Reactions of Haloalkanes

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Haloalkanes

- Contain a halogen atom covalently bonded to a carbon atom
- General formula: \( R-X \) where \( X \) is a halogen atom (F, Cl, Br, I) and \( R \) is the carbon chain.

Most halogens are more electronegative than carbon and so a dipole is induced and the C-X bond is polar.

\[
{}^{\delta+}C^{\delta-} \quad F^{\delta-} > C^{\delta+}Cl^{\delta-} > C^{\delta+}Br^{\delta-}
\]
### Naming haloalkanes

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

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-bromopropane</td>
<td><img src="structure.png" alt="1-bromopropane" /></td>
</tr>
<tr>
<td>2-chloro-2-methylbutane</td>
<td><img src="structure.png" alt="2-chloro-2-methylbutane" /></td>
</tr>
<tr>
<td>3-bromo-1-chloropentane</td>
<td><img src="structure.png" alt="3-bromo-1-chloropentane" /></td>
</tr>
<tr>
<td>1,2-dichloropropane</td>
<td><img src="structure.png" alt="1,2-dichloropropane" /></td>
</tr>
</tbody>
</table>

### Classifying haloalkanes

Haloalkanes can be classified according to how many carbons are attached to the C-X functional group.

- **Primary Haloalkane 1°**
  - One carbon attached to the carbon atom adjoining the halogen

- **Secondary Haloalkane 2°**
  - Two carbons attached to the carbon atom adjoining the halogen

- **Tertiary Haloalkane 3°**
  - Three carbons attached to the carbon atom adjoining the halogen
Nucleophilic Substitution Reactions of Haloalkanes

Nucleophile: electron pair donator e.g. :OH⁻, :NH₃, CN⁻

Substitution: swapping a halogen atom for another atom or groups of atoms

The **ATTACKING GROUP** is a **NUCLEOPHILE** (e.g. OH⁻, CN⁻, H₂O, NH₃) attracted to the δ⁺ carbon and donating a lone pair of electrons to form a new covalent bond.

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

Reactivity of haloalkanes

The rate of reaction 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</th>
<th>Bond enthalpy / kJmol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-I</td>
<td>238</td>
</tr>
<tr>
<td>C-Br</td>
<td>276</td>
</tr>
<tr>
<td>C-Cl</td>
<td>338</td>
</tr>
<tr>
<td>C-F</td>
<td>484</td>
</tr>
</tbody>
</table>
Comparing the rate of hydrolysis reactions

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

**Water** is a poor nucleophile but it can react slowly with haloalkanes in a substitution reaction.

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

Aqueous silver nitrate is added to a haloalkane and 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 haloalkane and so the rate of formation of the precipitate can be used to compare the reactivity of the different haloalkanes.

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

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

\[ \text{Ag}^+ (aq) + \text{I}^- (aq) \rightarrow \text{AgI} (s) \]

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

The precipitate forms:
- AgI (s) - yellow precipitate
- AgBr (s) - cream precipitate
- AgCl (s) - white precipitate

Reaction of haloalkanes with **aqueous** hydroxide ions

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

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

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

**Mechanism:** Nucleophilic Substitution

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

**Equation:**

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{Br} (l) + \text{K}^+\text{OH}^- (aq) \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} (l) + \text{K}^+\text{Br}^- (aq) \]

1-bromopropane \( \rightarrow \) propan-1-ol

\[ \text{H} \quad \text{H} \quad \text{H} \quad \text{Br} \quad + \text{KOH} \rightarrow \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{O} \quad + \text{KBr} \]

KEY
Nucleophilic substitution mechanism, $S_{N2}$

Bromoethane [Primary haloalkane] + aqueous hydroxide ions

The attacking group is a NUCLEOPHILE, OH$^-$. It is attracted to the slightly positive carbon atom and has a lone pair of electrons which can form a new covalent bond.

This mechanism goes through a TRANSITION STATE: the C-OH bond is forming at the same time as the C-Br bond is breaking.

Overall, there has been SUBSTITUTION of a Br atom for a −OH group.
Nucleophilic substitution mechanism, $S_N^1$

2-methyl-2-bromobutane $\text{[Tertiary haloalkane]} + \text{aqueous hydroxide ions}$

An intermediate **CARBOCATION** is formed. The OH **NUCLEOPHILE** attacks the positively charged carbon, using its lone pair to form a covalent bond.

Overall, there has been **SUBSTITUTION** of a Br atom for a –OH group.

$S_N^1$ or $S_N^2$?

The form of nucleophilic substitution known as $S_N^2$ is a bimolecular process; in the initial step there is collision between the haloalkane and the nucleophile.

The alternative mechanism, $S_N^1$, involves the initial breaking of the C-X bond to form a carbocation, which is then attacked by the nucleophile.

$S_N^1$ is favoured for tertiary haloalkanes where there is steric hindrance to attack (lots of bulky alkyl groups get in the way of the incoming nucleophile) and a more stable tertiary carbocation intermediate is formed (the alkyl groups are electron releasing and reduce the charge density on the carbon atom).
**Reaction of haloalkanes with ammonia**

*Change in functional group:* haloalkane $\rightarrow$ amine

- **Reagent:** NH$_3$ dissolved in ethanol
- **Conditions:** Heating under pressure (in a sealed tube)
- **Mechanism:** Nucleophilic Substitution
- **Type of reagent:** Nucleophile, :NH$_3$

**Equation:**

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{Br} \ (l) + 2\text{NH}_3 \ (\text{alc}) \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2 \ (l) + \text{NH}_4\text{Br} \ (aq)
\]

```
\[
\begin{array}{c}
\text{H} & \text{C} & \text{C} & \text{Br} \\
\text{H} & \text{H} & \text{H} & \text{H}
\end{array}
\begin{array}{c}
\text{H} & \text{C} & \text{C} & \text{NH}_2 \\
\text{H} & \text{H} & \text{H} & \text{H}
\end{array}
\]
```

1-bromopropane  propylamine

**Nucleophilic substitution mechanism**

For formation of primary amine from haloalkane

```
\[
\begin{array}{c}
\text{H}_3\text{C} & \text{C} & \text{Cl} \\
\text{H} & \text{H}
\end{array}
\begin{array}{c}
\text{H}_3\text{C} & \text{C} & \text{Cl}^{-} \\
\text{H} & \text{H} & \text{NH}_3
\end{array}
\begin{array}{c}
\text{H}_3\text{C} & \text{C} & \text{NH}_2 \\
\text{H} & \text{H}
\end{array}
\]
```

This reaction does not give a good yield and various other side products are formed.
Reaction of haloalkanes with KCN

**Change in functional group:** haloalkane $\rightarrow$ nitrile

**Reagent:** KCN dissolved in ethanol

**Conditions:** Heating under reflux

**Mechanism:** Nucleophilic Substitution

**Type of reagent:** Nucleophile, :CN$^-$

**Equation:**

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{Br} & \quad + \quad \text{CN}^- \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{CN} & \quad + \quad \text{Br}^- \\
\end{align*}
\]

1-bromopropane $\rightarrow$ butanenitrile

Nucleophilic substitution mechanism

cyanide ion with bromoethane

The C in the CN$^-$ ion counts as part of the carbon chain so remember to add one carbon to the name. E.g. Bromoethane turns into propanenitrile.
Reaction of haloalkanes with *alcoholic* hydroxide ions

**Change in functional group:** haloalkane → alkene

**Reagents:** Potassium (or sodium) hydroxide

**Conditions:** In *ethanolic solution*; Heat

**Mechanism:** Elimination

**Type of reagent:** Base, OH⁻

**Equation:**

$$\text{CH}_3\text{CH}_2\text{CH}_2\text{Br} (l) + \text{K}^+\text{OH}^- \text{(alc)} \rightarrow \text{CH}_3\text{CHCH}_2 (g) + \text{K}^+\text{Br}^- + \text{H}_2\text{O}$$

**Diagram: 1-bromopropane → propene**

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**Elimination mechanism**

2-bromopropane + alcoholic hydroxide ions

**Diagram:**

The hydroxide ion, OH⁻, acts as a *BASE* and removes a *proton* (hydrogen ion). The proton comes from a carbon atom *adjacent* to the one bonded to the bromine.
Elimination from unsymmetrical haloalkanes

What alkenes could this form when reacted with alcoholic KOH?

The OH\(^-\) removes a proton from a carbon atom adjacent to the carbon bearing the halogen. 2-chloro-2-methylbutane is unsymmetrical and there are two adjacent carbon atoms. Hydrogen can be removed from either and a mixture of isomeric alkenes is formed.

Apparatus used for Elimination Reaction

Ceramic wool soaked in KOH in ethanol and halogenoalkane

Gaseous alkene

HEAT
Elimination or substitution?

The products of reactions between haloalkanes and OH\(^{-}\) are **influenced by the solvent that the NaOH is dissolved in.**

Both reactions can take place simultaneously and a mixture of alkenes and alcohols may be formed. However, the **choice of solvent can favour one reaction.**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Product</th>
<th>Role of OH(^{-})</th>
<th>Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>Alcohol</td>
<td>Nucleophile</td>
<td><strong>Nucleophilic substitution</strong></td>
</tr>
<tr>
<td>Alcohol</td>
<td>Alkene</td>
<td>Base</td>
<td>Elimination</td>
</tr>
</tbody>
</table>

**KEY**