# Edexcel International AS Chemistry

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## Organic Chemistry: Halogenoalkanes

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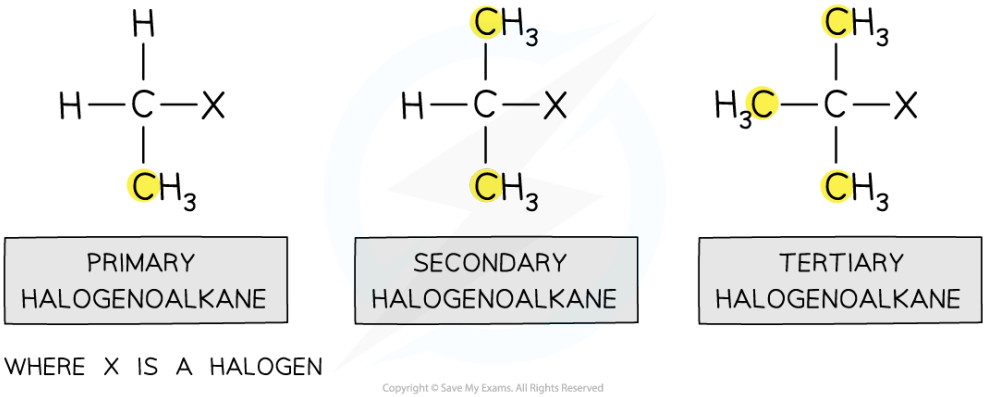
# Halogenoalkanes – Introduction

## Naming halogenoalkanes

- We use the prefixes
  - **Fluoro** for fluorine
  - **Chloro** for chlroine
  - **Bromo** for bromine
  - **Iodo** for iodine
- The name of the halogenoalkane is based on the orignal alkane
  - So $CH_3CH_2CH_2Br$ would be 1–bromopropane
- The position of the halogen atom must be taken into account
  - So $CH_3CH(Br)CH_3$ would be 2–bromopropane
- Finally the substituents are listed alphabetically
  - So $CH_3CH(Cl)CH_2Br$ would be 1–bromo-2–chloropropane

## Classifying halogenoalkanes

- Halogenoalkanes can be classified as **primary**, **secondary** or **tertiary** depending on the number of carbon atoms attached to the C-X functional group
  - 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



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## Examiner Tips and Tricks

You are also expected to be able to draw structural, displayed and skeletal formulae of halogenoalkanes

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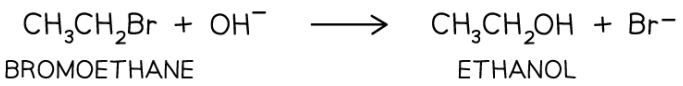
# Halogenoalkanes – Reactions

- A **nucleophile** is an electron-rich species that can **donate** a pair of electrons
  - 'Nucleophile' means 'nucleus / positive charge loving' as nucleophiles are attracted to positively charged species
  - **Nucleophilic** refers to reactions that involve a nucleophile

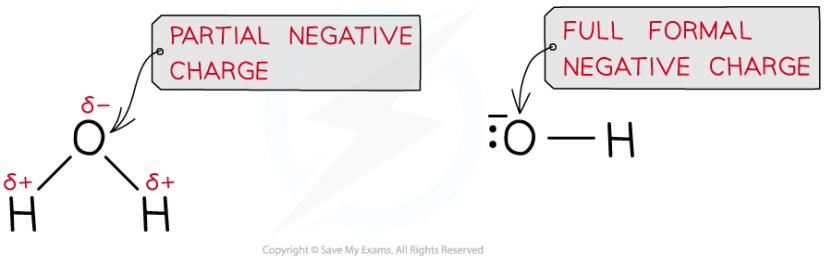
## Formation of alcohols

- The nucleophile in this reaction is the **hydroxide ion**, **$OH^-$**
- An aqueous solution of sodium hydroxide (NaOH) or potassium hydroxide (KOH) is used, with a small amount of ethanol as a co-solvent to help dissolve the halogenoalkane
  - Water must be the primary solvent, if ethanolic conditions are used instead, elimination will occur, forming an alkene
- This reaction is very slow at room temperature, so the reaction mixture is warmed
- This is an example of a **hydrolysis reaction** and the product is an alcohol
  - The rate of this reaction depends on the type of halogen in the halogenoalkane
  - The stronger the C-X bond, the slower the rate of the reaction
  - In terms of bond enthalpy, C-F > C-Cl > C-Br > C-I
  - Fluoroalkanes do not react at all, but iodoalkanes have a very fast rate of reaction




***The halogen is replaced by the nucleophile, $OH^-$***

- This reaction could also be done with water as the nucleophile, but it is very slow
  - The hydroxide ion is a better nucleophile than water as it carries a full negative charge
  - In water, the oxygen atom only carries a partial charge





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***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 the aqueous alkali***

**Reaction with water**

- The water molecule is a weak nucleophile, but it will eventually substitute for the halogen
- This occurs much more slowly compared to when warm aqueous sodium hydroxide is used
- An alcohol is produced
  - $RX + H_2O \rightarrow ROH + H^+ + X^-$
  - $CH_3CH_2Br + H_2O \rightarrow CH_3CH_2OH + H^+ + Br^-$
- If silver nitrate solution in ethanol is added to the solution, the silver ions will react with the halide ions as soon as they form, giving a silver halide precipitate
  - $Ag^+ (aq) + X^- (aq) \rightarrow AgX (s)$

## Formation of nitriles

- The nucleophile in this reaction is the **cyanide ion, $CN^-$**
- An **ethanolic solution** of **potassium cyanide** (KCN in ethanol) is **heated under reflux** with the halogenoalkane
- The product is a **nitrile**
  - E.g. bromoethane is heated under reflux with ethanolic potassium cyanide to form propanenitrile



***The halogen is replaced by a cyanide group, $CN^-$***

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

## Formation of primary amines by reaction with ammonia

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- The nucleophile in this reaction is the ammonia molecule, $NH_3$
- An **ethanolic solution** of **excess** ammonia ($NH_3$ in ethanol) is **heated under pressure** with a **primary** halogenoalkane
  - An excess of ammonia is used because the product is more reactive than ammonia so further substitution reactions could occur
- The product is a **primary amine**
  - E.g. bromoethane reacts with excess ethanolic ammonia when heated under pressure to form ethylamine

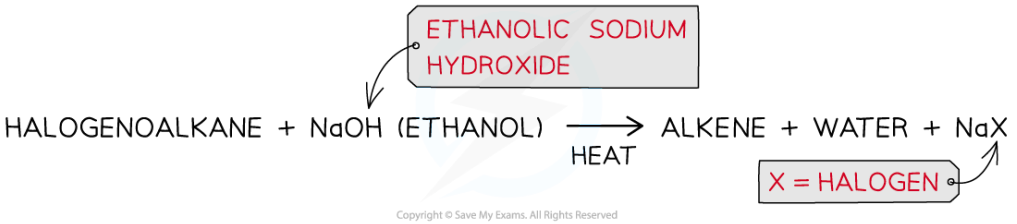
$$\underset{\text{BROMOETHANE}}{CH_3CH_2Br} + NH_3 \longrightarrow \underset{\text{ETHYLAMINE}}{CH_3CH_2NH_2} + HBr$$



***The halogen is replaced by an amine group, $NH_2$***

## Formation of alkenes

- 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
  - E.g. bromoethane is heated with ethanolic sodium hydroxide to form ethene






***Production of an alkene from a halogenoalkane by reacting it with ethanolic sodium hydroxide and heating it***


$$C_2H_5Br + NaOH\ (ETHANOL) \xrightarrow{HEAT} C_2H_4 + NaBr + H_2O$$

*Hydrogen bromide is eliminated to form ethene*

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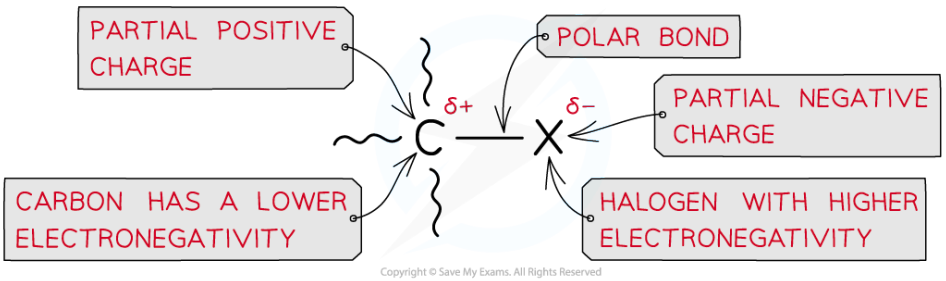
# Nucleophilic Substitution – Mechanism

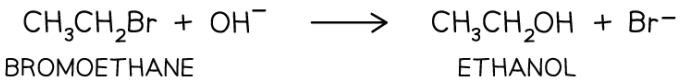
- A **nucleophilic substitution** reaction is one in which a **nucleophile** attacks a carbon atom which carries a **partial positive charge**
- An atom that has a **partial negative charge** is replaced by the nucleophile
- Halogenoalkanes will undergo nucleophilic substitution reactions due to the polar C-X bond (where X is a halogen)




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

## Mechanism with aqueous potassium hydroxide

- In the following reaction a halogenoalkane reacts with aqueous alkali to form an alcohol




***The halogen is replaced by a nucleophile, $OH^-$***

- The mechanism for the reaction is as follows


***Nucleophilic substitution reaction of bromoethane and aqueous alkali (e.g. NaOH)***

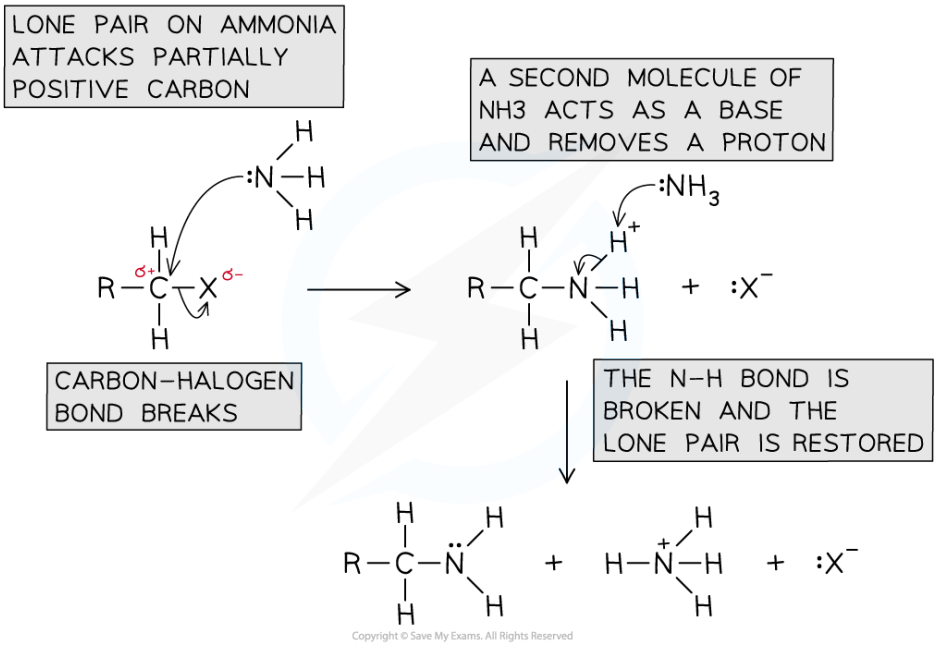
## Mechanism with ammonia

- When ammonia reacts with a haloalkane a nucleophilic substitution reaction takes place forming a primary amine
  - For example chloromethane reacts with ammonia in two steps to make methylamine and ammonium chloride

$$CH_3Cl + NH_3 \rightarrow [CH_3NH_3]^+Cl^-$$

$$[CH_3NH_3]^+Cl^- + NH_3 \rightarrow CH_3NH_2 + NH_4{+}Cl^-$$

- **Excess** ammonia is used to prevent further substitution and favour the formation of a primary amine




***The mechanism of nucleophilic substitution between ammonia and a halogenoalkane***

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# Halogenoalkanes – Hydrolysis

## Measuring the rate of hydrolysis

- Acidified aqueous silver nitrate can be used to measure the rate of hydrolysis of halogenoalkanes
- The following method is used:
  - Set up three test tubes in a 50 °C water bath, with a mixture of ethanol and acidified silver nitrate
  - Add a few drops of a chloroalkane, bromoalkane and an iodoalkane to each test tube and start a stop watch
  - Time how long it takes for the precipitates to form
- 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 haloalkane

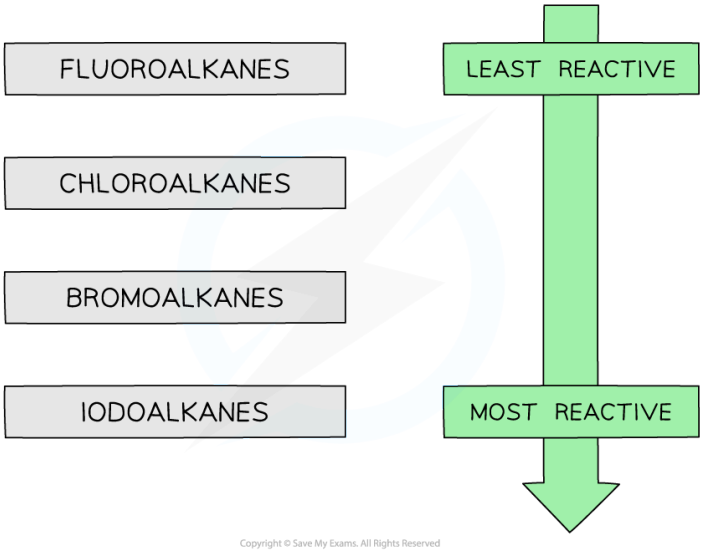
## Haloalkane Precipitates Table

| Halogenoalkane | Precipitate |
|---|---|
| Chlorides | White (silver chloride) |
| Bromides | Cream (silver bromide) |
| Iodides | Pale yellow (silver iodide) |



- The precipitates will form as the reaction progresses and the halide ions are formed
  - The yellow silver iodide precipitate is the fastest **nucleophilic substitution** reaction
    - This is because the C-I bond has the lowest bond enthalpy, so it is the easiest to break and will cause the $I^-$ ions to form the fastest
  - The white chloride precipitate is the slowest nucleophilic substitution reaction
    - This is because the C-Cl bond has the highest bond enthalpy, so it is the hardest to break and will cause the $Cl^-$ ions to form the slowest
- Silver fluoride is soluble, so a precipitate will not be formed in this reaction

- This confirms that fluoroalkanes are the least reactive and iodoalkanes are the most reactive halogenoalkanes
    - It can be predicted that the formation of silver astatide would be even quicker than silver iodide




***The trend in reactivity of haloalkanes***

- A similar experiment can be set up to compare the rate of hydrolysis in primary, secondary and tertiary halogenoalkanes
    - The halogen involved and the overall molecular formula of the halogenoalkane must remain the same
    - E.g. 1–chlorobutane (primary), 2–chlorobutane (secondary) and 2–chloro-2–methylpropane (tertiary)
- Results would show that:
    - The tertiary halogenoalkane / 2–chloro-2–methylpropane reacts the quickest
    - The primary halogenoalkane / 1–chlorobutane reacts the slowest
    - Therefore, the secondary halogenoalkane / 2–chlorobutane is in the middle
        - Although, the explanation for this is not required at AS level, it is required at A-level
        - The rate of hydrolysis is determined by the use of either an $S_N1$ or an $S_N2$ reaction mechanism

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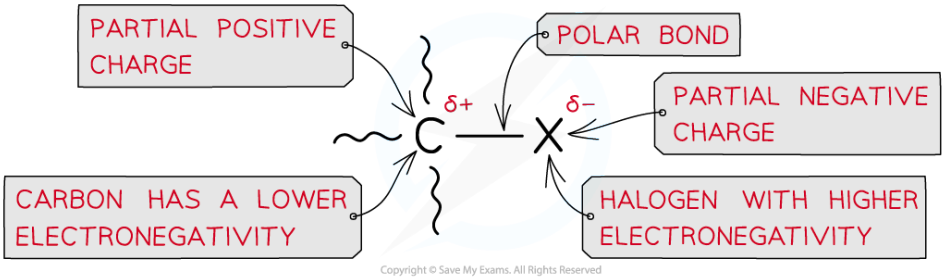
# Reactivity & Bond Enthalpy

- Halogenoalkanes contain at least one halogen atom covalently bonded to a carbon atom within the molecules structure
- Due to the difference in electronegativity between the halogen and carbon atoms:
  - The carbon-halogen, C-X, bond is polar
  - The carbon atom has a δ+ charge
  - The halogen atom has a δ- charge




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

- As the electronegativity down the group decreases, so does the polarity of the bond
  - This suggests that fluoroalkanes would be the quickest to react but the strength of the bond is another important and greater factor

## Bond Enthalpy

- 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

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



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- 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 of the halogenoalkane will therefore **heterolytically** break to form the alcohol
  - For example

$$CH_3CH_2I + OH^- \rightarrow CH_3CH_2OH + I^-$$

- 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