CIE AS Chemistry

Your notes

15.1 Halogenoalkanes

Contents

Producing Halogenoalkanes

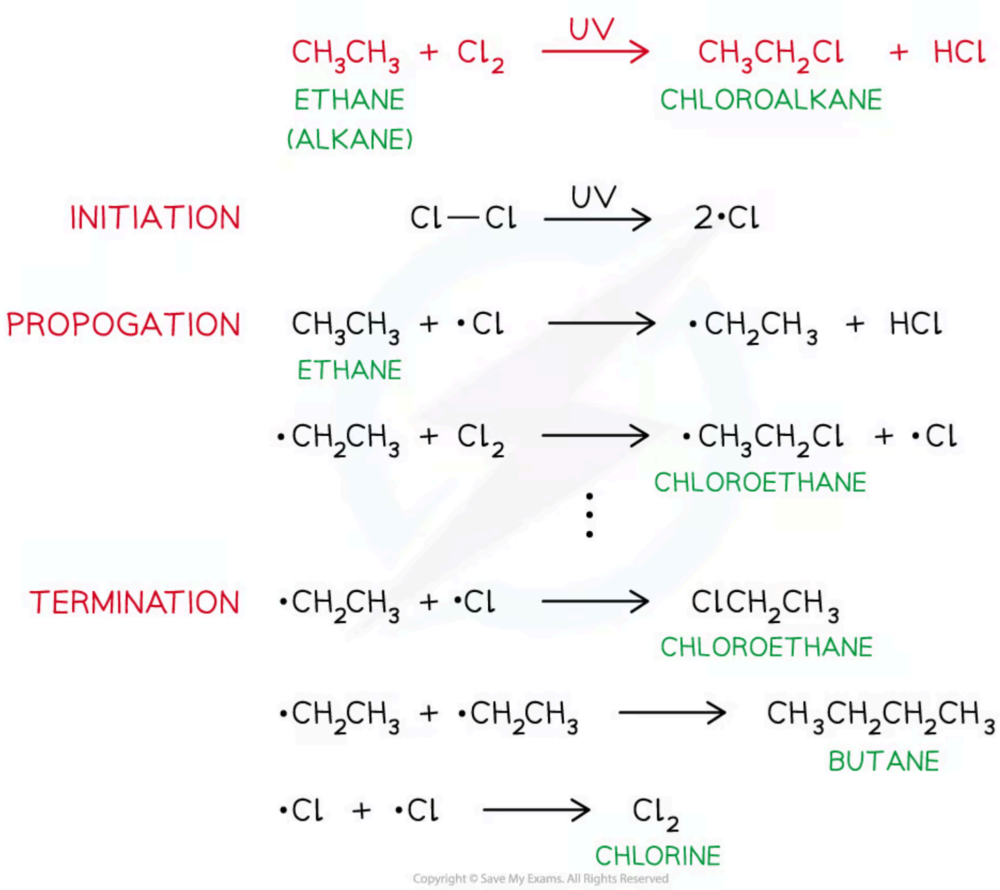
Production of Halogenoalkanes: Substitution & Addition Reactions

- **Halogenoalkanes** are alkanes that have one or more halogens
- They can be produced from:
  - **Free-radical substitution** of **alkanes**
  - **Electrophilic addition** of **alkenes**
  - **Substitution** of an **alcohol**

Free-radical substitution of alkanes

- Ultraviolet light (UV) is required for the reaction to start off
- A **free-radical substitution reaction** is a three-step reaction consisting of initiation, propagation and termination steps
- In the **initiation step,** the halogen bond is broken by energy from the UV light to produce two radicals in a **homolytic fission** reaction
- The **propagation step** refers to the **progression** (growing) of the substitution reaction in a **chain type reaction**
- The **termination step** is when the chain reaction **terminates** (stops) due to two free radicals reacting together and forming a single unreactive molecule

Free-radical substitution reactions of alkanes

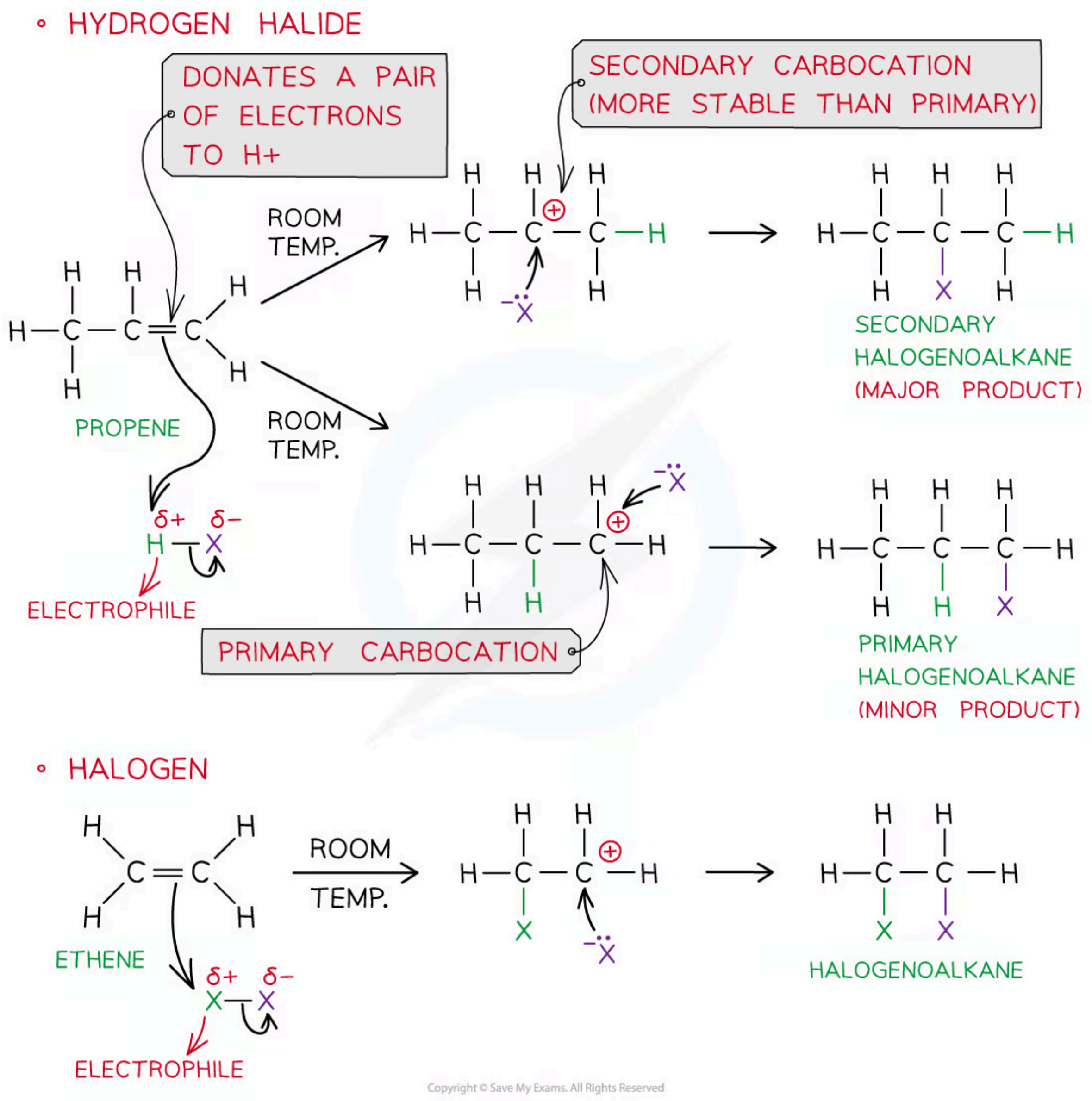


Free-radical substitution reactions of alkanes produce halogenoalkanes

Electrophilic addition

- Halogenoalkanes can also be produced from the addition of **hydrogen halides** (HX) or **halogens** (X_2) at **room temperature** to alkenes
- In hydrogen halides, the hydrogen acts as the electrophile and accepts a pair of electrons from the C-C bond in the alkene
  - The major product is the one in which the halide is bonded to the most substituted carbon atom (**Markovnikov's rule)**
- In the addition of halogens to alkenes, one of the halogen atoms acts as an electrophile and the other as a nucleophile

Electrophilic addition to alkenes



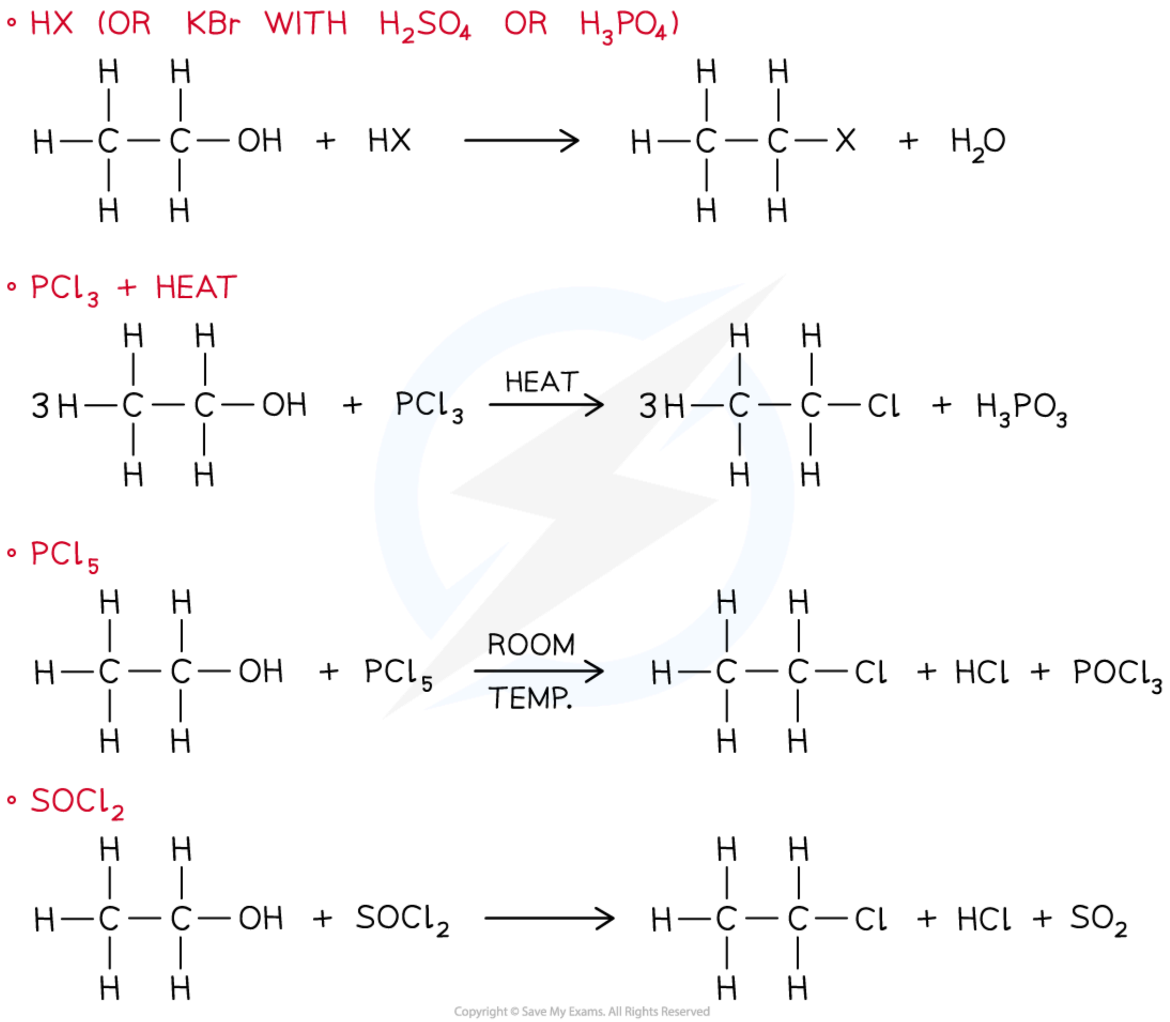
Electrophilic addition of hydrogen halides or hydrogen at room temperatures to alkenes results in the formation of halogenoalkanes

Substitution of alcohols

- In the **substitution of alcohols** an alcohol group is replaced by a halogen to form a halogenoalkane

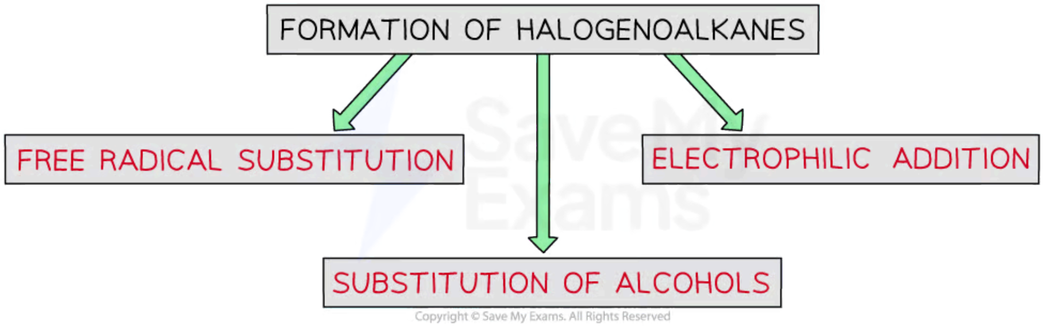
- The subustition of the alcohol group for a halogen can be achieved by reacting the alcohol with:
- HX (or KBr with H_2SO_4 or H_3PO_4 to make HX)
- PCl_3 and heat
- PCl_5 at room temperature
- $SOCl_2$

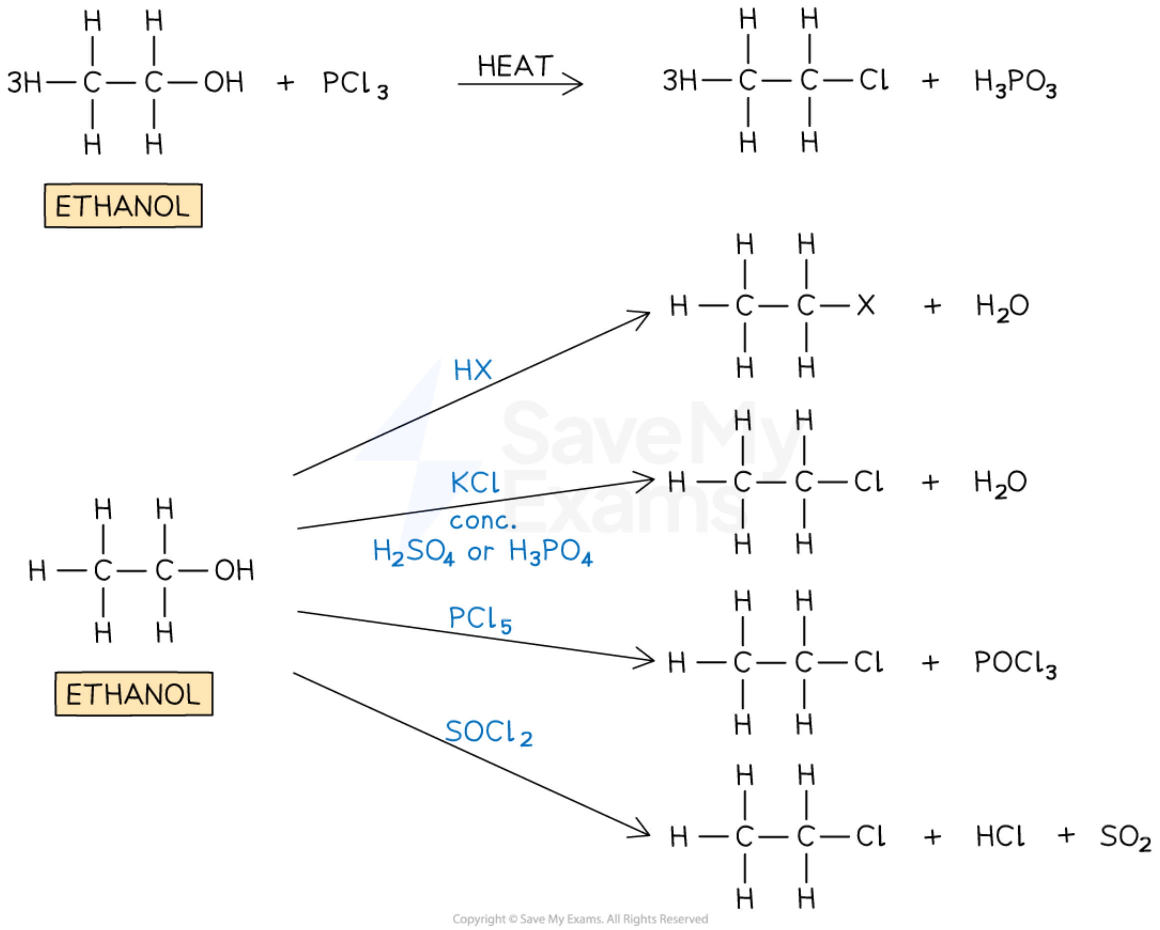
Substitution of alcohols



Substitution of alcohols produces halogenoalkanes

Different methods of forming halogenoalkanes





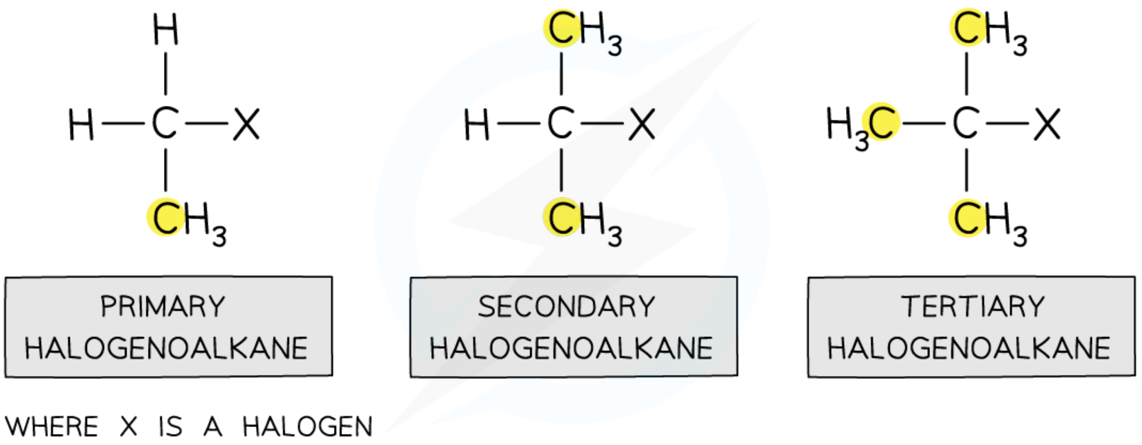
Overview of the different ways to produce halogenoalkanes

Your notes

Classifying Halogenoalkanes

- Depending on the carbon atom the halogen is attached to, halogenoalkanes can be classified as **primary**, **secondary** and **tertiary**
  - A **primary halogenoalkane** is when a halogen is attached to a carbon that itself is attached to one other alkyl group
  - A **secondary halogenoalkane** is when a halogen is attached to a carbon that itself is attached to two other alkyl groups
  - A **tertiary halogenoalkane** is when a halogen is attached to a carbon that itself is attached to three other alkyl groups

Primary, secondary and tertiary halogenoalkanes



The number of alkyl groups attached determines if the halogenoalkane is primary, secondary or tertiary

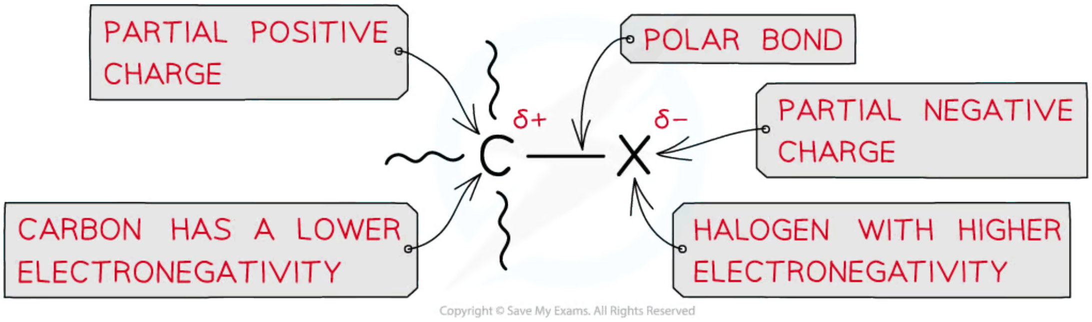
Substitution Reactions of Halogenoalkanes

Nucleophilic Substitution Reactions of Halogenoalkanes

- **Halogenoalkanes** are much more reactive than alkanes due to the presence of the **electronegative** halogens
  - The halogen-carbon bond is polar causing the carbon to carry a partial positive and the halogen a partial negative charge

- A **nucleophilic substitution** reaction is one in which a **nucleophile** attacks a carbon atom which carries a **partial positive charge**
- An atom that has a **partial negative charge** is replaced by the nucleophile

Explaining the polarity of a carbon-halogen bond



Due to large differences in electronegativity between the carbon and halogen atom, the C-X bond is polar

Reaction with NaOH

- The reaction of a halogenoalkane with **aqueous alkali** results in the formation of an alcohol
- The halogen is **replaced** by the OH^-
- The **aqueous hydroxide** (OH^- ion) behaves as a **nucleophile** by donating a pair of electrons to the carbon atom bonded to the halogen
- For example, bromoethane reacts with aqueous alkali when heated to form ethanol
  - Hence, this reaction is a **nucleophilic substitution**
  - The halogen is replaced by a nucleophile, $:OH^-$

$$CH_3CH_2Br + :OH^- \rightarrow CH_3CH_2OH + :Br^-$$

Reaction with KCN

- The **nucleophile** in this reaction is the **cyanide**, CN^- ion

- **Ethanolic solution** of **potassium cyanide** (KCN in ethanol) is **heated under reflux** with the halogenoalkane
- The product is a **nitrile**
  - For example, bromoethane reacts with ethanolic potassium cyanide when heated under reflux to form propanenitrile
  - The halogen is replaced by a nucleophile, $:CN^-$

$$\mathbf{CH_3CH_2Br + :CN^- \rightarrow CH_3CH_2CN + :Br^-}$$

- The nucleophilic substitution of halogenoalkanes with KCN adds an **extra** carbon atom to the carbon chain
- This reaction can therefore be used by chemists to make a compound with one more carbon atom than the best available organic starting material

Reaction with NH_3

- The **nucleophile** in this reaction is the **ammonia**, NH_3 molecule
- An **ethanolic solution** of **excess ammonia** (NH_3 in ethanol) is **heated under pressure** with the halogenoalkane
- For example, bromoethane reacts with excess ethanolic ammonia when heated under pressure to form ethylamine
  - The product is a **primary amine**
  - The halogen is replaced by an amine group NH_2

$$\mathbf{CH_3CH_2Br + NH_3 \rightarrow CH_3CH_2NH_2 + HBr}$$

- It is very important that the ammonia is in excess as the product of the nucleophilic substitution reaction, the **ethylamine**, can act as a nucleophile and attack another bromoethane to form the **secondary amine**, **diethylamine**

Reaction with aqueous silver nitrate

- Halogenoalkanes can be broken down **under reflux** by water to form **alcohols**
- The breakdown of a substance by water is also called **hydrolysis**

- For example, bromoethane reacts with aqueous silver nitrate solution to form ethanol
- This reaction is classified as a nucleophilic substitution reaction with **water molecules** in aqueous **silver nitrate** solution acting as nucleophiles, **replacing** the halogen in the halogenoalkane

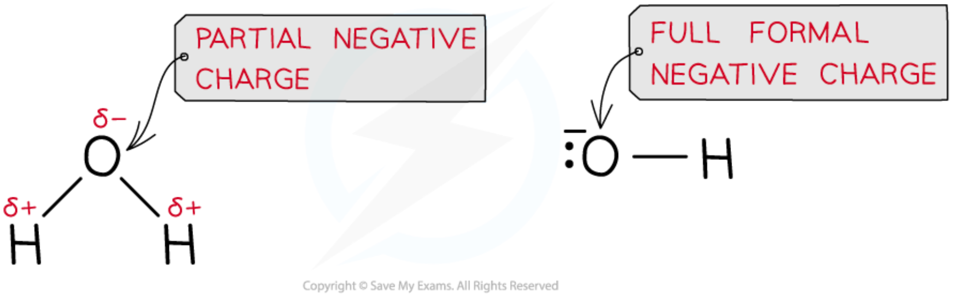
$$\mathbf{C_2H_5Br + H_2O \xrightarrow{\text{reflux}} C_2H_5OH + HBr}$$

Nucleophilic substitution with OH^-

In nucleophilic substitution with OH^-, the bond that forms and the bond that breaks must both involve the carbon atom that is bonded to the leaving group

- This reaction is similar to the nucleophilic substitution reaction of halogenoalkanes with aqueous alkali, however, hydrolysis with water is much **slower** than with the OH^- ion in alkalis
    - The hydroxide ion is a better nucleophile than water as it carries a full formal negative charge
    - In water, the oxygen atom only carries a partial negative charge

Comparing water and the hydroxide ion as nucleophiles



A hydroxide ion is a better nucleophile as it has a full formal negative charge whereas the oxygen atom in water only carries a partial negative charge; this causes the nucleophilic substitution reaction with water to be much slower than with aqueous alkali

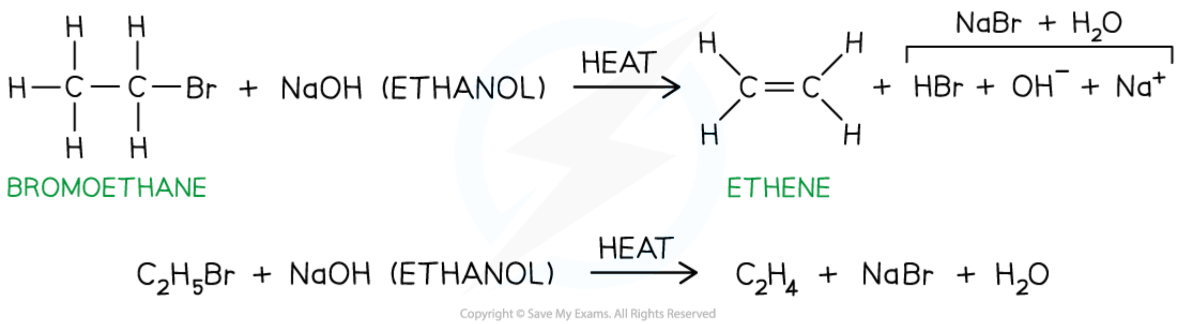
- The halogenoalkanes have different **rates of hydrolysis**, so this reaction can be used as a **test** to identify halogens in a halogenoalkane by measuring how long it takes for the test tubes containing the halogenoalkane and aqueous silver nitrate solutions to become **opaque**

Elimination Reactions of Halogenoalkanes

Elimination Reactions of Halogenoalkanes

- In an **elimination** reaction, an organic molecule loses a small molecule
  - In the case of halogenoalkanes, this small molecule is a hydrogen halide (eg. HCl)
- The halogenoalkanes are **heated** with **ethanolic sodium hydroxide** causing the C-X bond to break **heterolytically,** forming an X^- ion and leaving an alkene as an organic product
  - For example, bromoethane reacts with **ethanolic sodium hydroxide** when heated to form ethene

The elimination reaction of bromoethane with ethanolic sodium hydroxide



Hydrogen bromide is eliminated to form ethene

Exam Tip

The reaction conditions in a reaction are extremely important

If **NaOH(ethanol)** is used, an **elimination** reaction takes place to form an **alkene** from a halogenoalkane

If **NaOH(aq)** is used, a **nucleophilic substitution** reaction takes place to form an **alcohol** from a halogenoalkane.

SN1 & SN2

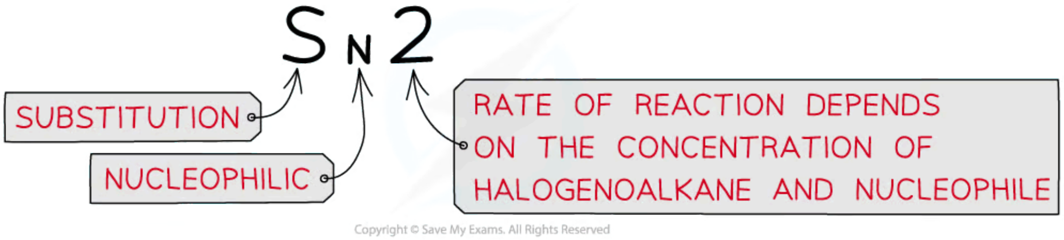
Halogenoalkanes: SN1 & SN2 Mechanisms

- In **nucleophilic substitution** reactions involving halogenoalkanes, the halogen atom is replaced by a nucleophile
- These reactions can occur in two different ways (known as **S_N2** and **S_N1** reactions) depending on the structure of the halogenoalkane involved

S_N2 reactions

- In **primary halogenoalkanes,** the carbon that is attached to the halogen is bonded to **one alkyl group**
- These halogenoalkanes undergo nucleophilic substitution by an **S_N2** mechanism
  - 'S' stands for 'substitution'
  - 'N' stands for 'nucleophilic'
  - '2' means that the rate of the reaction (which is determined by the slowest step of the reaction) depends on the concentration of both the halogenoalkane and the nucleophile ions

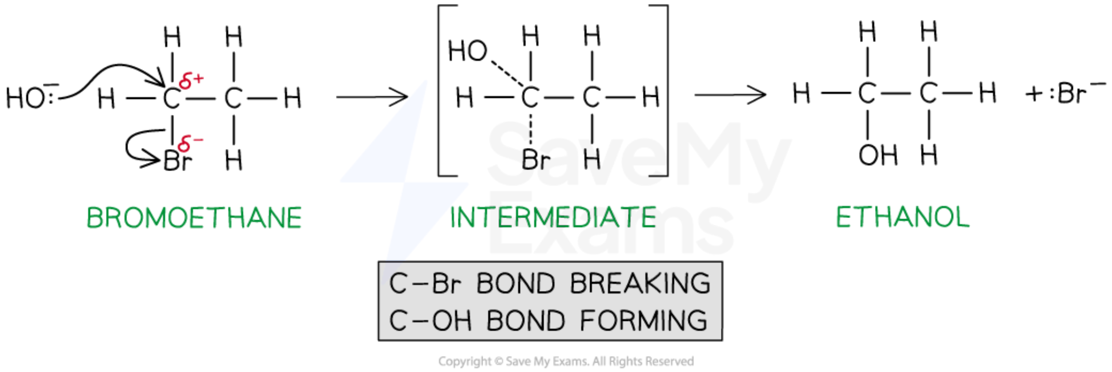
Defining an S_N2 mechanism



Each term in the S_N2 expression has a specific meaning

- The S_N2 mechanism is a **one-step** reaction
  - The nucleophile donates a pair of electrons to the δ+ carbon atom to form a new bond
  - At the same time, the C-X bond is breaking and the halogen (X) takes both electrons in the bond (**heterolytic fission**)
  - The halogen leaves the halogenoalkane as an X^- ion
- For example, the nucleophilic substitution of bromoethane by hydroxide ions to form ethanol

The nucleophilic substitution of bromoethane by hydroxide ions

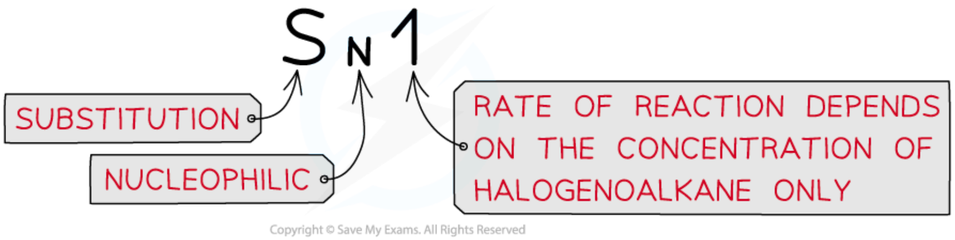


In this mechanism, the bromoethane is a primary halogenoalkane

S_N1 reactions

- In **tertiary halogenoalkanes,** the carbon that is attached to the halogen is bonded to **three alkyl groups**
- These halogenoalkanes undergo nucleophilic substitution by an **S_N1** mechanism
  - 'S' stands for 'substitution'
  - 'N' stands for 'nucleophilic'
  - '1' means that the rate of the reaction (which is determined by the slowest step of the reaction) depends on the concentration of only one reagent, the **halogenoalkane**

Defining an S_N1 mechanism

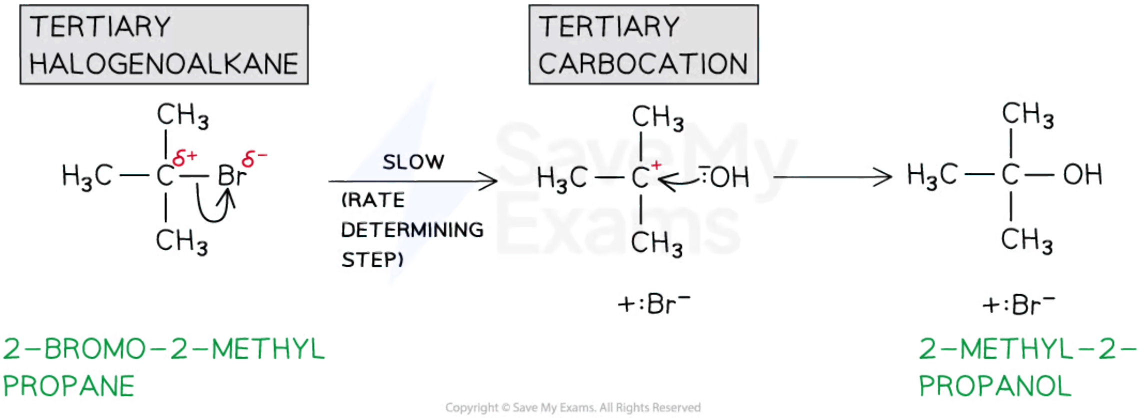


Each term in the S_N1 expression has a specific meaning

- The S_N1 mechanism is a two-step reaction
  - In the first step, the C-X bond breaks **heterolytically** and the halogen leaves the halogenoalkane as an X^- ion (this is the **slow** and **rate-determining step**)
  - This forms a **tertiary carbocation** (which is a tertiary carbon atom with a positive charge)
  - In the second step, the tertiary carbocation is attacked by the **nucleophile**

- For example, the nucleophilic substitution of 2-bromo-2-methylpropane by hydroxide ions to form 2-methyl-2-propanol

The nucleophilic substitution of 2-bromo-2-methylpropane by hydroxide ions

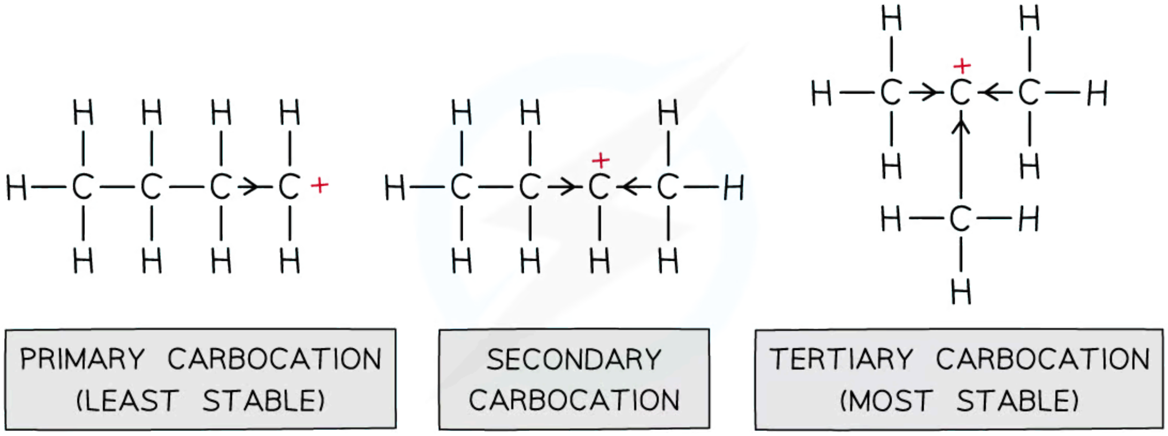


In this mechanism, the 2-bromo-2-methylpropane is a tertiary halogenoalkane

Carbocations

- In the S_N1 mechanism, a **tertiary carbocation** is formed
- This is not the case for S_N2 mechanisms as a **primary carbocation** would have been formed which is much **less** stable than tertiary carbocations
- This has to do with the **positive inductive effect** of the alkyl groups attached to the carbon which is bonded to the halogen atom
  - The alkyl groups push electron density towards the positively charged carbon, reducing the **charge density**
  - In tertiary carbocations, there are three alkyl groups stabilising the carbocation whereas in primary carbocations there is only one alkyl group
  - This is why tertiary carbocations are much more stable than primary ones

Stability of primary, secondary and tertiary carbocations



The carbocations become more stable moving from primary to secondary to tertiary

- **Secondary halogenoalkanes** undergo a **mixture** of both S_N1 and S_N2 reactions depending on their structure

Reactivity of Halogenoalkanes

Reactivity of Halogenoalkanes

- The halogenoalkanes have different **rates** of **substitution reactions**
- Since substitution reactions involve **breaking** the **carbon-halogen** bond the **bond energies** can be used to explain their different reactivities

Halogenoalkane Bond Energy Table

Bond	Bond Energy / kJ mol^{-1}
C–F	467 (strongest bond)
C–Cl	346
C–Br	290
C–I	228 (weakest bond)

- The table above shows that the C-I bond requires the least energy to break, and is therefore the **weakest** carbon-halogen bond
- During substitution reactions the C-I bond will therefore **heterolytically** break as follows:

$$R_3C{-}I + OH^- \rightarrow R_3C{-}OH + I^-$$

halogenoalkane alcohol

- The C-F bond, on the other hand, requires the most energy to break and is, therefore, the **strongest** carbon-halogen bond
- Fluoroalkanes will therefore be less likely to undergo substitution reactions

Aqueous silver nitrate

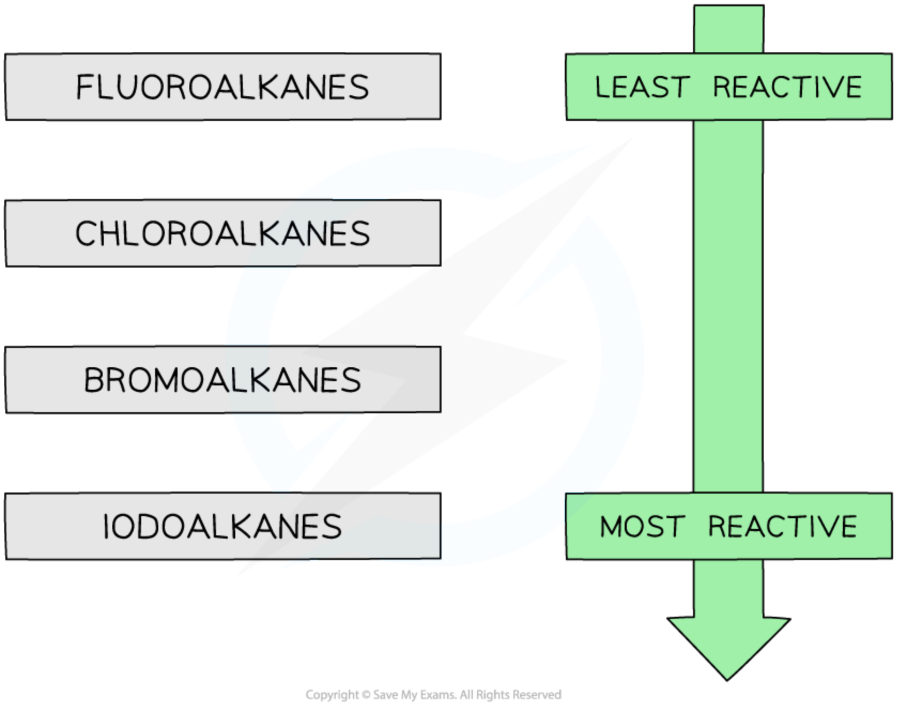
- Reacting halogenoalkanes with **aqueous silver nitrate solution** will result in the formation of a **precipitate**
- The **rate of formation** of these precipitates can also be used to determine the reactivity of the halogenoalkanes

Halogenoalkane Precipitates Table

Halogenoalkane	Precipitate
Chlorides	White (silver chloride)
Bromides	Cream (silver bromide)
Iodides	Yellow (silver iodide)

- The formation of the pale yellow silver iodide is the fastest (fastest **nucleophilic substitution** reaction) whereas the formation of the silver fluoride is the slowest (slowest **nucleophilic substitution** reaction)
- This confirms that fluoroalkanes are the least reactive and iodoalkanes are the most reactive halogenoalkanes

The trend in reactivity of halogenoalkanes



The halogenoalkanes become more reactive as you move down the group