

# 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*

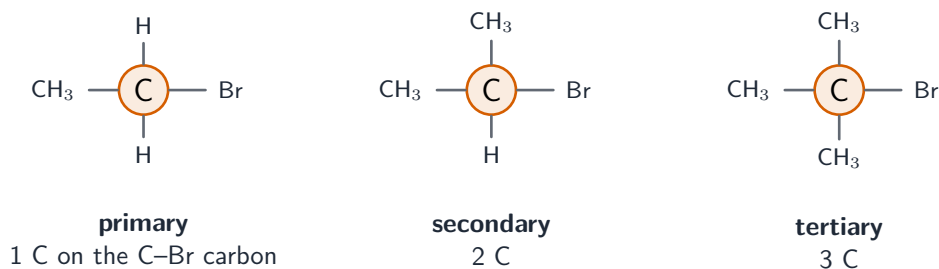
Image: Nave do Conhecimento, CC0 (commons.wikimedia.org)

### Making halogenoalkanes

- **free-radical substitution** 自由基取代 of an alkane with  $\text{Cl}_2$  or  $\text{Br}_2$  in ultraviolet light.
- **electrophilic addition** 亲电加成 of an alkene with a halogen  $\text{X}_2$  or a hydrogen halide  $\text{HX}$ .
- substitution of an **alcohol** 醇, for example by  $\text{HX}$ , by  $\text{PCl}_5$ , by  $\text{PCl}_3$  with heat, or by  $\text{SOCl}_2$ .

### 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, 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*

Image: Aleksander Sobolewski, CC BY-SA 4.0 (commons.wikimedia.org)

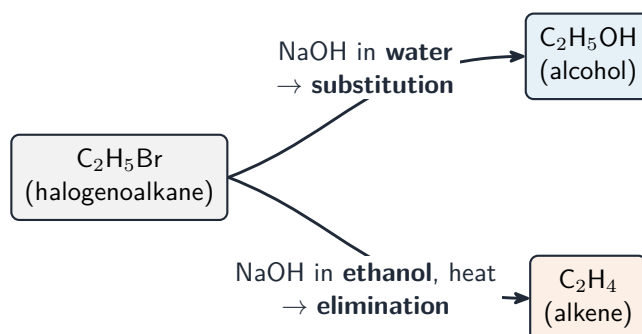
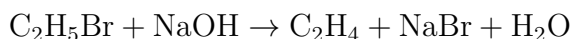
Reagent and conditions	Product
NaOH(aq), heat	an alcohol
KCN in ethanol, heat	a <b>nitrile</b> 腈 (adds one carbon to the chain)
NH <sub>3</sub> in ethanol, heated under pressure	an <b>amine</b> 胺

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. The conditions decide which reaction wins:

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



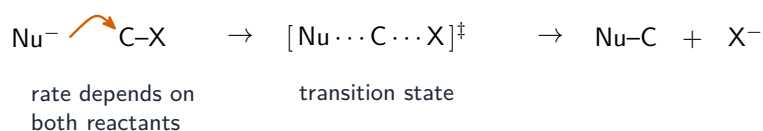
*The same halogenoalkane: NaOH in water substitutes to an alcohol, while NaOH in ethanol (with heat) eliminates to an alkene*

## The S<sub>N</sub>1 and S<sub>N</sub>2 mechanisms

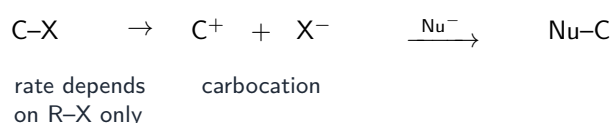
Nucleophilic substitution can follow two routes:

- **S<sub>N</sub>2**: 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<sub>N</sub>1**: 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<sub>N</sub>2: one step



### S<sub>N</sub>1: two steps



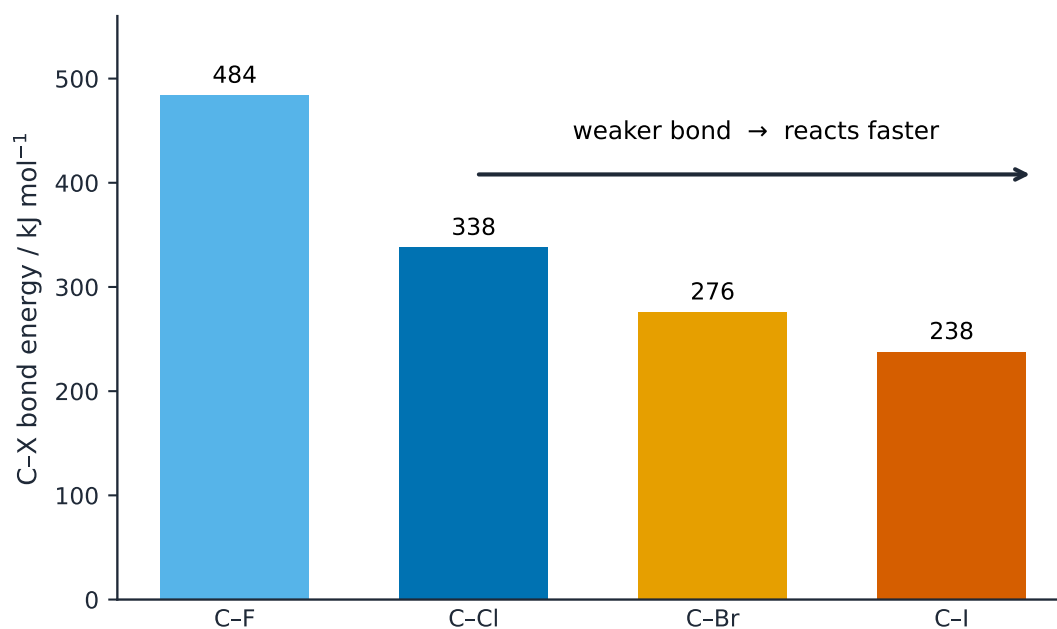
*S<sub>N</sub>2 is a single step through a crowded transition state; S<sub>N</sub>1 is two steps via a carbocation*

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*