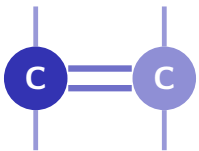
Hydrocarbons

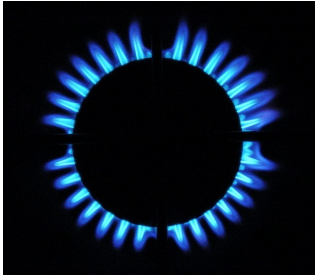
A-Level Chemistry ▪ Topic 14

A-Level Chemistry



What we will cover

1. Alkanes: making & combustion
2. Free-radical substitution
3. Alkenes & their reactions
4. The bromine test
5. Addition polymerisation
6. Markovnikov's rule



methane, the simplest alkane

1 Alkanes

Alkanes: making and combustion

complete 完全燃烧

plenty of $O_2 \rightarrow CO_2 + H_2O$

incomplete 不完全燃烧

too little $O_2 \rightarrow CO$ + soot

Alkanes 烷烃 (C_nH_{2n+2}) are made by **hydrogenation** 氢化 of alkenes or **cracking** 裂化; they are unreactive (strong, non-polar bonds).

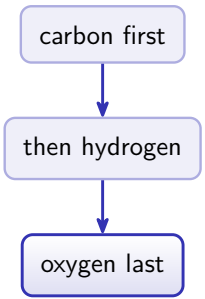
Two ways to make an alkane

hydrogenation 氢化 add H_2 across the C=C of an **alkene** 烯烃, over a Pt or Ni catalyst with heat

cracking 裂化 break a long-chain alkane into shorter ones by heating over Al_2O_3

Cracking turns heavy fractions of **crude oil** 原油 into lower-M_r alkanes *and* alkenes – a **fraction** 馏分 being molecules of similar boiling point. That is why it is worth doing: the short chains are what is in demand.

Balance a combustion equation in a fixed order



Oxygen goes last because it is the only element that appears twice on the right.

C_6H_{14} burning completely

6 carbons $\Rightarrow 6\,CO_2$;
14 hydrogens $\Rightarrow 7\,H_2O$;
right-hand oxygens $= 12 + 7 = 19$, so
$C_6H_{14} + \frac{19}{2}O_2 \rightarrow 6\,CO_2 + 7\,H_2O$

Two ways to make an alkene

elimination 消去 — remove HX from a **halogenoalkane** 卤代烷 with NaOH dissolved in *ethanol*, and heat

dehydration 脱水 — remove water from an **alcohol** 醇 over hot Al_2O_3, or with concentrated sulfuric acid

NaOH in ethanol eliminates to an alkene; NaOH in water substitutes to an alcohol. The solvent decides the product.

Reactions of the C=C, reagent by reagent

Reagent and conditions	**Product**
H_2, Ni catalyst, heat	alkane
a **hydrogen halide** 卤化氢 (HX), room temperature	halogenoalkane
X_2 (e.g. Br_2), room temperature	dihalide
steam, H_3PO_4, high T and p	alcohol
cold, dilute 冷稀 acidified $KMnO_4$	a **diol** 二醇 – two OH added
hot, concentrated 热浓 acidified $KMnO_4$	the C=C is broken apart

The last one is how the exam asks you to locate a double bond: what each half turns into tells you where it was. Write oxidation with [O].

Reading a broken C=C backwards

What each carbon becomes depends only on how many hydrogens it had:

no H
stops at a **ketone** 酮

one H
pushed on to a carboxylic acid

two H
oxidised all the way to CO_2

$$(CH_3)_2C{=}CHCH_3 + 3[O] \longrightarrow CH_3COCH_3 + CH_3COOH$$

Run it backwards – which is how the question is set. Given the products, put the two carbonyl carbons back together with a double bond and you have the original alkene.

Why alkanes are so unreactive

strong bonds	C–H and C–C are strong, so a lot of energy is needed to break either
no polarity	they have almost no **polarity** 极性, so a polar reagent finds nothing to attack

So alkanes react only with something aggressive enough to break a bond evenly – **ultra-violet light** 紫外光 making **free radicals** 自由基. That is **homolytic fission** 均裂: one electron to each atom. Break it *unevenly* and you get ions – **heterolytic fission** 异裂.

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.

Free-radical substitution

Alkanes react with a halogen in **UV light** 紫外线:

- **initiation** 引发 – UV makes radicals
- **propagation** 增长 – carries the chain
- **termination** 终止 – two radicals join

Free-radical substitution, in detail

1. initiation $Cl_2 \xrightarrow{UV} 2\,Cl^{\bullet}$

UV light splits Cl–Cl into two radicals

2. propagation $Cl^{\bullet} + C_2H_6 \longrightarrow C_2H_5^{\bullet} + HCl$

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

each radical makes a new radical, so the chain continues

3. termination $Cl^{\bullet} + C_2H_5^{\bullet} \longrightarrow C_2H_5Cl$

two radicals join, ending the chain

Alkanes react with a halogen in **UV light** 紫外线, in three steps:

initiation 引发 – UV splits a halogen into radicals.

propagation 增长 – each step makes another radical, carrying the chain.

termination 终止 – two radicals join and the chain stops.

2 Alkenes

Alkenes and their reactions

Alkenes 烯烃 (C_nH_{2n}) have a reactive C=C, attacked by **electrophilic addition** 亲电加成:

- H_2/Ni $\rightarrow$ alkane; steam $\rightarrow$ alcohol
- HX $\rightarrow$ halogenoalkane; X_2 $\rightarrow$ dihalide

The bromine test

shake with orange bromine water

with an **alkene**

turns colourless
(decolourised)

with an **alkane**

stays orange
(no reaction)

Shake with orange **bromine water** 溴水:

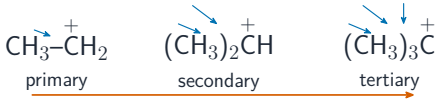
> An alkene decolourises it (electrophilic addition); an alkane leaves it orange.

Addition polymerisation

ethene (monomer) poly(ethene)

In **addition polymerisation** 加成聚合, many alkene molecules open their C=C and join into one long chain – with no other product. Ethene → poly(ethene), a **polymer** 聚合物.

Mechanism and Markovnikov's rule

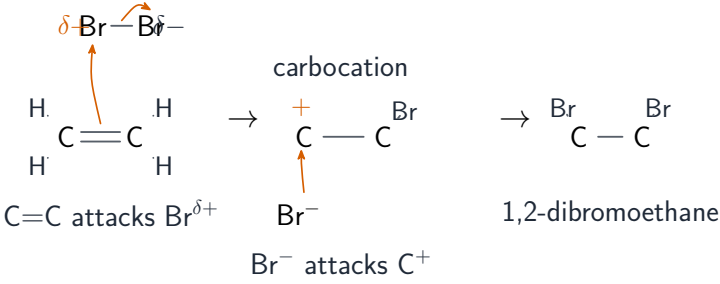


Markovnikov: HBr adds so the *more stable* carbocation forms

A **carbocation** 碳正离子 forms in electrophilic addition.

> Alkyl groups push electrons in (the **inductive effect** 诱导效应), so tertiary > secondary > primary – the more stable one forms (**Markovnikov's rule** 马氏规则).

The mechanism and Markovnikov's rule



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

Combustion

complete: alkane + O_2 → CO_2 + H_2O

incomplete: alkane + less O_2 → CO + soot + H_2O

Complete combustion gives CO2 and water; incomplete also gives CO and soot

Exam tips

- **Alkanes**: free-radical substitution needs **UV light** – show initiation, propagation and termination with the radical dots.
- **Alkenes**: electrophilic addition via a **carbocation**; draw curly arrows from the $C = C$.
- **Markovnikov**: H adds to the carbon with more H's, via the **more stable carbocation** (alkyl groups are electron-releasing).
- Test for $C = C$: **bromine water decolourises** (orange $\rightarrow$ colourless) – state the observation.

3 Recap

Worked example – which product is major?

But-1-ene reacts with HBr. Name the major product and explain why.

- The C=C π electrons attack the $\delta+$ H of H–Br: electrophilic addition.
- Two **carbocations** 碳正离子 are possible: a secondary one or a primary one.
- Alkyl groups push electron density in, spreading the charge, so the secondary is more stable.
- Br^- attacks it: major product 2-bromobutane.

Always route through the more stable carbocation. Stability: tertiary $>$ secondary $>$ primary.

Topic 14 – key takeaways

1 Alkanes

combustion; free-radical substitution in UV

2 Alkenes

electrophilic addition across C=C

3 Bromine test

alkene decolourises bromine water

4 Markovnikov

the more stable carbocation forms

Check yourself

1. What two products does incomplete combustion add?
2. What light is needed for free-radical substitution?
3. What does an alkene do to bromine water?
4. Which carbocation is most stable: 1°, 2° or 3°?

Answers **1.** carbon monoxide and soot **2.** ultraviolet **3.** decolourises it **4.** tertiary (3°)