Halogenoalkanes

Nucleophiles, naming and classifying halogenoalkanes, their reactions with a range of reagents, nucleophilic substitution mechanisms, rates of hydrolysis, and how they are made.

Nucleophiles and polar bonds

A **nucleophile** is an electron-pair donor: it attacks a $\delta+$ atom using a lone pair. Examples are OH^-, CN^- and NH_3.

Reaction mechanisms depend on bond polarity. The C–X bond in a halogenoalkane is polar, because halogens are more electronegative than carbon ($C^{\delta+}-X^{\delta-}$), so the carbon is attacked by nucleophiles.

Halogenoalkanes have the general formula $C_nH_{2n+1}X$. They are named with a prefix: chloro-, bromo-, iodo-, e.g. 1-bromobutane, 2-chloro-2-methylpropane.

- **Primary**: the carbon bonded to the halogen is attached to one other carbon (e.g. 1-bromopropane).
- **Secondary**: attached to two other carbons (2-bromopropane).
- **Tertiary**: attached to three other carbons (2-bromo-2-methylpropane).

Reactions of halogenoalkanes

Reagent	Conditions	Product	Role of reagent
Aqueous KOH or NaOH	Warm, **reflux**	Alcohol	OH^- is a **nucleophile**: **substitution** (hydrolysis)
Ethanolic KOH	Hot, reflux	Alkene	OH^- is a **base**: **elimination**
Aqueous silver nitrate in ethanol	Warm	Halide precipitate and alcohol	H_2O is the nucleophile; used to measure rates
Ammonia in ethanol (excess)	Heat under pressure in a sealed tube	Primary amine	NH_3 is a nucleophile
Potassium cyanide in ethanol (alcoholic KCN)	Reflux	Nitrile	CN^- is a nucleophile

Reaction with cyanide lengthens the carbon chain by one carbon: $CH_3CH_2Br + CN^- \rightarrow CH_3CH_2CN + Br^-$. The nitrile can then be hydrolysed to a carboxylic acid or reduced to an amine.

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The choice of solvent controls substitution or elimination: **aqueous** gives substitution, **ethanolic** gives elimination.

Mechanism: nucleophilic substitution (primary halogenoalkanes)

With hydroxide ions (shown for bromoethane):

1. The OH^- ion uses a lone pair to attack the $\delta+$ carbon (curly arrow from the lone pair to carbon).
2. At the same time the C–Br bond breaks **heterolytically** (curly arrow from the bond to Br) and Br^- leaves.

It takes place in **one step**, through a transition state in which the carbon is partly bonded to both OH and Br.

With ammonia the first step gives $CH_3CH_2NH_3^+Br^-$, and a second ammonia molecule removes an H^+ to give the amine, $CH_3CH_2NH_2$.

> **NOTE**
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> A second substitution can happen on the amine product, so an excess of ammonia is used to give mostly the primary amine.

Relative rates of hydrolysis

Add aqueous silver nitrate in ethanol to a halogenoalkane in a warm water bath. The halide ion formed gives a precipitate. The **faster the precipitate appears**, the faster the hydrolysis.

- By **structure**: tertiary > secondary > primary.
- By **halogen**: iodo > bromo > chloro. The rate depends on the **C–X bond enthalpy**: C–I is the weakest and breaks most easily, C–Cl is the strongest. (The polarity of the bond does not explain it, since C–Cl is the most polar.)

Precipitate colours: $AgCl$ white, $AgBr$ cream, AgI yellow.

> **TRY IT**
>
> Explain why 1-iodobutane hydrolyses faster than 1-chlorobutane.

The C–I bond is weaker than the C–Cl bond (lower bond enthalpy, because the iodine atom is larger and its bonding electrons are further from the nucleus), so it needs less energy to break and the rate is faster.

Core Practical 5 compares the rates of hydrolysis of a number of halogenoalkanes. Keep the volume, concentration, temperature and the amount of silver nitrate the same, and time the appearance of the

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precipitate.

Making a halogenoalkane: Core Practical 6

Tertiary alcohols react with concentrated hydrochloric acid at room temperature, so 2-chloro-2-methylpropane is made from 2-methylpropan-2-ol:

$$(CH_3)_3COH + HCl \rightarrow (CH_3)_3CCl + H_2O$$

The method:

1. Shake the alcohol with concentrated HCl in a **separating funnel**, releasing the pressure often.
2. Run off the lower aqueous layer and keep the upper organic layer.
3. **Wash** with sodium hydrogencarbonate solution to remove the remaining acid (vent the funnel because CO_2 forms).
4. **Dry** with anhydrous sodium sulfate or calcium chloride.
5. **Distil**, collecting the fraction at the boiling temperature of the product (51 °C).

> **NOTE**
>
> 1-Bromobutane is made from butan-1-ol with potassium bromide and 50% sulfuric acid under reflux, then distilled, washed and dried in the same way.

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