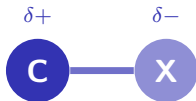


Halogen Compounds

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

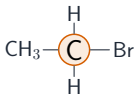


volatile halogenoalkanes

1

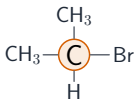
Halogenoalkanes

Three classes



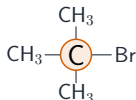
primary

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 $\text{C}=\text{C}$ gives one place only.

Nucleophilic substitution

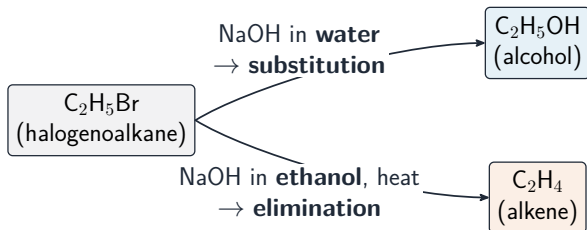


The polar carbon is attacked by a **nucleophile** 亲核试剂:

- $\text{NaOH(aq)} \rightarrow$ an **alcohol** 醇
- $\text{KCN} \rightarrow$ a **nitrile** 腈 (adds a carbon)
- $\text{NH}_3 \rightarrow$ 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

S_N2: one step

Nucleophile attacks **as** the halogen leaves, through a crowded **transition state** 过渡态.



Primary halogenoalkanes

S_N1: two steps

C—X breaks first to a **carbocation** 碳正离子; then Nu[−] attacks. Rate depends **only** on the halogenoalkane.

Tertiary: the carbocation is well stabilised

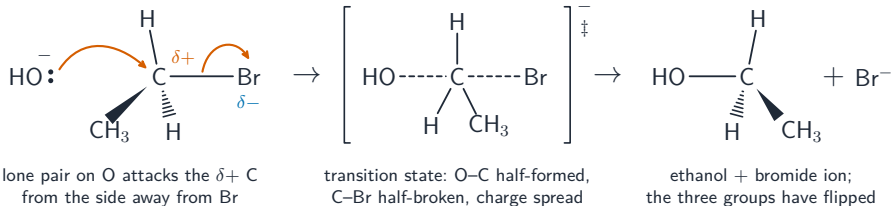
2

Mechanism and rate

S_N2 : one step

S_N2 双分子 – one step through a crowded **transition state** 过渡态; typical of **primary** halogenoalkanes.

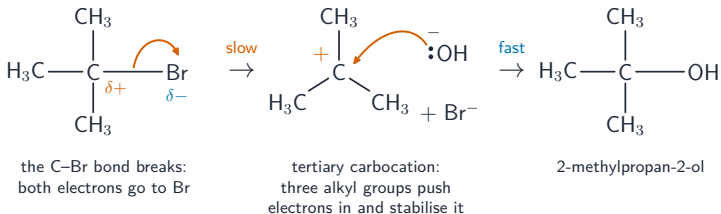
S_N2 (primary, e.g. bromoethane): one step



S_N1: two steps

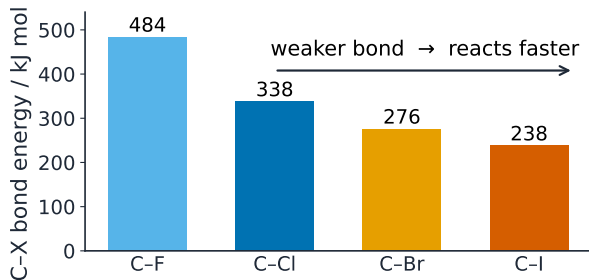
S_N1 单分子 – two steps via a **carbocation** 碳正离子; typical of **tertiary** halogenoalkanes.

S_N1 (tertiary, e.g. 2-bromo-2-methylpropane): two steps



The inductive effect of three alkyl groups stabilises the tertiary carbocation.

Different reactivities



rate: $\text{RI} > \text{RBr} > \text{RCl}$ (weaker C-X $\Rightarrow$ 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 = $k[\text{RBr}][\text{OH}^-]$.
- (b) **Tertiary**: bulky groups block attack, but the tertiary cation is stable.
- $\Rightarrow S_N1$: two steps via the cation; rate = $k[\text{RBr}]$ 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, NH₃ replace the halogen

3

Mechanism

S_N2 (primary) vs S_N1 (tertiary)

4

Reactivity

weaker C–X → 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