

15.1 Halogenoalkanes

Name: _____ Class: _____ Date: _____

Total: 12 marks

KEY WORDS elimination 消去 • secondary 仲 • tertiary 叔 • nucleophilic substitution 亲核取代 • primary 伯

Objective

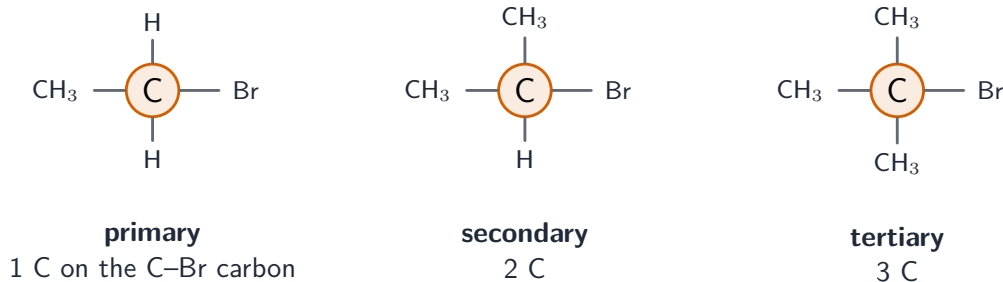
Build the skills to answer exam questions on **halogenoalkanes** 卤代烷 — **nucleophilic substitution** 亲核取代, **elimination** 消去, the **S_N1/S_N2** mechanisms, and the trend in reactivity.

You must be able to:

- classify halogenoalkanes and describe their nucleophilic substitution reactions
- describe the elimination reaction and the S_N1 and S_N2 mechanisms
- explain the different reactivities in terms of C–X bond strength

1 Worked examples

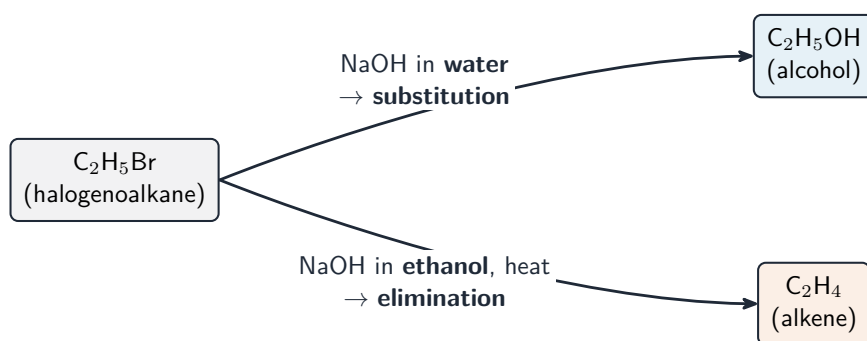
■ Classes and nucleophilic substitution



Primary/secondary/tertiary = 1/2/3 carbons joined to the carbon bearing the halogen

The polar C–X carbon is attacked by **nucleophiles**: NaOH(aq) → alcohol; KCN/ethanol → nitrile (+1 C); NH₃/ethanol/pressure → amine. **Test the halogen** with AgNO₃ in ethanol (white AgCl, cream AgBr, yellow AgI).

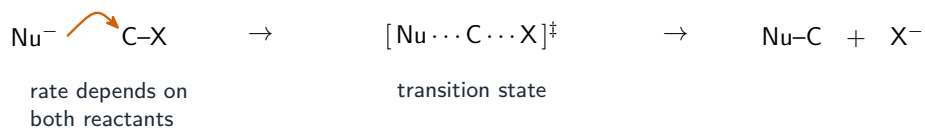
■ Substitution vs elimination



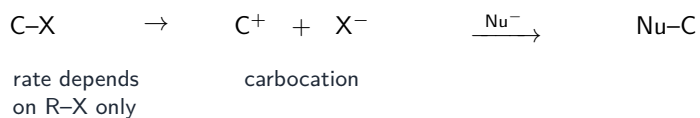
$\text{NaOH(aq)} \rightarrow \text{substitution (alcohol)}$; $\text{NaOH in ethanol} + \text{heat} \rightarrow \text{elimination (alkene)}$

■ $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$

$\text{S}_{\text{N}}2$: one step



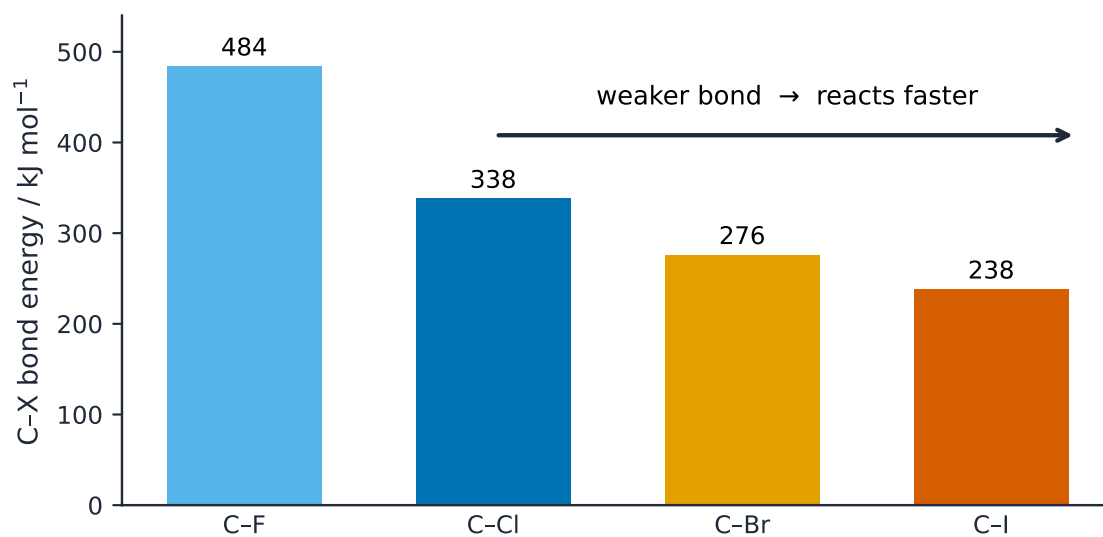
$\text{S}_{\text{N}}1$: two steps



$\text{S}_{\text{N}}2$: one step (rate depends on both). $\text{S}_{\text{N}}1$: via a carbocation (rate depends only on the halogenoalkane)

Primary $\rightarrow$ mostly $\text{S}_{\text{N}}2$; tertiary $\rightarrow$ mostly $\text{S}_{\text{N}}1$ (stable carbocation).

■ Reactivity



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

The weaker the C-X bond, the faster — iodoalkanes react fastest, chloroalkanes slowest

2 Practice

2.1 State the reagent and condition to convert a halogenoalkane into an alcohol. [2]

2.2 Name the organic product when a halogenoalkane reacts with KCN in ethanol. [1]

3 Exam-style questions

3.1 Which conditions favour **elimination** of a halogenoalkane to an alkene? [1]

- A NaOH in water, warm
- B NaOH in ethanol, heat
- C aqueous silver nitrate
- D KCN in ethanol

3.2 Which halogenoalkane reacts **fastest** with aqueous silver nitrate? [1]

- A 1-chlorobutane

- **B** 1-bromobutane
 - **C** 1-iodobutane
 - **D** they react at the same rate
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3.3 (a) Describe the S_N2 mechanism for the reaction of bromoethane with hydroxide ions. [3]

(b) Explain why tertiary halogenoalkanes tend to react by the S_N1 mechanism. [2]

3.4 Explain why iodoalkanes are more reactive than chloroalkanes in substitution reactions. [2]

Solutions

2.1 aqueous sodium hydroxide, NaOH(aq) ; and heat.

2.2 a nitrile.

3.1 B. NaOH in ethanol with heat favours elimination.

3.2 C. The C-I bond is weakest, so the iodoalkane reacts fastest.

3.3 (a) the OH^- nucleophile attacks the $\delta+$ carbon (curly arrow from the lone pair); at the same time the C-Br bond breaks, with both electrons going to Br ; passing through a transition state with both half-bonded, giving ethanol and Br^- .

(b) the tertiary carbocation is stabilised by three electron-pushing alkyl groups, so the C-X bond breaks first to form it ($\text{S}_{\text{N}}1$).

3.4 the C-I bond is weaker (lower bond energy) than C-Cl , so it breaks more easily, making the substitution faster.