

Halogen compounds

A-Level Chemistry 9701 · Topic 15 revision notes

Everything from the 2 lessons of this topic on a few pages: the key idea of each lesson, the diagram to remember, the points to learn and the traps examiners set. Read it, cover it, test yourself.

1. Halogenoalkanes

2. SN1 and SN2 mechanisms

thelucidstem.com

1 Halogenoalkanes

Syllabus 15.1

Halogenoalkanes contain a polar $C^{\delta+}-X^{\delta-}$ bond, so the carbon is attacked by **nucleophiles**. They are classed as primary, secondary or tertiary by how many carbons are attached to the C-X carbon. With **aqueous NaOH** they give alcohols; with **KCN in ethanol**, nitriles (one extra carbon); with **ammonia in ethanol under pressure**, amines: all **nucleophilic substitution**. With **NaOH in ethanol** they undergo **elimination** to alkenes. The rate of hydrolysis is governed by **bond strength**, not polarity: C-I is the weakest bond, so iodoalkanes react fastest.

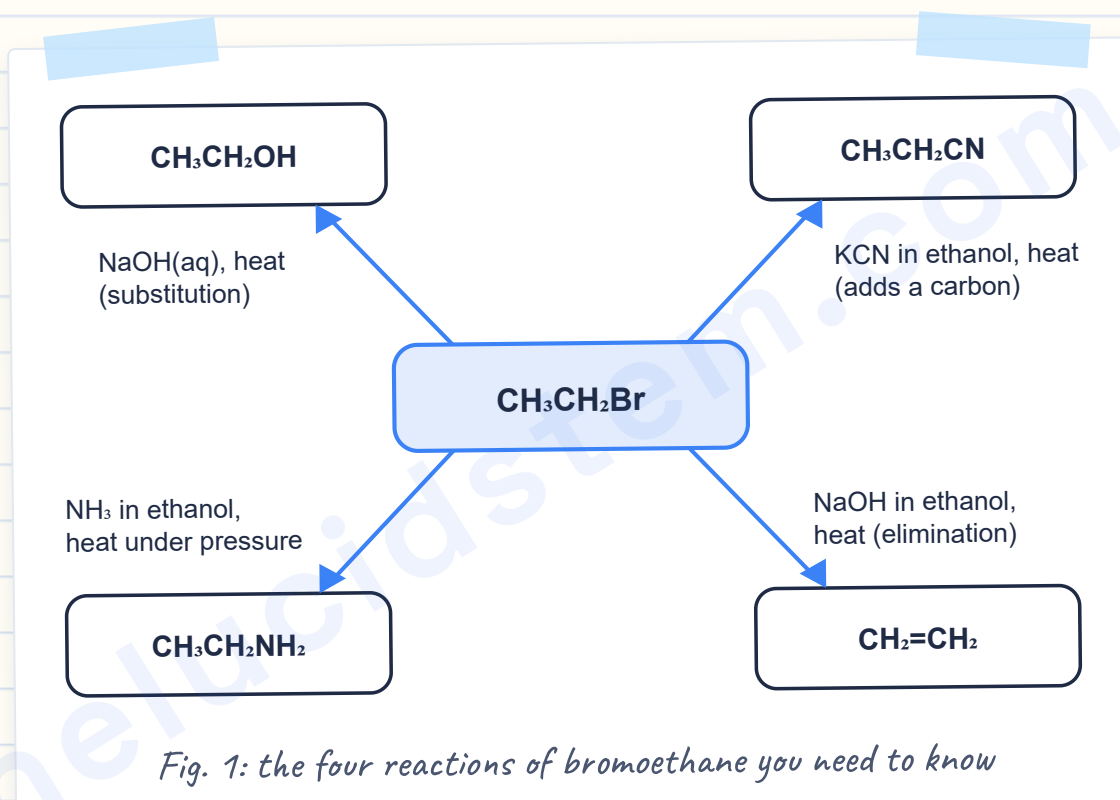


Fig. 1: the four reactions of bromoethane you need to know

Aqueous substitutes; ethanolic eliminates.

- ✓ **NaOH(aq)** → alcohol; **KCN/ethanol** → nitrile (+1 C).
- ✓ **NH_3 /ethanol, pressure** → amine.
- ✓ **NaOH/ethanol** → alkene.
- ✓ **Rate:** $C-I > C-Br > C-Cl$ (bond strength).

Watch out!

Aqueous NaOH gives substitution (an alcohol); **ethanolic** NaOH gives elimination (an alkene). For the rate of hydrolysis, bond **strength** wins over bond polarity: iodoalkanes react fastest. KCN is the reagent that lengthens the carbon chain.

2 SN1 and SN2 mechanisms

Syllabus 15.1

S_N2 (substitution, nucleophilic, bimolecular) happens in **one step**: the nucleophile attacks the δ^+ carbon from the side opposite the halogen while the C-X bond breaks, through a **transition state** with partial bonds. It is typical of **primary** halogenoalkanes, and its rate depends on both reactants. **S_N1** happens in **two steps**: the C-X bond breaks heterolytically (slowly) to give a **carbocation**, which the nucleophile then attacks (quickly). It is typical of **tertiary** halogenoalkanes, because the tertiary carbocation is stabilised by three alkyl groups and the crowded carbon blocks a backside attack. Its rate depends only on the halogenoalkane.

SN2: one step (primary)



SN1: two steps (tertiary)

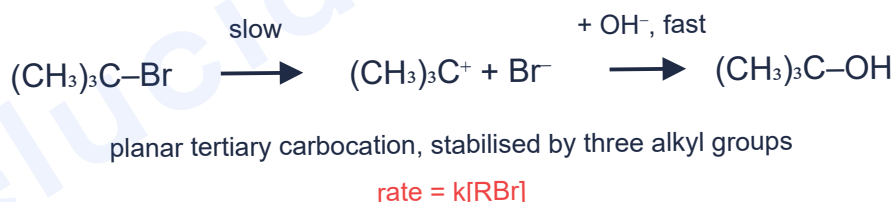


Fig. 1: the S_N2 and S_N1 routes compared

Primary S_N2; tertiary S_N1.

- ✓ **S_N2**: one step, transition state, rate = $k[\text{RX}][\text{Nu}]$.
- ✓ **S_N1**: two steps, carbocation, rate = $k[\text{RX}]$.
- ✓ **Tertiary**: steric hindrance plus stable carbocation.
- ✓ **Arrows** from lone pairs and bonds.

Watch out!

Curly arrows start from the **lone pair** on OH^- , not from the minus sign, and the arrow from the C-X bond must point to the halogen. In S_N2 draw the transition state in square brackets with partial bonds and an overall negative charge; S_N2 has **no** carbocation.