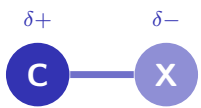
Halogen Compounds

A-Level Chemistry ▪ Topic 15

A-Level Chemistry



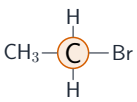
What we will cover

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

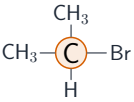
volatile halogenoalkanes

1 Halogenoalkanes

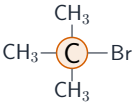
Three classes



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.

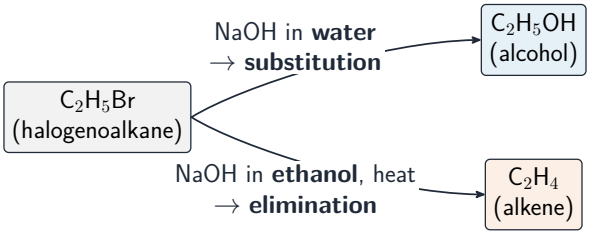
Nucleophilic substitution

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

- NaOH(aq) $\rightarrow$ 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)

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).

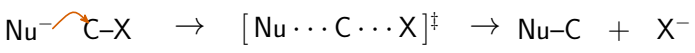
2 Mechanism and rate

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.

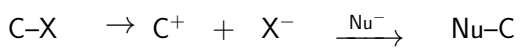
S_N2: one step



rate depends on both reactants

transition state

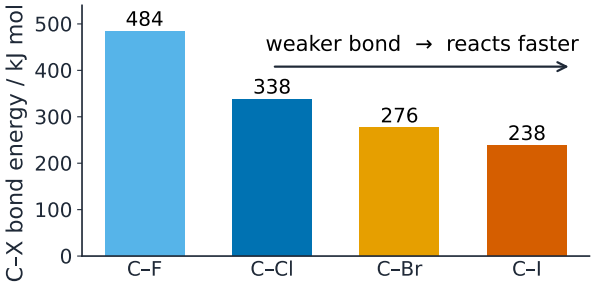
S_N1: two steps



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