Halogen compounds

Making halogenoalkanes, classification, nucleophilic substitution and elimination, the SN1 and SN2 mechanisms, and the effect of the C–X bond strength on reactivity.

15.1 Halogenoalkanes

Preparation

- Free-radical substitution of an alkane with Cl_2 or Br_2 in UV light.
- Electrophilic addition to an alkene with X_2 or $HX(g)$ at room temperature.
- Substitution of an alcohol: with $HX(g)$; KCl with concentrated H_2SO_4 or H_3PO_4; PCl_3 with heat; PCl_5; or $SOCl_2$. If generating HBr from a bromide salt, a non-oxidising acid such as H_3PO_4 avoids oxidation of bromide/HBr by concentrated sulfuric acid. For example $CH_3CH_2OH + PCl_5 \rightarrow CH_3CH_2Cl + POCl_3 + HCl$.

Classification

A halogenoalkane is **primary**, **secondary** or **tertiary** according to whether the carbon bonded to the halogen is attached to one, two or three other carbon atoms.

Nucleophilic substitution

The C–X bond is polar ($C^{\delta+}-X^{\delta-}$), so the carbon is attacked by **nucleophiles**.

Reagent and conditions	Product	Nucleophile
NaOH(aq), heat	alcohol	OH^-
KCN in ethanol, heat	nitrile (one more carbon)	CN^-
NH_3 in ethanol, heated under pressure	amine	NH_3
$AgNO_3(aq)$ in ethanol	halide precipitate (water is the nucleophile)	H_2O

Example: $CH_3CH_2Br + OH^- \rightarrow CH_3CH_2OH + Br^-$.

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Elimination

With **NaOH in ethanol** and heat, HBr is lost to give an **alkene**: $CH_3CH_2Br + NaOH \rightarrow CH_2{=}CH_2 + NaBr + H_2O$ (the hydroxide acts as a **base**). Aqueous NaOH gives substitution; ethanolic NaOH gives elimination.

Mechanisms: SN1 and SN2

- **SN2** (one step, bimolecular): the nucleophile attacks the carbon **from the side opposite the halogen** as the C–X bond breaks. There is a single **transition state** with both the nucleophile and halogen partly bonded. **Primary** halogenoalkanes react this way; a tertiary carbon is too crowded for the nucleophile. The rate depends on both the halogenoalkane and the nucleophile.
- **SN1** (two steps, unimolecular): the C–X bond breaks first (slow), forming a **carbocation** and X^-; the nucleophile then attacks the carbocation (fast). **Tertiary** halogenoalkanes react this way, because alkyl groups stabilise the carbocation by their **inductive effect**. The rate depends only on the halogenoalkane. If the carbon is chiral the product is a **racemic mixture**, since the nucleophile can attack the planar carbocation from either side.
- **Secondary** halogenoalkanes react by a mixture of both, depending on structure.

Draw the curly arrows: the lone pair on the nucleophile to the carbon; the C–X bond to the halogen.

Reactivity and C–X bond strength

The rate of hydrolysis **increases from chloro- to bromo- to iodo-**, because the C–X bond energy decreases down the group (C–Cl 340, C–Br 280, C–I 240 kJ mol^{-1}); the bond strength, not the polarity, decides the rate. This is shown with **aqueous silver nitrate in ethanol** and warming: the halide precipitate forms fastest for iodoalkanes (yellow AgI), then bromoalkanes (cream AgBr), and slowest for chloroalkanes (white AgCl). Fluoroalkanes do not react.

> **TRY IT**
>
> Explain why 2-bromo-2-methylpropane reacts by SN1 but 1-bromobutane by SN2.

In the tertiary compound the carbocation is stabilised by three alkyl groups, and the carbon is too hindered for backside attack. In the primary compound the carbon is easy to attack and the primary carbocation would be unstable.

Identify the reacting carbon before choosing a route

Classification depends on the carbon directly bonded to X, not the total carbon count. In 1-bromo-2-methylpropane, the CH_2Br carbon is bonded to one other carbon and is primary despite branching

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nearby. In 2-bromo-2-methylpropane, the C–Br carbon is bonded to three carbons and is tertiary. This distinction helps predict steric accessibility and carbocation stability.

Worked example: $CH_3CHBrCH_2CH_3$ is secondary. Substitution replaces Br with the incoming group without changing the carbon skeleton unless the nucleophile itself contains carbon. With cyanide the new product is $CH_3CH(CN)CH_2CH_3$, which contains **five** carbons. The nitrile carbon must be included when naming the product and considering subsequent hydrolysis.

> **TRY IT**
>
> Classify $CH_3CH_2CH_2Cl$ and $(CH_3)_3CCl$.

Answer: Primary and tertiary respectively. Count other carbons attached directly to the carbon carrying chlorine, not hydrogens on the entire molecule.

SN2: concerted bond making and breaking

In an SN2 step, nucleophile approach and departure of the leaving group occur together. Draw one arrow from a nucleophile lone pair to the electrophilic carbon and another from C–X to X. A transition state is not a stable intermediate that could accumulate in a flask. Backside approach explains inversion at a stereogenic reacting carbon when the product remains chiral.

Worked mechanism: hydroxide attacks bromoethane while the C–Br pair moves to Br. The products are ethanol and bromide. No free primary carbocation is required. Under a simple SN2 rate law, doubling hydroxide at fixed bromoethane doubles rate; doubling both concentrations gives four times the rate. These observations connect mechanism to **rate equations**.

SN1: ionisation followed by capture

In the first slow step, the C–X bond pair moves to X, leaving a carbocation. The nucleophile attacks in a later step. The planar carbon centre permits attack from either face, giving racemisation in the idealised model if a chiral product is formed. Real product ratios can be influenced by ion-pair and solvent effects; the key syllabus explanation is loss of stereochemical specificity through a planar intermediate.

A tertiary carbon is crowded for a concerted backside attack and can form a relatively stabilised carbocation. A primary carbon has the opposite combination. Secondary compounds depend more sensitively on solvent and conditions, so structure guides a prediction rather than guaranteeing one mechanism in all environments.

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In a simple SN1 hydrolysis, why may increasing nucleophile concentration have little effect on measured rate?

Answer: The rate-determining step is C–X ionisation and does not involve the nucleophile. The nucleophile is still required for product formation, but it does not enter that simple slow-step rate law.

Substitution and elimination compete

Hydroxide can donate a pair to carbon as a nucleophile or remove a proton as a base. Aqueous conditions favour substitution; hot ethanolic conditions favour elimination. These are preferred pathways, not an assertion that the other process becomes chemically impossible. For elimination, the removed hydrogen must be on a carbon adjacent to the carbon carrying X.

Worked example: 2-bromobutane can eliminate HBr to produce but-1-ene or but-2-ene, and but-2-ene has cis/trans forms. Draw each possible adjacent carbon and check duplicate structures by symmetry. Bromoethane has only one relevant carbon arrangement and gives ethene. A compound without a suitable adjacent hydrogen cannot undergo the ordinary elimination route merely because it contains bromine.

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Give reagents and conditions to make ethanol and ethene separately from bromoethane.

Answer: Heat with aqueous NaOH for ethanol. Heat with NaOH in ethanol for ethene. Include the solvent in each answer; “NaOH and heat” alone fails to distinguish the transformations.

Comparing hydrolysis rates fairly

Use matched halogenoalkane structures, equal concentrations, equal volumes and the same temperature when comparing C–Cl, C–Br and C–I. Ethanol helps mix the organic halogenoalkane with aqueous silver nitrate. Water hydrolyses the organic compound; silver ions reveal the released halide through precipitation. The time to visible precipitate is an indirect comparative measure of hydrolysis.

C–F is very strong, so a simple fluoroalkane is resistant under the usual test conditions. The greater polarity of C–F does not compensate for the bond-breaking difficulty. Do not infer that a yellow precipitate always means fastest reaction unless the samples and conditions are otherwise comparable.

Worked synthesis: bromoethane plus excess ethanolic ammonia gives ethylamine through substitution. Ammonia initially forms an alkylammonium species; another ammonia removes a proton, explaining the

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two-ammonia overall equation. Excess ammonia limits, but does not absolutely eliminate, further alkylation of the more nucleophilic amine product.

Chapter check: classify the reacting carbon, track carbon atoms when using cyanide, show lone-pair arrows and distinguish solvent-dependent substitution from elimination.

References and further reading

Scope follows section 15 of the **Cambridge 9701 syllabus for 2025–2027**. **Chemguide's Cambridge topic index** links to alternative explanations. The worked exercises and added diagrams are original teaching examples; numerical examples are illustrative unless a specific source is identified.

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