



REACTIONS OF HALOGENOALKANES 1

NUCLEOPHILIC SUBSTITUTION

Halogenoalkanes are susceptible to attack by **nucleophiles** (lone pair donors) such as OH^- , CN^- and NH_3 .

This is because the halogen atom is more electronegative than carbon atoms and so the C of the C-halogen bond is δ^+ .

In a **substitution** reaction, the halogen atom is replaced by another atom/group.

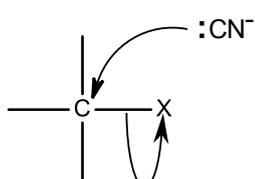
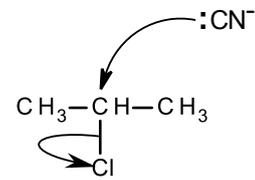
The rate of the reaction is partly affected by the strength of the C-halogen bond. The longer the bond, the weaker the bond, the more easily it breaks and the faster the reaction. Therefore, in terms of rate: $\text{C-I} > \text{C-Br} > \text{C-Cl} > \text{C-F}$.

NUCLEOPHILIC SUBSTITUTION 1 – reaction with warm, aqueous NaOH

Reagent	NaOH
Conditions	aqueous, warm
What happens	halogen atom is replaced by OH group
Overall equation	$\text{R-X} + \text{NaOH} \longrightarrow \text{R-OH} + \text{NaX}$
Mechanism	<p>nucleophilic substitution</p>
Example 1	<p>e.g. bromoethane + aqueous NaOH</p> $\text{CH}_3\text{-CH}_2\text{-Br} + \text{NaOH} \longrightarrow \text{CH}_3\text{-CH}_2\text{-OH} + \text{NaBr}$ <p>nucleophilic substitution</p>
Example 2	<p>e.g. 2-chloropropane + aqueous NaOH</p> $\begin{array}{c} \text{CH}_3\text{-CH-CH}_3 \\ \\ \text{Cl} \end{array} + \text{NaOH} \longrightarrow \begin{array}{c} \text{CH}_3\text{-CH-CH}_3 \\ \\ \text{OH} \end{array} + \text{NaCl}$ <p>nucleophilic substitution</p>

Example 3	e.g. 1-bromopropane + aqueous NaOH
Example 4	e.g. 2-iodo-3-methylbutane + aqueous NaOH

NUCLEOPHILIC SUBSTITUTION 2 – reaction with KCN

Reagent	KCN
Conditions	ethanolic, warm
What happens	halogen atom is replaced by CN group
Overall equation	$R-X + KCN \longrightarrow R-CN + KX$
Mechanism	<p>nucleophilic substitution</p> 
Example 5	<p>e.g. 2-chloropropane + ethanolic KCN</p> $\begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}_3 \\ \\ \text{Cl} \end{array} + \text{KCN} \longrightarrow \begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}_3 \\ \\ \text{CN} \end{array} + \text{KCl}$ <p>nucleophilic substitution</p> 

Example 6	e.g. 1-bromobutane + ethanolic KCN
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NUCLEOPHILIC SUBSTITUTION 3 – reaction with NH₃

Reagent	NH ₃
Conditions	Excess concentrated ammonia dissolved in ethanol at pressure in a sealed container
What happens	first molecule of NH ₃ : halogen atom is replaced by NH ₂ group second molecule of NH ₃ : leads to formation of NH ₄ X
Overall equation	$R-X + 2 NH_3 \longrightarrow R-NH_2 + NH_4X$
Mechanism	<p>nucleophilic substitution</p>
Example 7	<p>e.g. 2-chloropropane + excess conc NH₃</p> $ \begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}_3 \\ \\ \text{Cl} \end{array} + 2 \text{NH}_3 \longrightarrow \begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}_3 \\ \\ \text{NH}_2 \end{array} + \text{NH}_4\text{Cl} $ <p>nucleophilic substitution</p>
Example 8	e.g. 2-bromo-3-methylbutane + excess conc NH ₃

ELIMINATION	<p>When halogenoalkanes react with OH⁻ ions, an elimination reaction can compete with the nucleophilic substitution reaction.</p> <p>Elimination is favoured if hot, ethanolic KOH is used instead of warm, aqueous NaOH.</p> <p>In elimination, an H and X are removed from adjacent C atoms giving an alkene.</p> <p>In elimination, the OH⁻ ion acts as a base. In substitution, the OH⁻ ion acts as a nucleophile.</p>
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ELIMINATION – reaction with hot, ethanolic KOH	
Reagent	KOH
Conditions	Ethanolic, hot
What happens	<p>The halogen atom and one H atom from an adjacent C atom is removed giving an alkene (note that elimination cannot happen if there is no H on an adjacent C atom).</p> <p>A mixture of alkenes could be formed depending on which of the adjacent C atoms the H is lost from.</p>
Overall equation	$ \begin{array}{c} & \\ \text{---C} & \text{---C---} \\ & \\ \text{H} & \text{X} \end{array} + \text{KOH} \longrightarrow \begin{array}{c} & \\ \text{---C} & =\text{C---} \\ & \end{array} + \text{KX} + \text{H}_2\text{O} $
Mechanism	<p style="text-align: center;">elimination</p>
Example 9	<p>e.g. 2-chloropropane + hot, ethanolic KOH</p> $ \begin{array}{c} \text{CH}_3\text{---CH---CH}_3 \\ \\ \text{Cl} \end{array} + \text{KOH} \longrightarrow \text{CH}_3\text{---CH=CH}_2 + \text{KCl} + \text{H}_2\text{O} $ <p style="text-align: center;">elimination</p>
Example 10	e.g. 2-bromobutane + hot, ethanolic KOH (to give but-2-ene)