Hydrocarbons

Alkanes (combustion, free-radical substitution, cracking, pollution from engines) and alkenes (preparation, electrophilic addition, oxidation, addition polymers and carbocation stability).

14.1 Alkanes

Alkanes are saturated hydrocarbons, C_nH_{2n+2}. They are generally **unreactive** because the C–C and C–H bonds are strong and have **little polarity**, so polar reagents (acids, bases, nucleophiles) do not attack them.

Preparation of alkanes

- Hydrogenation of an alkene: H_2 with a Pt or Ni catalyst and heat.
- **Cracking** of a longer alkane: heat with Al_2O_3, e.g. $C_{10}H_{22} \rightarrow C_8H_{18} + C_2H_4$. Cracking converts heavy fractions of crude oil into more useful, shorter alkanes (for petrol) and alkenes (for polymers and other products).

Combustion

Complete: $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$. **Incomplete** combustion, with limited oxygen, gives **carbon monoxide** (toxic) and carbon (soot).

Free-radical substitution

Alkanes react with chlorine or bromine in **ultraviolet light**: $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$.

1. **Initiation:** $Cl_2 \rightarrow 2Cl\cdot$ (homolytic fission by UV light).
2. **Propagation:** $Cl\cdot + CH_4 \rightarrow \cdot CH_3 + HCl$, then $\cdot CH_3 + Cl_2 \rightarrow CH_3Cl + Cl\cdot$. The radical is regenerated, so it is a chain reaction.
3. **Termination:** two radicals combine: $Cl\cdot + Cl\cdot \rightarrow Cl_2$, $\cdot CH_3 + Cl\cdot \rightarrow CH_3Cl$ or $\cdot CH_3 + \cdot CH_3 \rightarrow C_2H_6$.

Further substitution gives a mixture (CH_2Cl_2, $CHCl_3$, CCl_4), and a side product from termination such as ethane.

Note Academy

Environmental consequences of the internal combustion engine

Engine exhaust contains **CO**, **oxides of nitrogen** and **unburnt hydrocarbons**. CO is toxic; NO_x forms acid rain and smog; hydrocarbons contribute to smog. A **catalytic converter** removes them: $2CO + 2NO \rightarrow 2CO_2 + N_2$.

Constructing a radical chain mechanism

Initiation creates radicals from non-radical starting material. Propagation consumes one radical and forms another, allowing the sequence to continue. Termination consumes radicals without generating replacements. The distinction depends on the species involved, not whether a step produces the desired organic product. Methyl radical plus chlorine forms chloromethane in a propagation step; methyl radical plus chlorine radical also forms chloromethane, but is termination.

Worked example — bromination of ethane: initiation is $Br_2 \xrightarrow{UV} 2Br\cdot$. Propagation steps are $Br\cdot + C_2H_6 \rightarrow HBr + C_2H_5\cdot$ and $C_2H_5\cdot + Br_2 \rightarrow C_2H_5Br + Br\cdot$. Termination can form Br_2, bromoethane or butane through radical combinations. Add the propagation steps and cancel radicals to recover the overall substitution equation.

UV light supplies energy for homolytic bond fission; it is a condition, not a catalyst molecule. Multiple substitutable hydrogens and further reactions of halogeno products generate mixtures. Using excess alkane favours monosubstitution relative to repeated halogenation, but does not turn the process into a perfectly selective synthesis.

> **TRY IT**
>
> Classify $CH_3\cdot + CH_3\cdot \rightarrow C_2H_6$ and explain why ethane can appear during chlorination of methane.

Answer: It is termination: two radicals combine and no radical remains. Methyl radicals formed during propagation can meet and create this side product even though the intended product is chloromethane.

Combustion, cracking and environmental chemistry

Balance hydrocarbon combustion by matching carbon to CO_2, hydrogen to H_2O, then oxygen last. Fractional oxygen coefficients are acceptable unless whole numbers are requested. Incomplete combustion can produce CO or carbon because oxygen supply is insufficient for full oxidation. A higher amount of carbon in a fuel molecule does not alone determine whether combustion is complete.

Worked example: $2C_4H_{10} + 13O_2 \rightarrow 8CO_2 + 10H_2O$. Burning 0.100 mol butane completely needs 0.650 mol oxygen and gives 0.400 mol carbon dioxide. A cracking equation has different products: for example $C_{10}H_{22} \rightarrow C_6H_{14} + C_4H_8$, conserving every atom without consuming oxygen.

Note Academy

14.2 Alkenes

Alkenes are unsaturated hydrocarbons, C_nH_{2n}, containing a C=C double bond (one σ and one π bond). The π bond is a region of high electron density, so alkenes are attacked by **electrophiles**.

Preparation of alkenes

- **Elimination of HX** from a halogenoalkane: ethanolic NaOH, heat.
- **Dehydration of an alcohol:** heated Al_2O_3 catalyst, or concentrated H_2SO_4 (or H_3PO_4) with heat.
- Cracking of longer alkanes.

Reactions

Reagent	Conditions	Product
H_2	Pt or Ni, heat	alkane
H_2O (steam)	H_3PO_4 catalyst	alcohol
$HX(g)$	room temperature	halogenoalkane
X_2	room temperature	dihalogenoalkane
Cold dilute acidified $KMnO_4$		diol (purple to colourless)
Hot concentrated acidified $KMnO_4$		C=C cleaved

Hot concentrated acidified $KMnO_4$ oxidatively splits the C=C bond. A $=CH_2$ end gives CO_2 and water, a =CHR end gives a **carboxylic acid** RCOOH, and a $=CR_2$ end gives a **ketone**. The products identify the position of the double bond in a larger molecule.

Test for C=C: shake with **aqueous bromine**; an alkene decolourises it (orange-brown to colourless).

Addition polymerisation: many alkene monomers join, for example $n\,CH_2{=}CH_2 \rightarrow [-CH_2CH_2-]_n$ (see the chapter on polymerisation).

Electrophilic addition mechanism

For Br_2 with ethene, the π electrons polarise the Br–Br bond. Electron movement begins from the π bond towards $Br^{\delta+}$, with the Br–Br bond pair moving to the other Br. Addition ultimately gives 1,2-dibromoethane. Bromination is commonly represented through a bridged bromonium intermediate; use the representation specified by the course or question, and do not treat decolourisation alone as proof of a free carbocation.

Note Academy

For HBr and propene the electrophile is $H^{\delta+}$ and the carbocation formed is $CH_3{}^+CHCH_3$.

Carbocation stability and Markovnikov's rule

Alkyl groups are **electron-donating (a positive inductive effect)**. They spread the positive charge, so **tertiary > secondary > primary** carbocations in stability. The more stable carbocation forms preferentially, so H adds to the carbon with **more hydrogen atoms** (Markovnikov addition). From propene and HBr the major product is **2-bromopropane** (via the secondary carbocation), not 1-bromopropane.

> **TRY IT**
>
> Hot concentrated acidified $KMnO_4$ turns an alkene into propanone and ethanoic acid. Deduce the alkene.

Propanone comes from $(CH_3)_2C=$ and ethanoic acid from $=CHCH_3$. The alkene is $(CH_3)_2C=CHCH_3$, 2-methylbut-2-ene.

A complete HBr addition explanation

For propene, a curly arrow starts at C=C and points to the H of HBr. Another starts at the H–Br bond and ends on bromine. Adding H to the terminal carbon leaves a secondary carbocation on the middle carbon; the opposite orientation would give a less stable primary carbocation. Bromide then donates a lone pair to the positive carbon to form 2-bromopropane.

The major-product prediction compares **intermediate stability**, not simply which finished product looks more symmetrical. Alkyl groups stabilise positive charge through electron donation. State both possible carbocations where a question asks why one product predominates. The alternative route may still give a minor product; Markovnikov orientation is not a claim that every addition under every possible condition behaves identically.

> **TRY IT**
>
> Predict the major product from but-1-ene and HBr under the ordinary electrophilic-addition conditions, and justify it.

Answer: 2-bromobutane, via a secondary carbocation. The alternative placement of H would produce a primary carbocation and favour the less important 1-bromobutane route.

Note Academy

Conditions determine the oxidation product

Cold dilute acidified manganate(VII) adds hydroxyl groups across C=C to form a diol. Hot concentrated acidified reagent can cleave the double bond. For cleavage predictions, mark the two original alkene carbons and determine what each was attached to: two carbon groups lead to a ketone fragment, one carbon group and one H lead to a carboxylic acid, and a terminal CH_2 can be fully oxidised to CO_2 and water.

Worked example: but-2-ene splits into two ethanoic-acid fragments. But-1-ene gives propanoic acid plus carbon dioxide under vigorous oxidative-cleavage conditions. The latter equation shortens the identifiable organic fragment because the terminal carbon is lost as CO_2; atom counting explains the difference.

To reverse such a deduction, remove the oxygen added at the two carbonyl/acid positions and reconnect the corresponding carbons with C=C. Check total carbon count and whether the proposed alkene could give cis/trans isomers. A cleavage product can reveal connectivity without uniquely determining the original stereoisomer.

> **TRY IT**
>
> An alkene gives only propanone on symmetrical oxidative cleavage. Suggest its structure.

Answer: $(CH_3)_2C=C(CH_3)_2$, 2,3-dimethylbut-2-ene. Each double-bond carbon carries two methyl groups, so each side becomes propanone. It has no cis/trans pair because each carbon has two identical substituents.

Distinguishing addition products and tests

Hydrogenation removes unsaturation without adding oxygen or halogen. Hydration adds H and OH, while halogen addition adds two halogen atoms. All preserve the original carbon skeleton unless another process occurs. For bromine-water testing, give the observation and inference separately: orange-brown colour disappears, supporting reactive unsaturation under the test conditions. Other groups can also consume bromine, so an unfamiliar multifunctional compound needs additional evidence.

The dihalogenoalkane is the standard product model for halogen addition under appropriate conditions. In aqueous media, solvent participation can affect detailed products; do not use a qualitative bromine-water observation as a complete preparative product analysis. The exam question's reagents and solvent determine the expected structure.

> **TRY IT**
>
> How could ethene be converted into ethanol, and how could ethanol be converted back into ethene?

Note Academy

Answer: Hydrate ethene using steam with a phosphoric-acid catalyst under suitable industrial conditions. Dehydrate ethanol using heated aluminium oxide or a suitable concentrated acid with heat. One is addition and the reverse functional-group transformation is elimination.

Chapter check: balance radical steps, distinguish propagation from termination, show electron-pair sources in addition, and state both reagent concentration and temperature for oxidation. Continue to **halogenoalkane substitution** and **alcohol chemistry**.

References and further reading

Scope follows section 14 of the **Cambridge 9701 syllabus for 2025–2027**. **Chemguide's Cambridge topic index** links to alternative explanations. The worked exercises and added diagrams are original teaching examples; numerical examples are illustrative unless a specific source is identified.

Note Academy