

Hydrocarbons: alkanes and alkenes (AS Chemistry notes)

These notes cover the hydrocarbons part of the Cambridge International AS Chemistry syllabus (9701): where alkanes come from, why they are so unreactive, how they burn and how they react with halogens, how cracking turns long alkanes into more useful products, and the reactions of alkenes, including the electrophilic addition mechanism, Markovnikov's rule, oxidation with potassium manganate(VII) and addition polymerisation. The section on pollution links the chemistry to engines and the environment. Each mechanism is written out step by step so that you can draw it with curly arrows in the exam.

1. Hydrocarbons and crude oil

1.1 Key words

Hydrocarbon: a compound containing carbon and hydrogen only.

Saturated: containing only single bonds between carbon atoms (no C=C double bonds).

Unsaturated: containing at least one carbon to carbon double (or triple) bond.

Homologous series: a family of compounds with the same functional group and the same general formula, in which each member differs from the next by CH_2 , with similar chemical properties and a gradual trend in physical properties.

The alkanes have the general formula $\text{C}_n\text{H}_{2n+2}$ (methane CH_4 , ethane C_2H_6 , propane C_3H_8 , butane C_4H_{10}). Cycloalkanes such as cyclohexane have the formula C_nH_{2n} . The alkenes have one C=C double bond and the general formula C_nH_{2n} (ethene C_2H_4 , propene C_3H_6 , but-1-ene and but-2-ene C_4H_8).

1.2 Crude oil as a source of alkanes

Crude oil (petroleum) is a mixture of many hydrocarbons, mostly alkanes and cycloalkanes, with smaller amounts of arenes. Natural gas is mainly methane. Crude oil is separated by **fractional distillation**: the oil is vaporised and passed into a tall column that is hot at the bottom and cooler at the top. Each fraction condenses at the level where the temperature falls below its boiling range. Small molecules with weak intermolecular forces (instantaneous dipole to induced dipole forces) have low boiling points and leave near the top as refinery gas and petrol (gasoline). Large molecules with stronger intermolecular forces condense lower down as kerosene, diesel, fuel oil, and the residue gives bitumen.

Each fraction is still a mixture of compounds with similar boiling points, not a pure substance. Demand for the small, petrol-sized molecules is much higher than the amount present in crude oil, which is why the large molecules are cracked (section 4).

2. Alkanes: unreactivity and combustion



2.1 Why alkanes are unreactive

Alkanes do not react with acids, alkalis, or common oxidising agents such as acidified potassium manganate(VII) or acidified potassium dichromate(VI) under normal conditions. There are two reasons.

1. **Strong bonds.** The C–C and C–H bonds are strong, so a lot of energy is needed to break them and the activation energy of most reactions is high.
2. **Very low polarity.** Carbon and hydrogen have very similar electronegativities, so the C–H bond is almost non-polar. There are no partial charges ($\delta+$ or $\delta-$) to attract nucleophiles or electrophiles, and no lone pairs or π electrons to attack other species.

Alkanes therefore react only under harsh conditions: burning in oxygen, reaction with halogens in ultraviolet light, and cracking at high temperature.

2.2 Complete combustion

In plenty of oxygen, alkanes burn completely to carbon dioxide and water. The reaction is very exothermic, which is why alkanes are used as fuels.

Worked example: balancing a combustion equation

Write the equation for the complete combustion of octane, C_8H_{18} .

Step 1: carbon atoms give CO_2 : 8 C gives 8CO_2 .

Step 2: hydrogen atoms give water: 18 H gives $9\text{H}_2\text{O}$.

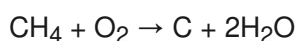
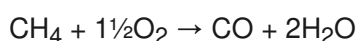
Step 3: count oxygen atoms needed: $(8 \times 2) + 9 = 25$ O atoms, which is 12.5O_2 .

$\text{C}_8\text{H}_{18} + 12\frac{1}{2}\text{O}_2 \rightarrow 8\text{CO}_2 + 9\text{H}_2\text{O}$, or doubled: $2\text{C}_8\text{H}_{18} + 25\text{O}_2 \rightarrow 16\text{CO}_2 + 18\text{H}_2\text{O}$

For any alkane: $\text{C}_n\text{H}_{2n+2} + (3n+1)/2 \text{O}_2 \rightarrow n\text{CO}_2 + (n+1)\text{H}_2\text{O}$.

2.3 Incomplete combustion

When the oxygen supply is limited (for example in a car engine cylinder, or a gas heater with a blocked flue), the carbon is not fully oxidised. Carbon monoxide or carbon (soot) forms instead of carbon dioxide.

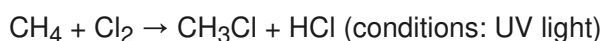


Carbon monoxide is toxic because it binds strongly to haemoglobin and reduces the amount of oxygen the blood can carry. It has no colour or smell. Soot particles (particulates) can cause breathing problems and blacken buildings.

3. Alkanes: free-radical substitution

3.1 The reaction

Alkanes react with chlorine or bromine in the presence of ultraviolet light (or sunlight). A hydrogen atom is replaced by a halogen atom, so this is a **substitution** reaction. In the dark at room temperature there is no reaction.



Free radical: a species with an unpaired electron.

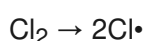
Homolytic fission: the breaking of a covalent bond in which each atom takes one electron from the shared pair, forming two free radicals.

Heterolytic fission: the breaking of a covalent bond in which one atom takes both electrons from the shared pair, forming a cation and an anion.

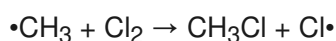
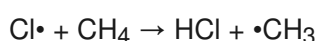
3.2 The mechanism, step by step

Free radicals are shown with a dot, for example $\text{Cl}\cdot$ and $\cdot\text{CH}_3$. In the mechanism, single-headed (fish-hook) arrows show the movement of single electrons, but at AS you are mainly asked to write the equations for each stage.

Stage 1: Initiation. UV light provides the energy to break the $\text{Cl}-\text{Cl}$ bond by homolytic fission. The $\text{Cl}-\text{Cl}$ bond is broken rather than $\text{C}-\text{H}$ because it is weaker.

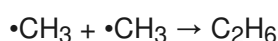
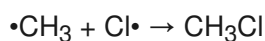
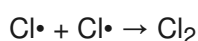


Stage 2: Propagation. A chlorine radical removes a hydrogen atom from methane, forming hydrogen chloride and a methyl radical. The methyl radical then reacts with a chlorine molecule, forming chloromethane and a new chlorine radical.



Each propagation step uses one radical and makes one radical, so the chain continues. One initiation step can lead to thousands of product molecules: this is a **chain reaction**.

Stage 3: Termination. Two radicals meet and join, forming a molecule. This removes radicals and stops a chain.



Exam tip: the formation of a small amount of ethane is evidence for the radical mechanism. Ethane can only form by two methyl radicals joining in a termination step. When asked for "a termination step that gives a product with a longer chain", always give two alkyl radicals joining.

3.3 Further substitution and mixtures of products

The free-radical reaction is hard to control. Chloromethane can itself be attacked by a chlorine radical, so further substitution happens:



Repeating this gives trichloromethane, CHCl_3 , and tetrachloromethane, CCl_4 . Using a large excess of methane makes it more likely that a chlorine radical hits a methane molecule rather than a chloromethane molecule, so monosubstitution is favoured. Using excess chlorine favours CCl_4 .

With longer alkanes, the halogen can replace a hydrogen atom on any carbon, so a mixture of structural isomers forms. For example, propane gives both 1-chloropropane and 2-chloropropane. This

is why free-radical substitution is a poor way to make a single pure halogenoalkane, and the products must be separated, for example by fractional distillation.

Worked example: counting monosubstituted isomers

How many different monochloro products can form from butane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$?

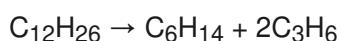
Look for hydrogen atoms in different environments. The two end CH_3 groups are equivalent, and the two middle CH_2 groups are equivalent. So there are two environments, giving 1-chlorobutane ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$) and 2-chlorobutane ($\text{CH}_3\text{CHClCH}_2\text{CH}_3$). Answer: 2 structural isomers. (2-chlorobutane is chiral, so it exists as a pair of optical isomers, formed in equal amounts.)

4. Cracking

4.1 What cracking is

Cracking: the breaking down of large alkane molecules into smaller, more useful molecules, which include alkanes and alkenes (and sometimes hydrogen).

Cracking is a **thermal decomposition**. C–C bonds in the long chain break, and because there are not enough hydrogen atoms to make two alkanes, at least one product must be an alkene.



The bonds break at random points, so a mixture of products forms. Any balanced equation that conserves carbon and hydrogen atoms and has an alkene among the products is acceptable.

4.2 Conditions

- **Thermal cracking:** high temperature (several hundred degrees Celsius) and often high pressure, with no catalyst.
- **Catalytic cracking:** a lower temperature (roughly 450 to 500 °C) with a catalyst such as aluminium oxide or a zeolite (an aluminosilicate). The catalyst lowers the activation energy and makes products suitable for petrol, including branched alkanes and arenes.

4.3 Why cracking is important

1. It matches supply to demand: crude oil contains more large molecules than are needed, and fewer of the short molecules used in petrol.
2. Shorter alkanes make better fuels because they vaporise and ignite easily. Branched alkanes burn more smoothly in engines.
3. The alkenes formed, especially ethene and propene, are feedstocks for polymers and for other chemicals such as ethanol.

5. Alkenes: structure of the double bond

5.1 The C=C double bond

A C=C double bond is made of one **σ bond**, formed by head-on overlap of orbitals along the line between the two nuclei, and one **π bond**, formed by sideways overlap of p orbitals above and below that line. Each carbon in C=C is sp^2 hybridised, and the atoms around the double bond are in one plane with bond angles of about 120° .

The π bond is weaker than the σ bond, and its electrons lie outside the line of the nuclei, so they are exposed. This region of high electron density attracts electrophiles. This is why alkenes are much more reactive than alkanes, and why their typical reaction is **addition**: the π bond breaks and two new σ bonds form.

Because the π bond prevents rotation about the C=C bond, alkenes such as but-2-ene show geometrical (cis/trans) isomerism when each carbon of the double bond carries two different groups.

6. Alkenes: electrophilic addition

Electrophile: a species that accepts a pair of electrons to form a new covalent bond. Electrophiles are positive ions or have a δ^+ atom.

Addition reaction: a reaction in which two molecules join to form a single product.

6.1 Summary of addition reactions of ethene

Reagent	Conditions	Product from ethene	Use or note
H ₂	Nickel catalyst, about 150 °C (platinum or palladium work at room temperature)	Ethane, CH ₃ CH ₃	Hydrogenation; used to harden vegetable oils into margarine
Br ₂ (or Cl ₂)	Room temperature, in the dark is fine (no UV needed)	1,2-dibromoethane, CH ₂ BrCH ₂ Br	Test for C=C: orange bromine water turns colourless
HBr (or HCl, HI)	Room temperature, gaseous HX or concentrated solution	Bromoethane, CH ₃ CH ₂ Br	Gives halogenoalkanes; unsymmetrical alkenes follow Markovnikov's rule
H ₂ O (steam)	Phosphoric acid catalyst, high temperature (about 300 °C) and high pressure (several MPa)	Ethanol, CH ₃ CH ₂ OH	Industrial manufacture of ethanol (hydration)

Hydrogenation is an addition reaction but it does not go by the electrophilic mechanism below; it happens on the surface of the metal catalyst. You only need its conditions and product.

6.2 Mechanism: ethene with hydrogen bromide

The H–Br bond is polar (H δ^+ –Br δ^-) because bromine is more electronegative than hydrogen.

- The π electrons of the C=C bond are attracted to the δ^+ hydrogen of HBr. A curly arrow is drawn from the middle of the double bond to the H atom.
- At the same time, the H–Br bond breaks heterolytically. A curly arrow is drawn from the H–Br bond to the Br atom, which takes both electrons and becomes Br $^-$.
- The hydrogen is now bonded to one carbon. The other carbon has lost its share of the π

electrons and carries a positive charge. This intermediate is a **carbocation**, CH_3CH_2^+ .

4. A lone pair on the bromide ion is attracted to the positive carbon. A curly arrow is drawn from a lone pair on Br^- to the C^+ , forming a $\text{C}-\text{Br}$ bond. The product is bromoethane.

Exam tip: drawing the mechanism

For full marks show: the dipole on $\text{H}-\text{Br}$ (δ^+ on H, δ^- on Br); a curly arrow starting from the $\text{C}=\text{C}$ bond and ending at the H; a curly arrow from the $\text{H}-\text{Br}$ bond to the Br; the carbocation with a full + charge on the correct carbon; Br^- with a lone pair; and a curly arrow from that lone pair to the C^+ . Curly arrows always start at a bond or lone pair and show the movement of a pair of electrons.

6.3 Mechanism: ethene with bromine

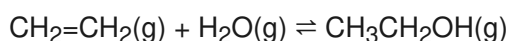
The $\text{Br}-\text{Br}$ bond is non-polar, so how does bromine act as an electrophile?

1. As a bromine molecule approaches the region of high electron density in the π bond, the electrons in $\text{Br}-\text{Br}$ are repelled away from the near bromine atom. This **induces a dipole**: the near Br becomes δ^+ and the far Br becomes δ^- .
2. The π electrons attack the δ^+ bromine atom (curly arrow from $\text{C}=\text{C}$ to the near Br), and the $\text{Br}-\text{Br}$ bond breaks heterolytically (curly arrow from the $\text{Br}-\text{Br}$ bond to the far Br), forming Br^- .
3. A carbocation forms: $\text{CH}_2\text{Br}-\text{CH}_2^+$.
4. The bromide ion uses a lone pair to bond to the positive carbon, forming 1,2-dibromoethane, $\text{CH}_2\text{BrCH}_2\text{Br}$.

When bromine water is used rather than pure bromine, water molecules are present in large excess and can also attack the carbocation, so the main organic product is 2-bromoethanol, $\text{CH}_2\text{BrCH}_2\text{OH}$. Either way, the orange colour disappears, so the test for an alkene still works.

6.4 Hydration with steam

Industrially, ethene and steam are passed over a phosphoric acid catalyst at high temperature and pressure:



The reaction is reversible and exothermic, so only a small fraction of the ethene is converted on each pass; unreacted ethene is recycled. The acid catalyst provides H^+ , which adds to the alkene to give a carbocation, and a water molecule then bonds to the carbocation and loses H^+ , regenerating the catalyst.

7. Markovnikov's rule and carbocation stability

7.1 Unsymmetrical alkenes give two possible products

Propene, $\text{CH}_3\text{CH}=\text{CH}_2$, is unsymmetrical. When HBr adds, the H can join either carbon of the double bond, so two products are possible: 2-bromopropane, $\text{CH}_3\text{CHBrCH}_3$, and 1-bromopropane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$. In practice 2-bromopropane is the major product.

Markovnikov's rule: when a hydrogen halide (HX) adds to an unsymmetrical alkene, the hydrogen atom attaches to the carbon of the double bond that already has more hydrogen atoms, and the halogen attaches to the carbon with fewer hydrogen atoms.

7.2 Primary, secondary and tertiary carbocations

Carbocations are classified by the number of alkyl groups bonded to the positive carbon.

- Primary: one alkyl group, for example $\text{CH}_3\text{CH}_2\text{CH}_2^+$.
- Secondary: two alkyl groups, for example $\text{CH}_3\text{CH}^+\text{CH}_3$.
- Tertiary: three alkyl groups, for example $(\text{CH}_3)_3\text{C}^+$.

Stability order: **tertiary > secondary > primary**.

7.3 Explaining the rule

Alkyl groups have a **positive inductive effect**: they push electron density towards the carbon they are attached to. This partly spreads out (stabilises) the positive charge on a carbocation. The more alkyl groups attached to the positive carbon, the more the charge is spread and the more stable the carbocation.

In the first step of the mechanism, the alkene can form either a primary or a secondary carbocation. The more stable carbocation forms faster, because the step that leads to it has a lower activation energy. So more of the product comes from the more stable carbocation.

Worked example: propene + HBr

Route A: H adds to the end carbon (CH_2), giving $\text{CH}_3\text{CH}^+\text{CH}_3$. The positive carbon has two methyl groups, so this is a **secondary** carbocation. Br^- then gives 2-bromopropane (**major** product).

Route B: H adds to the middle carbon, giving $\text{CH}_3\text{CH}_2\text{CH}_2^+$, a **primary** carbocation with one alkyl group. Br^- then gives 1-bromopropane (**minor** product).

The secondary carbocation is more stable because two alkyl groups donate electron density to the positive carbon, so route A is favoured.

The same idea applies to the hydration of propene with steam: the major product is propan-2-ol, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$, and the minor product is propan-1-ol. With 2-methylpropene, $(\text{CH}_3)_2\text{C}=\text{CH}_2$, the tertiary carbocation $(\text{CH}_3)_3\text{C}^+$ forms, so the major product with HBr is 2-bromo-2-methylpropane.

8. Oxidation of alkenes with potassium manganate(VII)

8.1 Cold, dilute, acidified KMnO_4

When an alkene is shaken with cold, dilute, acidified potassium manganate(VII), the π bond is broken and an OH group is added to each carbon of the original double bond. The product is a **diol**.



Observation: the purple solution turns colourless, because purple MnO_4^- is reduced to very pale (almost colourless) Mn^{2+} . This is another test for a $\text{C}=\text{C}$ bond. (In alkaline conditions a brown precipitate of MnO_2 forms instead.) Note that $[\text{O}]$ is used to represent oxygen from the oxidising agent in a balanced organic equation.

8.2 Hot, concentrated, acidified KMnO_4

Under these harsher conditions the $\text{C}=\text{C}$ double bond is broken completely (both the σ and π bonds),

and each carbon of the double bond becomes a C=O group. What you get depends on what is attached to each carbon of the double bond.

Group at one end of C=C	Product from that end	Example
=CH ₂ (two H atoms)	Methanoic acid, which is oxidised further to CO ₂ and H ₂ O	End carbon of propene gives CO ₂
=CHR (one H, one alkyl group)	Carboxylic acid, RCOOH	CH ₃ CH= gives ethanoic acid, CH ₃ COOH
=CRR' (two alkyl groups)	Ketone, RCOR'	(CH ₃) ₂ C= gives propanone, CH ₃ COCH ₃

Worked example: working out the products

Predict the products when 2-methylbut-2-ene, (CH₃)₂C=CHCH₃, is heated with concentrated acidified KMnO₄.

Step 1: split the molecule at the double bond: (CH₃)₂C= and =CHCH₃.

Step 2: the left-hand carbon has two alkyl groups, so it becomes a ketone: (CH₃)₂C=O, propanone.

Step 3: the right-hand carbon has one H and one methyl group, so it becomes a carboxylic acid: CH₃COOH, ethanoic acid.

Products: propanone and ethanoic acid.

This reaction is useful for finding the position of a double bond in an unknown alkene. Work backwards: identify the fragments from the products and join the two C=O carbons with a double bond. CO₂ among the products shows the alkene had a =CH₂ group at the end of the chain.

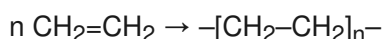
9. Addition polymerisation

9.1 How addition polymers form

Addition polymerisation: the joining together of many small unsaturated molecules (monomers) to form a long chain molecule (polymer), with no other product formed.

Repeat unit: the smallest group of atoms that, when repeated, makes up the polymer chain.

The π bond in each monomer breaks and the carbon atoms link to the next monomer by new σ bonds. The polymer is saturated. Industrially this needs high pressure and an initiator, or a catalyst (for example a Ziegler–Natta catalyst for poly(ethene) and poly(propene)).



9.2 Deducing repeat units and monomers

To draw the repeat unit, take the two carbon atoms of the C=C, make the double bond single, keep all the other groups on those carbons, and add a bond sticking out on each side (through the brackets).

Monomer	Polymer	Repeat unit
Ethene, $\text{CH}_2=\text{CH}_2$	Poly(ethene)	$-\text{CH}_2-\text{CH}_2-$
Propene, $\text{CH}_2=\text{CHCH}_3$	Poly(propene)	$-\text{CH}_2-\text{CH}(\text{CH}_3)-$
Chloroethene, $\text{CH}_2=\text{CHCl}$	Poly(chloroethene), PVC	$-\text{CH}_2-\text{CHCl}-$
Tetrafluoroethene, $\text{CF}_2=\text{CF}_2$	Poly(tetrafluoroethene), PTFE	$-\text{CF}_2-\text{CF}_2-$

Exam tip: in poly(propene) the CH_3 group is a branch, not part of the main chain. A common mistake is to draw the repeat unit as $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$. The main chain of any addition polymer contains only the two carbons that were in the $\text{C}=\text{C}$ bond of each monomer. To find the monomer from a polymer, pick out a two-carbon repeat unit in the main chain and put a double bond between those carbons.

9.3 Disposal of poly(alkenes)

Poly(alkenes) are chemically inert, like alkanes, because they are saturated and made of strong, non-polar $\text{C}-\text{C}$ and $\text{C}-\text{H}$ bonds. This is useful while they are in use but causes problems when they are thrown away.

- **Landfill:** they are non-biodegradable, so they last for a very long time and take up space. Litter harms wildlife, and small fragments (microplastics) spread through water and soil.
- **Combustion:** burning releases energy that can be used, but it produces CO_2 (a greenhouse gas), and incomplete combustion gives toxic CO . Burning PVC releases hydrogen chloride, an acidic and toxic gas, so incinerators need scrubbers to remove it, and toxic chlorinated compounds can also form.
- **Recycling:** saves crude oil and reduces landfill, but the plastics have to be collected and sorted by type.

10. Fuels, combustion and pollution

10.1 Pollutants from engines

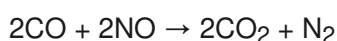
Pollutant	How it forms	Effect
Carbon dioxide, CO_2	Complete combustion of any hydrocarbon	Greenhouse gas, contributes to climate change
Carbon monoxide, CO	Incomplete combustion	Toxic: reduces the oxygen-carrying capacity of blood
Unburnt hydrocarbons	Fuel that passes through the engine without burning	Contribute to photochemical smog; some are carcinogenic. Methane is a greenhouse gas
Oxides of nitrogen, NO and NO_2	Nitrogen and oxygen from the air react at the very high temperature in the engine: $\text{N}_2 + \text{O}_2 \rightarrow 2\text{NO}$; then $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ in air	Acid rain (NO_2 forms nitric acid); photochemical smog; respiratory problems

Particulates (soot)	Incomplete combustion, especially of diesel	Lung and heart disease
Sulfur dioxide, SO ₂	Sulfur impurities in the fuel burn	Acid rain; reduced by removing sulfur from fuels at the refinery

Note that NO_x does not come from the fuel. It forms because the temperature inside the cylinder is high enough to overcome the large activation energy needed to break the strong N≡N triple bond.

10.2 Catalytic converters

A catalytic converter in the exhaust contains a ceramic honeycomb coated with a thin layer of metals such as platinum, palladium and rhodium. The honeycomb gives a large surface area for a small mass of expensive metal. The gases adsorb on the metal surface, react, and then desorb.



Unburnt hydrocarbons are also oxidised, for example: $\text{C}_8\text{H}_{18} + 25\text{NO} \rightarrow 8\text{CO}_2 + 12\frac{1}{2}\text{N}_2 + 9\text{H}_2\text{O}$

Converters only work once they are hot, so they are least effective during short journeys from cold. They remove CO, NO_x and unburnt hydrocarbons, but they do not reduce the CO₂ produced; in fact they convert CO into CO₂.

11. Summary of key reactions

Starting material	Reagent and conditions	Product	Type of reaction
Alkane	O ₂ , ignite	CO ₂ + H ₂ O (or CO, C)	Combustion (oxidation)
Alkane	Cl ₂ or Br ₂ , UV light	Halogenoalkane + HX	Free-radical substitution
Long alkane	High temperature, Al ₂ O ₃ or zeolite catalyst	Shorter alkane + alkene	Cracking (thermal decomposition)
Alkene	H ₂ , Ni catalyst, heat	Alkane	Addition (hydrogenation, reduction)
Alkene	Br ₂ , room temperature	Dibromoalkane	Electrophilic addition
Alkene	HBr, room temperature	Bromoalkane	Electrophilic addition
Alkene	Steam, H ₃ PO ₄ catalyst, high T and p	Alcohol	Electrophilic addition (hydration)
Alkene	Cold dilute acidified KMnO ₄	Diol	Oxidation
Alkene	Hot concentrated acidified KMnO ₄	Ketones, carboxylic acids, CO ₂	Oxidation (C=C broken)
Alkene	High pressure, initiator or catalyst	Poly(alkene)	Addition polymerisation

Quick check

1. Explain why alkanes are unreactive towards most reagents, such as acids, alkalis and acidified potassium manganate(VII). [2]

2. (a) Write balanced equations for the complete combustion of propane and for its incomplete combustion to form carbon monoxide and water. [2]
(b) Calculate the mass of carbon dioxide formed when 11.0 g of propane burns completely. (A_r : C = 12.0, H = 1.0, O = 16.0) [2]
3. Ethane reacts with bromine in ultraviolet light.
(a) Name the type of reaction and the mechanism. [1]
(b) Write equations for the initiation step and the two propagation steps. [3]
(c) Write an equation for a termination step that forms a hydrocarbon. [1]
4. 2-methylpropane, $(\text{CH}_3)_3\text{CH}$, reacts with chlorine in UV light. Give the structural formulae and names of the two monochloro products, and explain why free-radical substitution is not a good method for making one pure product. [4]
5. (a) Complete this cracking equation: $\text{C}_{14}\text{H}_{30} \rightarrow \text{C}_{10}\text{H}_{22} + \text{_____}$ [1]
(b) State the conditions used in catalytic cracking and give two reasons why oil companies crack long-chain alkanes. [3]
6. (a) Explain how nitrogen monoxide forms in a car engine, even though petrol contains no nitrogen. [2]
(b) Write an equation for the reaction in a catalytic converter that removes both carbon monoxide and nitrogen monoxide. [1]
(c) State one pollutant that a catalytic converter does not remove. [1]
7. Describe, with the help of the steps you would draw, the mechanism of the reaction between ethene and bromine. Name the mechanism and explain how a non-polar bromine molecule can act as an electrophile. [5]
8. Propene reacts with hydrogen bromide.
(a) Name the major product and the minor product. [2]
(b) Explain, in terms of the intermediates formed, why one product is the major product. [3]
9. But-2-ene, $\text{CH}_3\text{CH}=\text{CHCH}_3$, is reacted separately with (a) hydrogen, (b) steam and (c) cold, dilute, acidified potassium manganate(VII). For each, give the conditions and the name of the organic product. [6]
10. Predict the organic products when 2-methylbut-2-ene, $(\text{CH}_3)_2\text{C}=\text{CHCH}_3$, is heated with concentrated acidified potassium manganate(VII). State what you would observe. [3]
11. An alkene X has the molecular formula C_5H_{10} . When X is heated with concentrated acidified KMnO_4 , the only products are carbon dioxide, water and butanone, $\text{CH}_3\text{COCH}_2\text{CH}_3$. Deduce the structural formula and name of X. Explain your reasoning. [3]
12. (a) Draw the repeat unit of poly(chloroethene). [1]
(b) Explain why poly(chloroethene) is non-biodegradable and why burning it is a problem. [3]
(c) Part of a polymer chain is $-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{CH}(\text{CH}_3)-$. Name the monomer. [1]

1. The C–C and C–H bonds are strong, so a large amount of energy is needed to break them (high activation energy). The C–H bond is almost non-polar because carbon and hydrogen have similar electronegativities, so there are no δ^+ or δ^- sites to attract nucleophiles or electrophiles.

2. (a) Complete: $\text{C}_3\text{H}_8 + 5\text{O}_2 \rightarrow 3\text{CO}_2 + 4\text{H}_2\text{O}$.

Incomplete: $\text{C}_3\text{H}_8 + 3\frac{1}{2}\text{O}_2 \rightarrow 3\text{CO} + 4\text{H}_2\text{O}$ (or $2\text{C}_3\text{H}_8 + 7\text{O}_2 \rightarrow 6\text{CO} + 8\text{H}_2\text{O}$). Check oxygen: $3 + 4 = 7$ O atoms = $3\frac{1}{2}\text{O}_2$.

(b) $M_r(\text{C}_3\text{H}_8) = (3 \times 12.0) + (8 \times 1.0) = 44.0$. Moles of propane = $11.0 \div 44.0 = 0.250$ mol. From

the equation, 1 mol propane gives 3 mol CO_2 , so moles of $\text{CO}_2 = 0.750$ mol. $M_r(\text{CO}_2) = 44.0$, so mass = $0.750 \times 44.0 = 33.0$ g.

3. (a) Substitution; free-radical substitution.

(b) Initiation: $\text{Br}_2 \rightarrow 2\text{Br}\cdot$ (homolytic fission, using energy from UV light).

Propagation: $\text{Br}\cdot + \text{C}_2\text{H}_6 \rightarrow \text{HBr} + \cdot\text{C}_2\text{H}_5$

Propagation: $\cdot\text{C}_2\text{H}_5 + \text{Br}_2 \rightarrow \text{C}_2\text{H}_5\text{Br} + \text{Br}\cdot$

(c) $\cdot\text{C}_2\text{H}_5 + \cdot\text{C}_2\text{H}_5 \rightarrow \text{C}_4\text{H}_{10}$ (butane).

4. 2-methylpropane has hydrogen atoms in two environments: nine on the three CH_3 groups and one on the central CH.

Substituting a CH_3 hydrogen gives $(\text{CH}_3)_2\text{CHCH}_2\text{Cl}$, 1-chloro-2-methylpropane.

Substituting the central hydrogen gives $(\text{CH}_3)_3\text{CCl}$, 2-chloro-2-methylpropane.

The chlorine radical can remove any hydrogen atom, so a mixture of isomers forms. Further substitution also occurs (dichloro, trichloro products and so on), because the product can itself react with chlorine radicals. The products then have to be separated, so the yield of any one product is low.

5. (a) Carbon: $14 - 10 = 4$. Hydrogen: $30 - 22 = 8$. The missing product is C_4H_8 (butene, an alkene).

(b) Conditions: a temperature of about 450 to 500 °C with a catalyst of aluminium oxide or a zeolite. Reasons (any two): there is greater demand for short-chain alkanes such as petrol than crude oil supplies, so cracking matches supply to demand; shorter (and branched) alkanes make better fuels; cracking produces alkenes, which are used to make polymers and other chemicals such as ethanol.

6. (a) The temperature inside the engine cylinder is very high. This provides enough energy to overcome the high activation energy for breaking the strong $\text{N}\equiv\text{N}$ bond, so nitrogen and oxygen from the air react: $\text{N}_2 + \text{O}_2 \rightarrow 2\text{NO}$.

(b) $2\text{CO} + 2\text{NO} \rightarrow 2\text{CO}_2 + \text{N}_2$

(c) Carbon dioxide (also acceptable: sulfur dioxide or particulates).

7. Mechanism: electrophilic addition.

Step 1: as Br_2 approaches the $\text{C}=\text{C}$ bond, the high electron density of the π bond repels the electrons in $\text{Br}-\text{Br}$, inducing a dipole: the nearer Br becomes δ^+ and the further Br δ^- . This δ^+ atom is the electrophile.

Step 2: a curly arrow from the $\text{C}=\text{C}$ π bond to the δ^+ Br shows the π electrons forming a new $\text{C}-\text{Br}$ bond. A second curly arrow from the $\text{Br}-\text{Br}$ bond to the δ^- Br shows heterolytic fission, forming Br^- .

Step 3: the intermediate is a carbocation, $\text{CH}_2\text{BrCH}_2^+$.

Step 4: a curly arrow from a lone pair on Br^- to the positive carbon forms the second $\text{C}-\text{Br}$ bond. Product: 1,2-dibromoethane, $\text{CH}_2\text{BrCH}_2\text{Br}$.

8. (a) Major: 2-bromopropane, $\text{CH}_3\text{CHBrCH}_3$. Minor: 1-bromopropane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$.

(b) The first step forms a carbocation. If H adds to the end CH_2 carbon, a secondary carbocation, $\text{CH}_3\text{CH}^+\text{CH}_3$, forms; if H adds to the middle carbon, a primary carbocation, $\text{CH}_3\text{CH}_2\text{CH}_2^+$, forms. Alkyl groups are electron-donating (positive inductive effect), so the secondary carbocation, with two alkyl groups, has its charge spread more and is more stable. It forms faster (lower activation energy), so 2-bromopropane, formed from it, is the major product.

9. (a) Hydrogen with a nickel catalyst, heated (about 150 °C): butane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$.

(b) Steam with a phosphoric acid catalyst at high temperature and pressure: butan-2-ol, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$. Because but-2-ene is symmetrical, only one product forms.

(c) Cold, dilute, acidified KMnO_4 , shaken at room temperature: butane-2,3-diol, $\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}_3$.

10. Split at the $\text{C}=\text{C}$: $(\text{CH}_3)_2\text{C}=\text{CHCH}_3$ has two alkyl groups, so it gives a ketone, propanone, CH_3COCH_3 . $=\text{CHCH}_3$ has one H and one alkyl group, so it gives a carboxylic acid, ethanoic acid, CH_3COOH . Observation: the purple solution is decolourised (turns colourless).

11. Butanone, $\text{CH}_3\text{COCH}_2\text{CH}_3$, is a ketone, so one carbon of the double bond carried two alkyl groups (CH_3 and CH_2CH_3). CO_2 shows the other carbon was a terminal $=\text{CH}_2$. Joining the two $\text{C}=\text{O}$ carbons with a double bond gives $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_3$. Check the formula: 5 carbons and 10 hydrogens, C_5H_{10} . X is 2-methylbut-1-ene.

12. (a) $-\text{CH}_2-\text{CHCl}-$ with a bond extending from each end carbon through the brackets.

(b) The polymer chain is saturated and held together by strong, almost non-polar $\text{C}-\text{C}$ and $\text{C}-\text{H}$ bonds, so it is chemically inert and microorganisms cannot break it down. Burning it releases toxic hydrogen chloride gas (and CO_2 , and CO if combustion is incomplete), so the waste gases must be treated before release.

(c) The two-carbon repeat unit is $-\text{CH}_2-\text{CH}(\text{CH}_3)-$, so the monomer is propene, $\text{CH}_2=\text{CHCH}_3$.