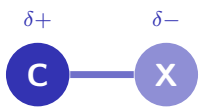
Halogen Compounds

A-Level Chemistry ▪ Topic 15

A-Level Chemistry

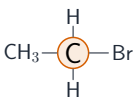


What we will cover

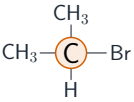
1. Three classes
2. Nucleophilic substitution
3. Substitution vs elimination
4. S_N1 & S_N2
5. Different reactivities

volatile halogenoalkanes

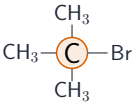
Three classes



primary
1 C on the C–Br carbon



secondary
2 C



tertiary
3 C

A **halogenoalkane** 卤代烷 has a C–X bond.

- **primary** 伯 – 1 carbon on the C–X carbon
- **secondary** 仲 – 2
- **tertiary** 叔 – 3

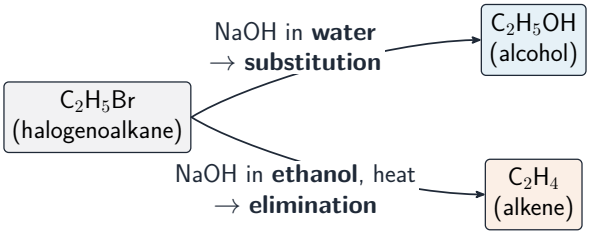
Nucleophilic substitution

The polar carbon is attacked by a **nucleophile** 亲核试剂:

- NaOH(aq) $\rightarrow$ an **alcohol** 醇
- KCN $\rightarrow$ a **nitrile** 腈 (adds a carbon)
- NH_3 $\rightarrow$ an **amine** 胺

Warm with **silver nitrate** 硝酸银 to identify the halogen.

Substitution vs elimination

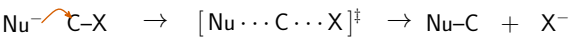


The conditions decide:

- NaOH in water → substitution (alcohol)
- NaOH in ethanol, heat → **elimination** 消去 (alkene)

S_N1 and S_N2

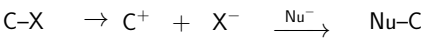
S_N2: one step



rate depends on both reactants

transition state

S_N1: two steps



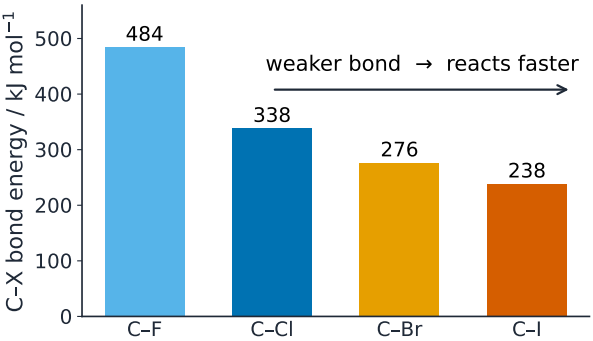
rate depends on R–X only

carbocation

- **S_N2** 双分子 – one step, a crowded **transition state** 过渡态; primary
- **S_N1** 单分子 – two steps via a **carbocation** 碳正离子; tertiary

The inductive effect stabilises the tertiary carbocation.

Different reactivities



Reactivity depends on the C–X **bond energy** 键能.

> The weaker the bond, the faster it reacts – so iodoalkanes react fastest, chloroalkanes slowest.

Worked example – S_N1 or S_N2?

Predict the mechanism for hydrolysis of (a) 1-bromobutane and (b) 2-bromo-2-methylpropane.

- (a) Primary: little steric hindrance, and a primary cation is too unstable to form.
- $\Rightarrow S_N2$: one step, OH^- attacks as Br leaves; rate $= k[RBr][OH^-]$.
- (b) Tertiary: bulky groups block attack, but the tertiary cation is stable.
- $\Rightarrow S_N1$: two steps via the cation; rate $= k[RBr]$ only.

Primary $\rightarrow S_N2$, tertiary $\rightarrow S_N1$, secondary $\rightarrow$ both. The rate equation is the exam's proof of which one ran.

Topic 15 – key takeaways

1 Classes

primary, secondary, tertiary

2 Substitution

NaOH(aq), KCN, NH_3 replace the halogen

3 Mechanism

S_N2 (primary) vs S_N1 (tertiary)

4 Reactivity

weaker C–X $\rightarrow$ faster; iodo fastest

Check yourself

1. NaOH in water gives which product?
2. NaOH in ethanol gives which product?
3. Which mechanism do tertiary halogenoalkanes favour?
4. Which halogenoalkane reacts fastest?

Answers **1.** an alcohol **2.** an alkene **3.** S_N1 **4.** the iodoalkane