3.3 Halogenoalkanes

Naming Halogenoalkanes

Based on original alkane, with a prefix indicating halogen atom:
- Fluoro for F;
- Chloro for Cl;
- Bromo for Br;
- Iodo for I.

Substituents are listed alphabetically

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.

- **Primary halogenoalkane**: One carbon attached to the carbon atom adjoining the halogen
- **Secondary halogenoalkane**: Two carbons attached to the carbon atom adjoining the halogen
- **Tertiary halogenoalkane**: Three carbons attached to the carbon atom adjoining the halogen

Reactions of Halogenoalkanes

- **Halogenoalkanes undergo either substitution or elimination reactions**

Organic reactions are classified by their mechanisms

1. Nucleophilic substitution reactions

- **Substitution**: swapping a halogen atom for another atom or groups of atoms
- **Nucleophile**: electron pair donor e.g. :OH, :NH$_3$, CN$^-$

- **The Mechanism**: We draw (or outline) mechanisms to show in detail how a reaction proceeds

The nucleophiles attack the positive carbon atom.

We use curly arrows in mechanisms (with two line heads) to show the movement of two electrons.

A curly arrow will always start from a lone pair of electrons or the centre of a bond.

The rate of these substitution reactions depends on the strength of the C-X bond.

The weaker the bond, the easier it is to break and the faster the reaction.

The iodoalkanes are the fastest to substitute and the fluoroalkanes are the slowest. The strength of the C-F bond is such that fluoroalkanes are very unreactive.

<table>
<thead>
<tr>
<th>Bond enthalpy / kJmol$^{-1}$</th>
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<tbody>
<tr>
<td>C-I</td>
</tr>
<tr>
<td>C-Br</td>
</tr>
<tr>
<td>C-Cl</td>
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<tr>
<td>C-F</td>
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Comparing the rate of hydrolysis reactions

**Hydrolysis** is defined as the splitting of a molecule (in this case a halogenoalkane) by a reaction with water:

\[
\text{CH}_3\text{CH}_2\text{X} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{X}^- + \text{H}^+
\]

**Aqueous silver nitrate** is added to a halogenoalkane. The halide leaving group combines with a silver ion to form a **silver halide precipitate**.

The precipitate only forms when the halide ion has left the halogenoalkane and so the rate of formation of the precipitate can be used to compare the reactivity of the different halogenoalkanes.

The quicker the precipitate is formed, the faster the substitution reaction and the more reactive the halogenoalkane.

The rate of these substitution reactions depends on the strength of the C-X bond. The weaker the bond, the easier it is to break and the faster the reaction.

**Water** is a poor nucleophile but it can react slowly with halogenoalkanes in a substitution reaction:

\[
\text{CH}_3\text{CH}_2\text{I} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{I}^- + \text{H}^+
\]

Aqueous silver nitrate is added to a halogenoalkane. The halide leaving group combines with a silver ion to form a silver halide precipitate.

Ag\(^{\text{aq}}\)\( + \) I\(^{-}\)(aq) \(\rightarrow\) AgI\(_{\text{(s)}}\) - yellow precipitate

The iodoalkane forms a precipitate with the silver nitrate first as the C-I bond is weakest and so it hydrolyses the quickest.

The quicker the precipitate is formed, the faster the substitution reaction and the more reactive the halogenoalkane.

The aqueous conditions needed is an important point. If the solvent is changed to ethanol an elimination reaction occurs.

**Nucleophilic substitution with aqueous hydroxide ions**

**Change in functional group**: halogenoalkane \(\rightarrow\) alcohol

**Reagent**: potassium (or sodium) hydroxide

**Conditions**: In aqueous solution; Heat under reflux

**Mechanism**: Nucleophilic Substitution

**Type of reagent**: Nucleophile, OH\(^-\)

\[
\text{HO}^-: + \text{CH}_3\text{CH}_2\text{Br} \rightarrow \text{CH}_3\text{CH}_2\text{OH} + :\text{Br}^-
\]

The aqueous conditions needed is an important point. If the solvent is changed to ethanol an elimination reaction occurs.

**Alternative mechanism for tertiary halogenoalkanes**

Tertiary halogenoalkanes undergo nucleophilic substitution in a different way.

Tertiary halogenoalkanes undergo this mechanism as the tertiary carbocation is stabilised by the electron releasing methyl groups around it. (See alkenes topic for another example of this). Also the bulky methyl groups prevent the hydroxide ion from attacking the halogenoalkane in the same way as the mechanism above.

The Br first breaks away from the halogenoalkane to form a carbocation intermediate.

The hydroxide nucleophile then attacks the positive carbon.
**Nucleophilic substitution with cyanide ions**

**Change in functional group:** halogenoalkane → nitrile  
**Reagent:** KCN dissolved in ethanol/water mixture  
**Conditions:** Heating under reflux  
**Mechanism:** Nucleophilic Substitution  
**Type of reagent:** Nucleophile, :CN⁻

![Reaction diagram with mechanism](image)

Note: the mechanism is identical to the above one.

This reaction increases the length of the carbon chain (which is reflected in the name). In the above example butanenitrile includes the C in the nitrile group.

**Naming Nitriles**

Nitrile groups have to be at the end of a chain. Start numbering the chain from the C in the CN.

- CH₂CH₂CN: propanenitrile
- H₃C—CH—CH₂—C≡N: 3-methylbutanenitrile
- CH₃

Note the naming: butanenitrile and not butannitrile.

**Nucleophilic substitution with ammonia**

**Change in functional group:** halogenoalkane → amine  
**Reagent:** NH₃ dissolved in ethanol  
**Conditions:** Heating under pressure (in a sealed tube)  
**Mechanism:** Nucleophilic substitution  
**Type of reagent:** Nucleophile, :NH₃

![Reaction diagram](image)

Naming amines:

In the above example propylamine, the propyl shows the 3 C's of the carbon chain.

Sometimes it is easier to use the IUPAC naming for amines e.g. Propan-1-amine

Further substitution reactions can occur between the halogenoalkane and the amines formed leading to a lower yield of the amine. Using excess ammonia helps minimise this.
2. Elimination reaction of halogenoalkanes

Elimination with alcoholic hydroxide ions

<table>
<thead>
<tr>
<th>Change in functional group: haloenoalkane → alkene</th>
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<tbody>
<tr>
<td>Reagents: Potassium (or sodium) hydroxide</td>
</tr>
<tr>
<td>Conditions: In ethanol; Heat</td>
</tr>
<tr>
<td>Mechanism: Elimination</td>
</tr>
<tr>
<td>Type of reagent: Base, OH⁻</td>
</tr>
</tbody>
</table>

Elimination: removal of small molecule (often water) from the organic molecule

\[
\text{CH}_3\text{C}H\text{H}_2\text{Br} + \text{KOH} \rightarrow \text{CH}_3\text{C}=\text{C}H + \text{KBr} + \text{H}_2\text{O}
\]

I-bromopropane → propene

Note the importance of the solvent to the type of reaction here.
Aqueous: substitution
Alcoholic: elimination

Often a mixture of products from both elimination and substitution occurs

With unsymmetrical secondary and tertiary haloenoalkanes two (or sometimes three) different structural isomers can be formed

The structure of the haloenoalkane also has an effect on the degree to which substitution or elimination occurs in this reaction.
Primary tends towards substitution
Tertiary tends towards elimination
Ozone Chemistry

The naturally occurring ozone ($O_3$) layer in the upper atmosphere is beneficial as it filters out much of the sun’s harmful UV radiation.

Ozone in the lower atmosphere is a pollutant and contributes towards the formation of smog.

Man-made chlorofluorocarbons (CFC's) caused a hole to form in the ozone layer.

Chlorine radicals are formed in the upper atmosphere when energy from ultra-violet radiation causes C–Cl bonds in chlorofluorocarbons (CFCs) to break.

The chlorine free radical atoms catalyze the decomposition of ozone, due to these reactions, because they are regenerated. (They provide an alternative route with a lower activation energy)

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Overall equation

$$2O_3 \rightarrow 3O_2$$

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These reactions contributed to the formation of a hole in the ozone layer.

Legislation to ban the use of CFCs was supported by chemists and that they have now developed alternative chlorine-free compounds.

HFCs (Hydro fluoro carbons) e.g. CH$_2$FCF$_3$ are now used for refrigerators and air-conditioners. These are safer as they do not contain the C-Cl bond.

The C-F bond is stronger than the C-Cl bond and is not affected by UV.