Halogen compounds

A-Level Chemistry

Halogenoalkanes

A **halogenoalkane** 卤代烷 is an alkane with one or more halogen atoms in place of hydrogen (a C–X bond, where X is a halogen).

Volatile halogenoalkanes were once widely used as refrigerants and aerosol propellants

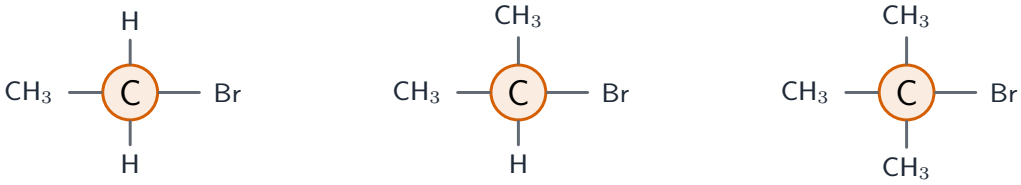
Image: Nave do Conhecimento, CC0 (commons.wikimedia.org)

Making halogenoalkanes

- **free-radical substitution** 自由基取代 of an alkane with Cl_2 or Br_2 in ultraviolet light.
- **electrophilic addition** 亲电加成 of an alkene with a halogen X_2 or a hydrogen halide HX.
- substitution of an **alcohol** 醇, for example by HX, by PCl_5, by PCl_3 with heat, or by $SOCl_2$.

Three classes

A halogenoalkane is **primary** 伯, **secondary** 仲 or **tertiary** 叔, depending on how many carbon atoms are joined to the carbon that holds the halogen (one, two or three).



primary
1 C on the C–Br carbon

secondary
2 C

tertiary
3 C

Primary, secondary and tertiary halogenoalkanes, set by how many carbons are joined to the carbon bearing the halogen

Nucleophilic substitution

The C–X bond is polar, so the carbon is slightly positive. A **nucleophilic substitution** 亲核取代 happens when a **nucleophile** 亲核试剂 (a lone-pair species) attacks that carbon and replaces the halogen.

Many halogenoalkane reactions are carried out by heating the mixture under reflux

Reagent and conditions	Product
NaOH(aq), heat	an alcohol
KCN in ethanol, heat	a **nitrile** 腈 (adds one carbon to the chain)
NH_3 in ethanol, heated under pressure	an **amine** 胺

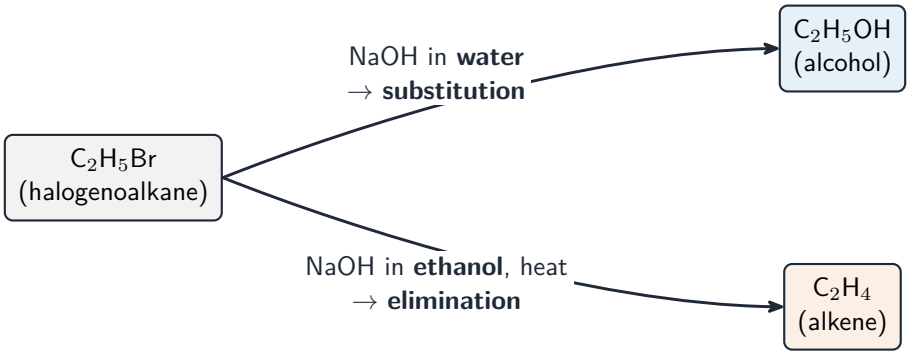
To **identify the halogen**, warm the halogenoalkane with **silver nitrate** 硝酸银 in ethanol. A silver halide **precipitate** 沉淀 forms, and its colour shows which halogen is present (white AgCl, cream AgBr, yellow AgI).

Elimination

The same halogenoalkane can instead undergo **elimination** 消去 to form an **alkene** 烯烃. The conditions decide which reaction wins:

- NaOH in **water** → nucleophilic substitution → an alcohol.
- NaOH in **ethanol**, heated → elimination → an alkene.

$$C_2H_5Br + NaOH \rightarrow C_2H_4 + NaBr + H_2O$$



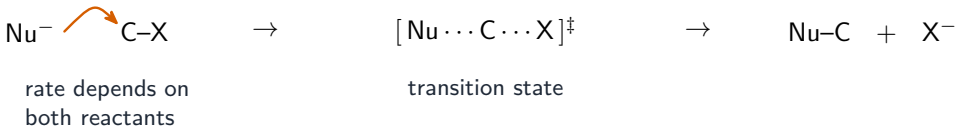
The same halogenoalkane: NaOH in water substitutes to an alcohol, while NaOH in ethanol (with heat) eliminates to an alkene

The S_N1 and S_N2 mechanisms

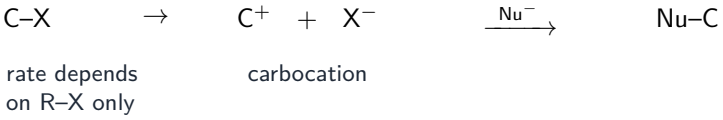
Nucleophilic substitution can follow two routes:

- **S_N2**: one step. The nucleophile attacks at the same time as the halogen leaves, passing through a crowded **transition state** 过渡态 where both are half-bonded. The rate depends on both the halogenoalkane and the nucleophile.
- **S_N1**: two steps. First the C–X bond breaks to give a **carbocation** 碳正离子; then the nucleophile attacks it. The rate depends only on the halogenoalkane.

S_N2: one step



S_N1: two steps



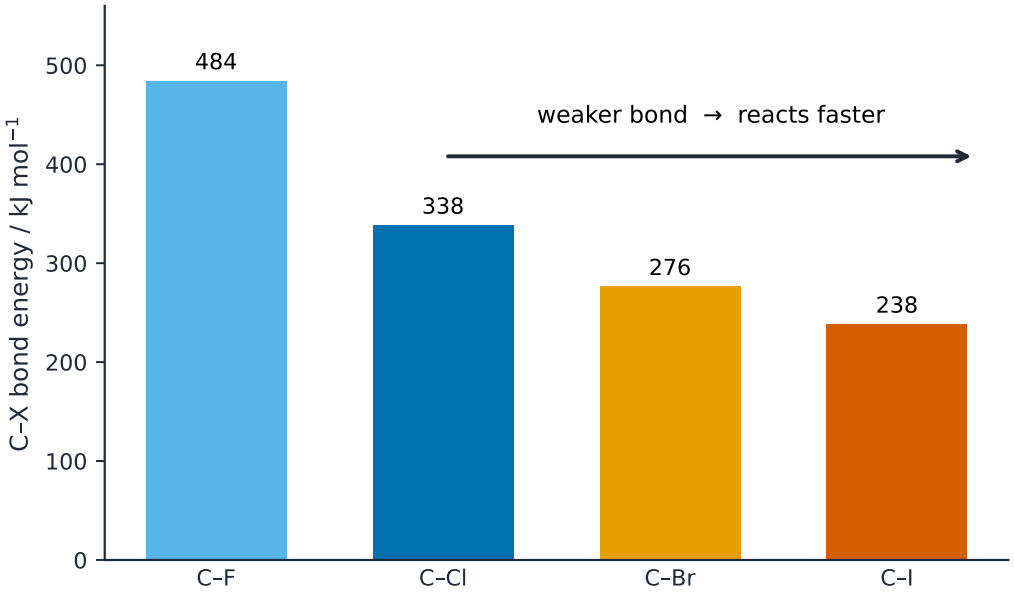
S_N2 is a single step through a crowded transition state; S_N1 is two steps via a carbocation

Alkyl groups push electrons towards the positive carbon (the **inductive effect** 诱导效应), so they stabilise the carbocation. This is why:

- **primary** halogenoalkanes mostly react by S_N2.
- **tertiary** halogenoalkanes mostly react by S_N1 (their carbocation is well stabilised).
- **secondary** halogenoalkanes use a mixture of the two.

Different reactivities

How fast a halogenoalkane reacts depends on the strength of the C–X bond, measured by its **bond energy** 键能. The C–I bond is the weakest, so iodoalkanes react fastest; the C–Cl bond is the strongest of the three, so chloroalkanes react slowest. So when tested with silver nitrate, an iodoalkane gives its precipitate first —its higher **reactivity** 反应活性 comes from the weaker C–X bond.



The weaker the C–X bond, the faster the halogenoalkane reacts —so iodoalkanes react fastest and chloroalkanes slowest

Worked example. Predict the mechanism for the hydrolysis of 1-bromobutane and of 2-bromo-2-methylpropane. Classify the halogenoalkane first. 1-bromobutane is **primary**: the carbon carrying the Br is barely shielded, so the nucleophile can attack the back of it and the mechanism is S_N2 - one step, with the rate depending on **both** the halogenoalkane and the nucleophile. 2-bromo-2-methylpropane is **tertiary**: three bulky methyl groups block that attack, but they also stabilise the carbocation formed once the Br leaves, so it goes S_N1 - two steps, with the rate depending on the halogenoalkane **only**. Decide from the **class** (primary → S_N2, tertiary → S_N1), and note that the tertiary one hydrolyses **faster** despite being the more crowded.

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.