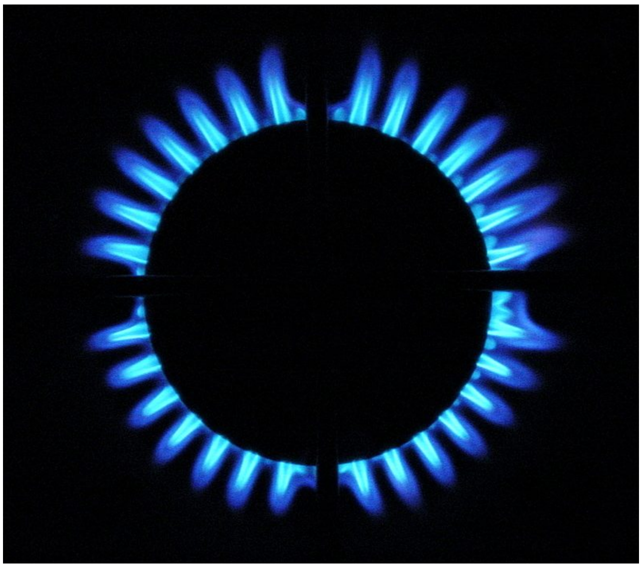
Hydrocarbons

A-Level Chemistry

Alkanes



Natural gas —mainly methane, the simplest alkane —burns on a stove.

Image: Marina Burity from Santo André, Brazil, CC BY-SA 2.0 (commons.wikimedia.org)

Alkanes 烷烃 are saturated hydrocarbons (general formula C_nH_{2n+2}).

Making alkanes

- **hydrogenation** 氢化: add hydrogen to an **alkene** 烯烃, using a Pt or Ni catalyst and heat.
- **cracking** 裂化: break a long-chain alkane into shorter ones by heating with Al_2O_3.

Combustion

In **combustion** 燃烧 an alkane burns in oxygen:

- **complete combustion** 完全燃烧 (plenty of oxygen) gives carbon dioxide and water.
- **incomplete combustion** 不完全燃烧 (not enough oxygen) gives water plus toxic **carbon monoxide** 一氧化碳 (CO) and soot (carbon).

Free-radical substitution

Alkanes react with chlorine or bromine by **free-radical substitution** 自由基取代, in **ultraviolet light** 紫外线. For ethane and chlorine the mechanism has three steps:

- **initiation** 引发—UV light splits the halogen into two **free radicals** 自由基: $Cl_2 \rightarrow 2\,Cl\cdot$

- **propagation** 增长—radicals react and make new radicals:

$$\mathrm{Cl}\cdot + \mathrm{C_2H_6} \rightarrow \mathrm{C_2H_5}\cdot + \mathrm{HCl} \qquad \mathrm{C_2H_5}\cdot + \mathrm{Cl_2} \rightarrow \mathrm{C_2H_5Cl} + \mathrm{Cl}\cdot$$

- **termination** 终止—two radicals join, ending the chain: $\mathrm{Cl}\cdot + \mathrm{C_2H_5}\cdot \rightarrow \mathrm{C_2H_5Cl}$

1. initiation

$\mathrm{Cl_2} \xrightarrow{\mathrm{UV}} 2\,\mathrm{Cl}^\bullet$

UV light splits Cl–Cl into two radicals

2. propagation

$\mathrm{Cl}^\bullet + \mathrm{C_2H_6} \longrightarrow \mathrm{C_2H_5}^\bullet + \mathrm{HCl}$

$\mathrm{C_2H_5}^\bullet + \mathrm{Cl_2} \longrightarrow \mathrm{C_2H_5Cl} + \mathrm{Cl}^\bullet$

each radical makes a new radical, so the chain continues

3. termination

$\mathrm{Cl}^\bullet + \mathrm{C_2H_5}^\bullet \longrightarrow \mathrm{C_2H_5Cl}$

two radicals join, ending the chain

Free-radical substitution in three steps: initiation makes radicals, propagation carries the chain, and termination ends it

Why cracking is useful, and why alkanes are unreactive

Cracking turns heavy fractions of **crude oil** 原油 into more useful, lower-M_r alkanes and alkenes. (A **fraction** 馏分 is a group of molecules with a similar boiling-point range.)

Alkanes are generally unreactive, especially towards polar reagents. This is because the C–H and C–C bonds are strong and have little **polarity** 极性, so there is no charge to attract an attacking species.

Environmental effects

Burning alkanes in an internal combustion engine gives off carbon monoxide, oxides of nitrogen and unburnt hydrocarbons. A catalytic converter removes these by turning them into harmless gases.

Alkenes

Cracking heavy fractions at a refinery produces alkenes for plastics and fuels.

Image: Walter Siegmund (talk), CC BY 2.5 (commons.wikimedia.org)

Alkenes have a C=C double bond (general formula C_nH_{2n}). The double bond is the functional group, so alkenes are reactive.

Making alkenes

- **elimination** 消去 of HX from a **halogenoalkane** 卤代烷, using NaOH dissolved in ethanol, with heat.
- **dehydration** 脱水 of an **alcohol** 醇, using a hot Al_2O_3 catalyst or concentrated sulfuric acid.
- cracking of a longer-chain alkane.

Reactions of alkenes

Most reactions are **electrophilic addition** 亲电加成 across the double bond:

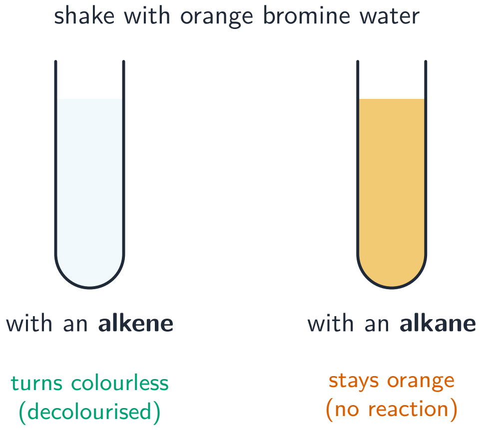
Reagent and conditions	Product
H_2, Pt/Ni catalyst, heat	alkane
steam 水蒸气 (H_2O), H_3PO_4 catalyst	alcohol
a **hydrogen halide** 卤化氢 (HX), room temperature	halogenoalkane
a halogen X_2	a di-substituted alkane

There are also two oxidation reactions with acidified $KMnO_4$:

- **cold, dilute** $KMnO_4$ adds two –OH groups to give a **diol** 二醇.
- **hot, concentrated** $KMnO_4$ breaks the C=C bond apart. The products (such as carboxylic acids or carbon dioxide) tell you where the double bond was.

Test for a $C=C$ bond

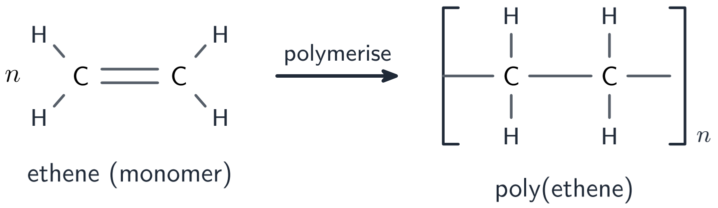
Shake the compound with orange **bromine water** 溴水. An alkene **decolourises** it (turns it colourless) by electrophilic addition. An alkane does not.



The bromine-water test: an alkene decolourises the orange bromine water, while an alkane leaves it orange

Addition polymerisation

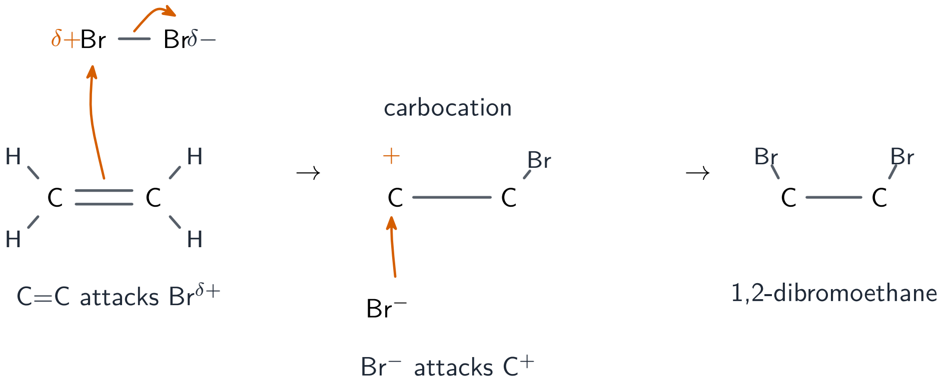
In **addition polymerisation** 加成聚合, many alkene molecules join into one long chain, with no other product. Ethene gives poly(ethene). The long-chain product is a **polymer** 聚合物.



Addition polymerisation: many ethene molecules open their double bonds and join into the long chain of poly(ethene)

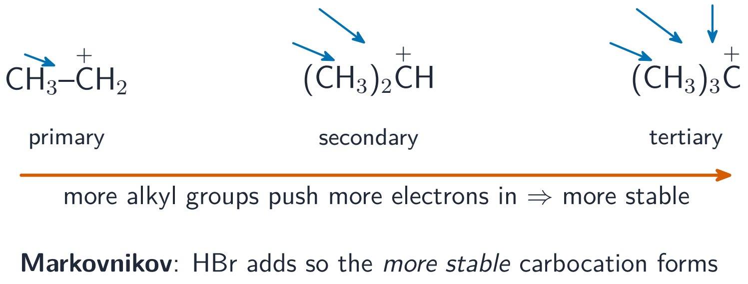
The mechanism and Markovnikov's rule

In electrophilic addition (for example bromine with ethene), the electron-rich $C=C$ attracts the electrophile. This forms a positive intermediate called a **carbocation** 碳正离子, which the negative part then attacks.



Electrophilic addition of bromine to ethene: the C=C attacks $Br^{\delta+}$*, a carbocation forms, then* Br^- *attacks it*

Alkyl groups push electrons towards the positive carbon —this is the **inductive effect** 诱导效应. So a carbocation with more alkyl groups is more stable: tertiary is more stable than secondary, which is more stable than primary. When HBr adds to propene, the more stable carbocation forms, so hydrogen adds to the carbon that already has more hydrogens. This pattern is **Markovnikov's rule** 马氏规则.



Carbocation stability rises from primary to tertiary as more alkyl groups push electrons in —the basis of Markovnikov's rule