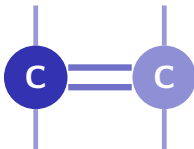


Hydrocarbons

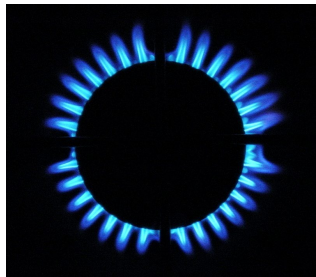
A-Level Chemistry ■ Topic 14

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



Alkanes: making and combustion

complete

plenty of $\text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$

incomplete

too little $\text{O}_2 \rightarrow \text{CO} + \text{soot}$

Alkanes ($\text{C}_n\text{H}_{2n+2}$) are made by **hydrogenation** of alkenes or **cracking** ; they are unreactive (strong, non-polar bonds).

Two ways to make an alkane

hydrogenation

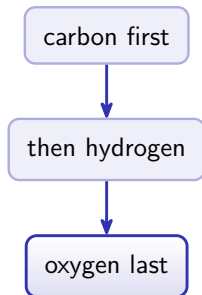
add H_2 across the $\text{C}=\text{C}$ of an **alkene**, over a Pt or Ni catalyst with heat

cracking

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

Cracking turns heavy fractions of **crude oil** into lower- M_r alkanes *and* alkenes – a **fraction** 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



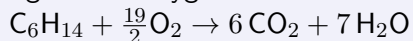
Oxygen goes last because it is the only element that appears **twice** on the right.

C₆H₁₄ burning completely

6 carbons $\Rightarrow$ 6 CO₂;

14 hydrogens $\Rightarrow$ 7 H₂O;

right-hand oxygens = 12 + 7 = 19, so



Two ways to make an alkene

elimination

remove HX from a **halogenoalkane** with NaOH dissolved in *ethanol*, and heat

dehydration

remove water from an **alcohol** 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 (HX), room temperature	halogenoalkane
X ₂ (e.g. Br ₂), room temperature	dihalide
steam, H ₃ PO ₄ , high <i>T</i> and <i>p</i>	alcohol
cold, dilute acidified KMnO ₄	a diol – two OH added
hot, concentrated 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

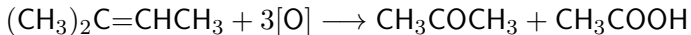
stops at a **ketone**

one H

pushed on to a
carboxylic acid

two H

oxidised all the
way to CO₂



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**, so a polar reagent finds nothing to attack

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

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** :

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

Free-radical substitution, in detail



UV light splits Cl-Cl into two radicals



each radical makes a new radical, so the chain continues



two radicals join, ending the chain

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

initiation – UV splits a halogen into radicals.

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

termination – two radicals join and the chain stops.



Alkenes and their reactions



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

- $H_2/Ni \rightarrow$ 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)



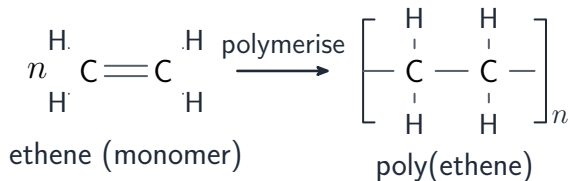
with an **alkane**

stays orange
(no reaction)

Shake with orange **bromine water** :

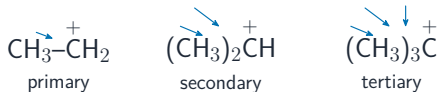
An alkene **decolourises** it (electrophilic addition); an alkane leaves it orange.

Addition polymerisation



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

Mechanism and Markovnikov's rule



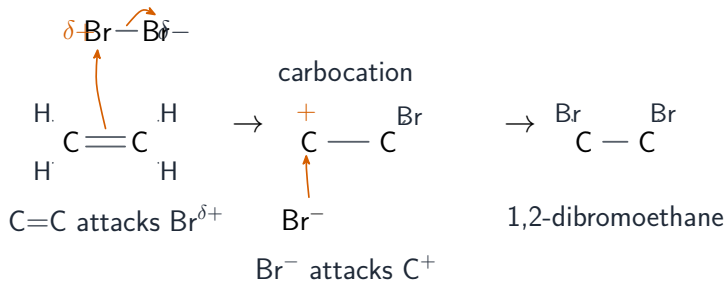
more alkyl groups push more electrons in $\Rightarrow$ more stable

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

A **carbocation** forms in electrophilic addition.

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

The mechanism and Markovnikov's rule



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

Combustion

complete: $\text{alkane} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$

incomplete: $\text{alkane} + \text{less O}_2 \rightarrow \text{CO} + \text{soot} + \text{H}_2\text{O}$

Complete combustion gives CO_2 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.



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 δ^+ H of H-Br: **electrophilic addition**.
- Two **carbocations** 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°)