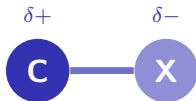


Halogen Compounds

A-Level Chemistry ■ Topic 15

A-Level Chemistry



What we will cover

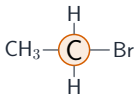
- 1 Three classes
- 2 Nucleophilic substitution
- 3 Substitution vs elimination
- 4 S_N1 & S_N2
- 5 Different reactivities



volatile halogenoalkanes

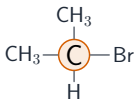


Three classes



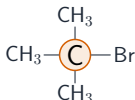
primary

1 C on the C-Br carbon



secondary

2 C



tertiary

3 C

A **halogenoalkane** has a C-X bond.

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

Two ways to make a halogenoalkane

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

free-radical substitution

an alkane with Cl_2 or Br_2 in ultraviolet light

electrophilic addition

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

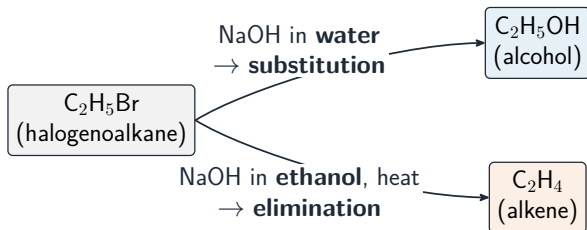


The polar carbon is attacked by a **nucleophile** :

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

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

Substitution vs elimination



The conditions decide:

- NaOH in **water** → substitution (alcohol)
- NaOH in **ethanol**, heat → **elimination** (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** where both are half-bonded.
- **S_N1**: two steps. First the C–X bond breaks to give a **carbocation** ; 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).

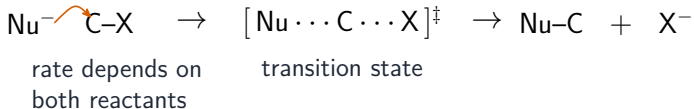


S_N1 and S_N2

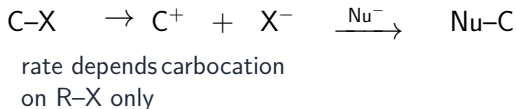
- **S_N2** – one step, a crowded **transition state** ; primary
- **S_N1** – two steps via a **carbocation** ; tertiary

The inductive effect stabilises the tertiary carbocation.

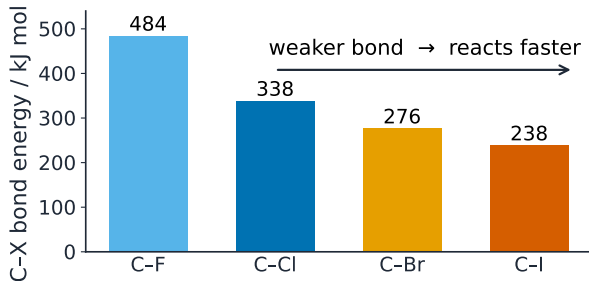
S_N2: one step



S_N1: two steps



Different reactivities



rate: $\text{RI} > \text{RBr} > \text{RCl}$ (weaker C-X $\Rightarrow$ faster)

Reactivity depends on the C-X **bond energy** .

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.



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