# Halogen Compounds

A-Level Chemistry ▪ Topic 15

A-Level Chemistry




## What we will cover

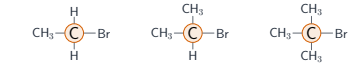
1. Three classes
2. Nucleophilic substitution
3. Substitution vs elimination
4. $S_N1$ & $S_N2$
5. Different reactivities

*volatile halogenoalkanes*

# 1 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



## Two ways to make a halogenoalkane

A **halogenoalkane** 卤代烷 is an alkane with one or more halogens in place of hydrogen – a C–X bond.

| | |
|---|---|
| **free-radical substitution 自由基取代** | an alkane with $Cl_2$ or $Br_2$ in ultraviolet light |
| **electrophilic addition 亲电加成** | an alkene with a halogen $X_2$, or with a hydrogen halide HX |

The route decides the product: radicals give a mixture, an addition across a C=C gives one place only.



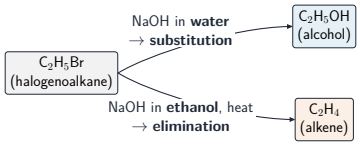
## Nucleophilic substitution

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

- NaOH(aq) → an **alcohol** 醇
- KCN → a **nitrile** 腈 (adds a carbon)
- $NH_3$ → 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)



## The $S_N1$ and $S_N2$ mechanisms

Nucleophilic substitution can follow two routes:

- **$S_N2$**: one step. The nucleophile attacks at the same time as the halogen leaves, passing through a crowded **transition state 过渡态** where both are half-bonded.
- **$S_N1$**: two steps. First the C–X bond breaks to give a **carbocation 碳正离子**; then the nucleophile attacks it. The rate depends only on the halogenoalkane.
- **primary** halogenoalkanes mostly react by $S_N2$.
- **tertiary** halogenoalkanes mostly react by $S_N1$ (their carbocation is well stabilised).

# 2 Mechanism and rate



## $S_N1$ and $S_N2$

- **$S_N2$** 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.

**$S_N2$: one step**

$$Nu^- \overset{\curvearrowright}{C}\text{–}X \rightarrow [Nu\cdots C\cdots X]^{\ddagger} \rightarrow Nu\text{–}C + X^-$$

rate depends on both reactants — transition state

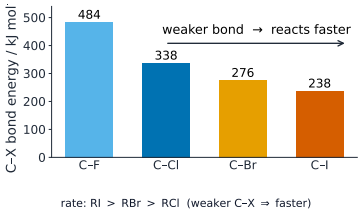
**$S_N1$: two steps**

$$C\text{–}X \rightarrow C^+ + X^- \xrightarrow{Nu^-} Nu\text{–}C$$

rate depends on R–X only — carbocation



## Different reactivities




rate: RI > RBr > RCl (weaker C–X ⇒ faster)

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

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



## Exam tips

- Draw **nucleophilic substitution** with a curly arrow from the nucleophile's lone pair to the $\delta+$ carbon and one from the C-X bond.
- Match mechanism to class: $S_N1$ **(tertiary, carbocation, two steps) vs** $S_N2$ (primary, one step, transition state).
- Reactivity is set by **bond enthalpy**: C-I is weakest, so iodoalkanes react fastest (not electronegativity).
- **Elimination** (hot, ethanolic KOH) vs **substitution** (warm, aqueous KOH) – the conditions decide the product; state them.

# 3 Recap



## 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