A-LEVEL CHEMISTRY • EXERCISE SHEET

15.1 Halogenoalkanes

Name: _____ Class: _____ Date: _____ **Total: 12 marks**

Objective

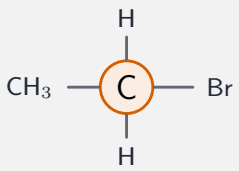
Build the skills to answer exam questions on **halogenoalkanes** 卤代烷—**nucleophilic substitution** 亲核取代, **elimination** 消去, the **S_N1/S_N2** mechanisms, and the trend in reactivity.

You must be able to:

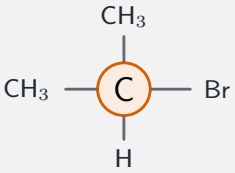
- classify halogenoalkanes and describe their nucleophilic substitution reactions
- describe the elimination reaction and the S_N1 and S_N2 mechanisms
- explain the different reactivities in terms of C–X bond strength

1 Worked examples

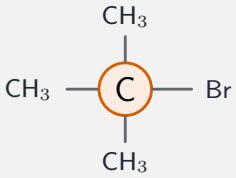
Classes and nucleophilic substitution



primary
1 C on the C–Br carbon



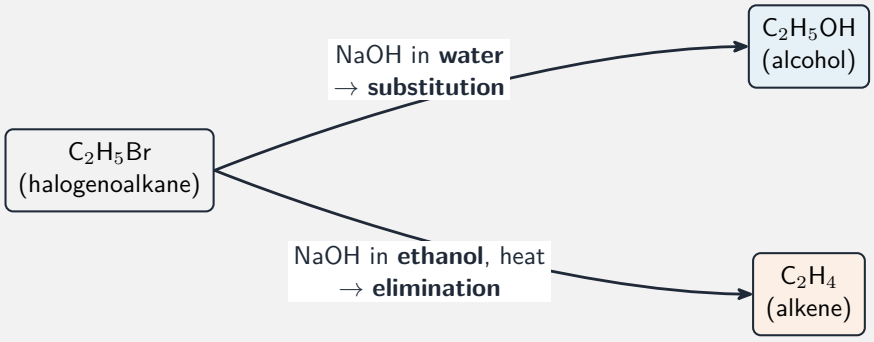
secondary
2 C



tertiary
3 C

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); NH /ethanol/pressure → amine. **Test the halogen** with AgNO in ethanol (white AgCl, cream AgBr, yellow AgI).



NaOH(aq) → substitution (alcohol); NaOH in ethanol + heat → elimination (alkene)

S_N1 and S_N2

S_N2: one step

$$\mathrm{Nu^-} + \mathrm{C{-}X} \rightarrow [\mathrm{Nu\cdots C\cdots X}]^{\ddagger} \rightarrow \mathrm{Nu{-}C} + \mathrm{X^-}$$

rate depends on both reactants — transition state

S_N1: two steps

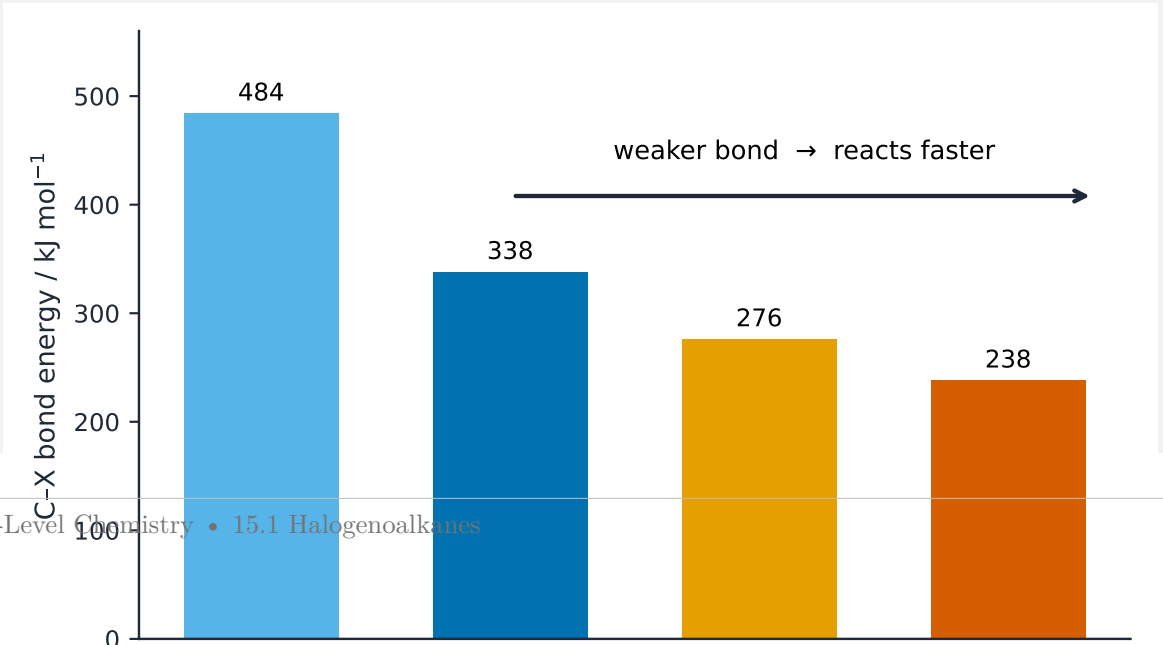
$$\mathrm{C{-}X} \rightarrow \mathrm{C^+} + \mathrm{X^-} \xrightarrow{\mathrm{Nu^-}} \mathrm{Nu{-}C}$$

rate depends on R–X only — carbocation

S_N2: one step (rate depends on both). S_N1: via a carbocation (rate depends only on the halogenoalkane)

Primary → mostly S_N2; tertiary → mostly S_N1 (stable carbocation).

Reactivity



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

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]

4 Go further

You are now ready for the real exam questions on this subtopic. Open the **15.1 Halogenoalkanes** past-paper sheet in the Library, or try these in **Practice mode**:

- 9701/11 N25 —Q30 (halogenoalkanes)
- 9701/12 N25 —Q31 (nucleophilic substitution)
- 9701/14 N25 —Q31 (mechanisms)

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 (S_N1).

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