

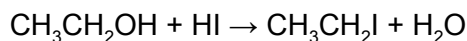
- **Primary** and **secondary** alcohols react **very, very slowly** with **hydrogen chloride**, HCl. **Tertiary** alcohols react rapidly with concentrated hydrochloric acid at room temperature:



- **Hydrogen bromide** reacts with alcohols. Typically the alcohol is treated with **potassium bromide** and **concentrated sulfuric acid** as these two reactants will produce hydrogen bromide:



- **Hydrogen iodide** reacts with alcohols. Typically the alcohol is treated with **potassium iodide** and **phosphoric(V) acid**. Phosphoric(V) acid is used in this reaction instead of **sulfuric acid** as sulfuric acid will readily **oxidise the iodide ions** to iodine.



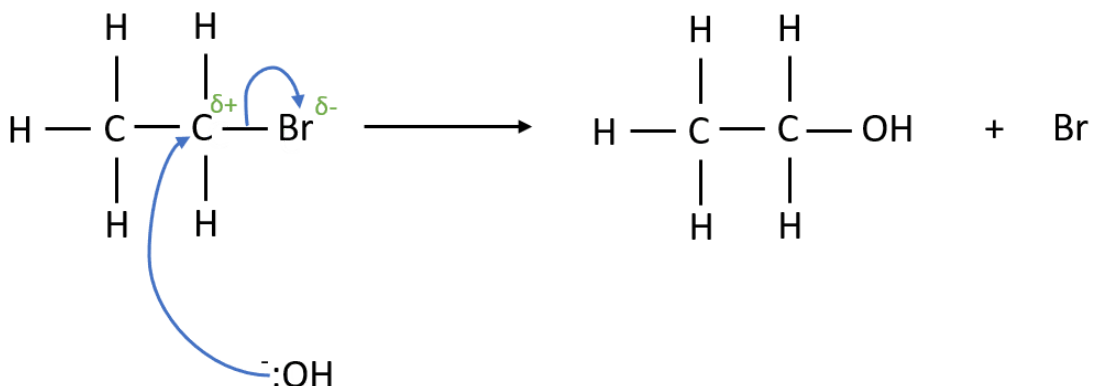
Nucleophilic Substitution of Halogenoalkanes

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 donate electrons**. Common nucleophiles are: OH^- , CN^- and NH_3 .

Hydrolysis

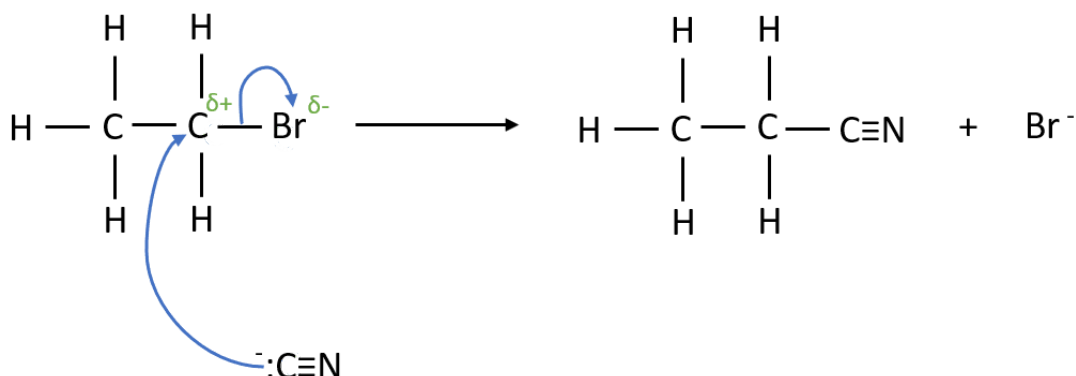
Hydrolysis occurs when a halogenoalkane undergoes nucleophilic substitution with a **hydroxide**.

For example bromoethane reacts to form ethanol. **Warm aqueous sodium hydroxide** is required:



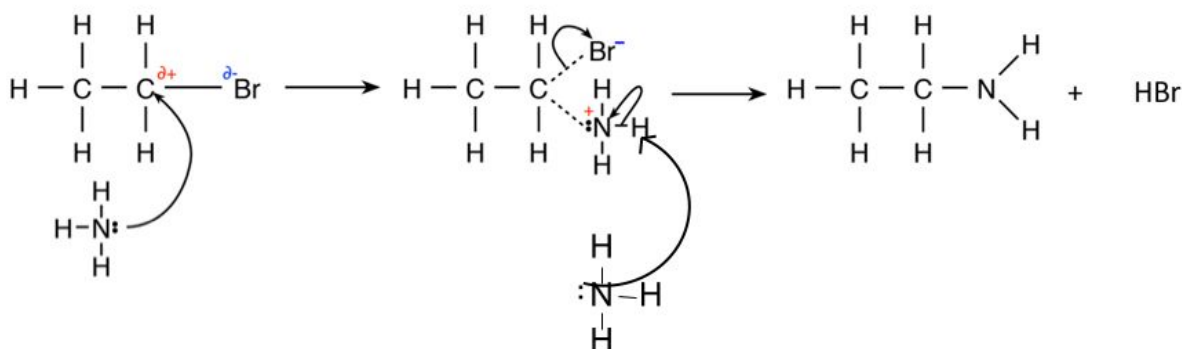
Formation of nitriles

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** under pressure.



Test for Halogenoalkanes

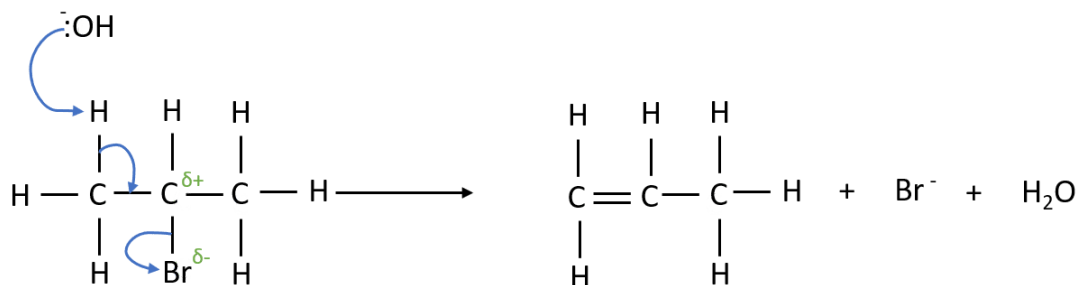
First the halogenoalkane is heated with some sodium hydroxide in a mixture with some ethanol and water. This is then acidified by adding nitric acid, which prevents unreacted hydroxide ions from reacting with the silver ions which would give a false positive precipitate. As these precipitates are often hard to distinguish, adding ammonia can help to confirm the result.

	Silver Nitrate (In ethanol)	Dilute NH ₃	Concentrated NH ₃
Cl-	White precipitate	Precipitate dissolves	Precipitate dissolves
Br-	Cream Precipitate	Precipitate remains	Precipitate dissolves
I-	Yellow precipitate	Precipitate remains	Precipitate remains



Elimination of Halogenoalkane

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 would occur.



S_N1 and S_N2 Mechanisms

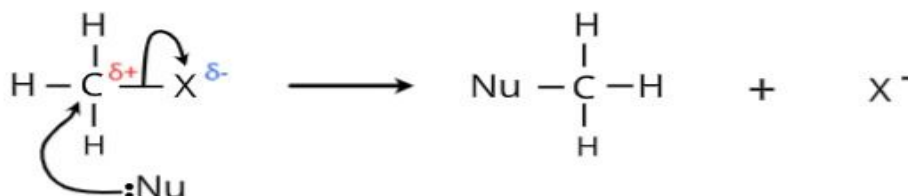
S_N1 and **S_N2** reactions are both types of **nucleophilic substitution**. In these reactions, a nucleophile replaces a leaving group.

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**.

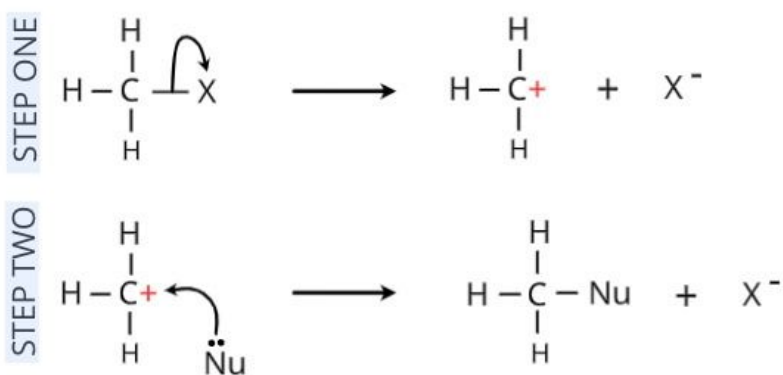
In the diagram below, :Nu is the nucleophile and X is a halogen:



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. The following diagram demonstrates the two steps:





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

