

Hydrocarbons

A-Level Chemistry 9701 · Topic 14 revision notes

Everything from the 4 lessons of this topic on a few pages: the key idea of each lesson, the diagram to remember, the points to learn and the traps examiners set. Read it, cover it, test yourself.

1. Alkanes

2. Free radical substitution

3. Alkenes

4. Electrophilic addition

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1 Alkanes

Syllabus 14.1

Alkanes are **saturated** hydrocarbons, C_nH_{2n+2} , with only single bonds and tetrahedral carbons. Their C-C and C-H bonds are **strong and almost non-polar**, so they are attacked by neither nucleophiles nor electrophiles, which makes them generally **unreactive**. They come from crude oil by **fractional distillation** and **cracking**. They burn: **complete combustion** gives CO_2 and H_2O ; in limited oxygen, **incomplete combustion** gives toxic CO and soot. Boiling points rise with chain length and fall with branching.

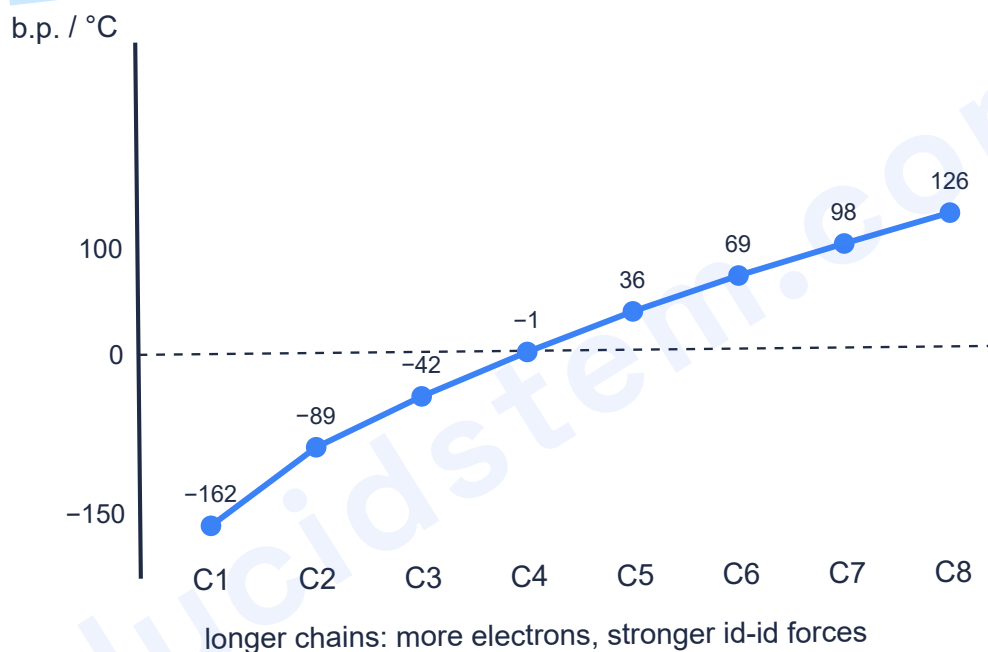


Fig. 1: boiling points of the straight-chain alkanes

Strong, non-polar bonds; good fuels.

- ✓ C_nH_{2n+2} , saturated, tetrahedral.
- ✓ **Cracking** gives shorter alkanes plus alkenes.
- ✓ **Balance** C, then H, then O.
- ✓ **Incomplete** combustion: CO and soot.

Watch out!

When balancing a combustion equation, balance C first, then H, then O last; if O needs a half, double everything. Alkanes do **not** decolourise bromine water in the dark: they react with halogens only by free-radical substitution in UV light.

2 Free radical substitution

Syllabus 14.1

Alkanes react with chlorine or bromine in **ultraviolet light** by **free radical substitution**.

Initiation: UV light breaks Cl-Cl by **homolytic fission** into two chlorine radicals.

Propagation: a radical reacts with a molecule to give a product and a new radical, so the chain continues. **Termination:** two radicals combine and the chain stops. Because radicals are so reactive, further substitution occurs and a **mixture** of products forms (CH_3Cl , CH_2Cl_2 , CHCl_3 , CCl_4 , and some ethane).

initiation



radicals are made

propagation



a radical is used and another made: a chain reaction

termination



two radicals meet:
the chain stops

Fig. 1: the three stages of the free radical substitution of methane by chlorine

Make, pass on, destroy radicals.

- ✓ **Initiation:** homolytic fission in UV light.
- ✓ **Propagation:** one radical in, one radical out.
- ✓ **Termination:** two radicals in, none out.
- ✓ **Mixture** of products from further substitution.

Watch out!

Radicals form by **homolytic fission** and carry an unpaired electron, shown by a dot. Every propagation step has **one radical on each side**; every termination step has **two radicals in and none out**. A step that makes HCl and a methyl radical is propagation, not termination.

3 Alkenes

Syllabus 14.2

Alkenes are **unsaturated**, C_nH_{2n} , with a $C=C$ made of a σ and a π bond. The π electrons are a region of high electron density above and below the plane, so alkenes undergo **addition**: with H_2 (Ni catalyst) to alkanes, with steam (H_3PO_4 catalyst) to alcohols, with HX to halogenoalkanes and with X_2 to dihalogenoalkanes. **Bromine water** turns from orange to colourless. Cold, dilute acidified $KMnO_4$ gives a **diol**; hot, concentrated acidified $KMnO_4$ **splits** the $C=C$, and the products reveal where the double bond was.

hot, concentrated, acidified $KMnO_4$ splits $C=C$

end of the $C=C$	product
$=CH_2$	CO_2 (and H_2O)
$=CHR$	$RCOOH$, a carboxylic acid
$=CRR'$	$RCOR'$, a ketone

e.g. $(CH_3)_2C=CHCH_3 \rightarrow$ propanone + ethanoic acid

cold, dilute $KMnO_4$ instead adds two OH groups: a diol

Fig. 1: the products of oxidising an alkene with hot, concentrated $KMnO_4$

The π bond adds; hot $KMnO_4$ splits.

- ✓ H_2/Ni , steam/ H_3PO_4 , HX , X_2 : all addition.
- ✓ **Bromine water**: orange to colourless.
- ✓ **Cold dilute $KMnO_4$** : diol.
- ✓ **Hot conc. $KMnO_4$** : $=CH_2 \rightarrow CO_2$, $=CHR \rightarrow RCOOH$, $=CR_2 \rightarrow$ ketone.

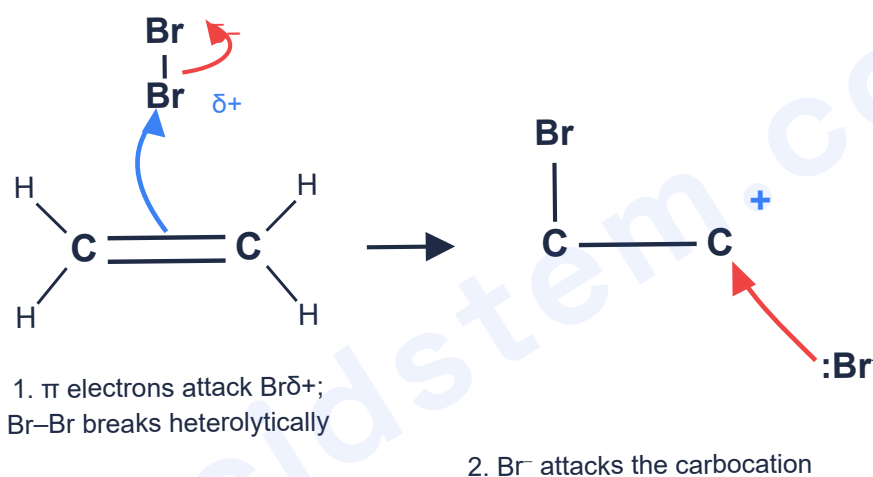
Watch out!

Cold, dilute $KMnO_4$ **adds** two OH groups (a diol); hot, concentrated $KMnO_4$ **breaks** the $C=C$. Do not mix them up. In the cleavage products, each carbon of the original $C=C$ becomes a $C=O$ carbon: $=CH_2$ goes all the way to CO_2 .

4 Electrophilic addition

Syllabus 14.2

In **electrophilic addition** the π electrons of the $C=C$ attack an **electrophile**. With Br_2 , the approaching π cloud **induces a dipole** in $Br-Br$; the π pair forms a bond to the $Br^{\delta+}$ atom while $Br-Br$ breaks heterolytically, giving a **carbocation** and Br^- , which then attacks the positive carbon. With HBr , $H^{\delta+}$ is the electrophile. Alkyl groups push electron density towards a positive carbon (the **positive inductive effect**), so carbocation stability is **tertiary > secondary > primary**. With an unsymmetrical alkene the major product comes from the more stable carbocation: propene + HBr gives mainly **2-bromopropane**.



product: 1,2-dibromoethane, CH_2BrCH_2Br

Fig. 1: electrophilic addition of bromine to ethene

π bond to electrophile, then anion to carbocation.

- ✓ **Arrow 1:** from $C=C$ to $H^{\delta+}$ or $Br^{\delta+}$.
- ✓ **Arrow 2:** from $H-Br$ or $Br-Br$ bond to Br .
- ✓ **Arrow 3:** from Br^- lone pair to C^+ .
- ✓ **Stability:** tertiary > secondary > primary.

Watch out!

The first curly arrow must start from the **$C=C$ double bond** (the π electrons) and point to the electrophile, not start at the bromine. Draw the carbocation with a full + charge on carbon, and the bromide ion with a lone pair and a - charge. The major product comes from the **more substituted** carbocation.

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