4 Introductory Organic Chemistry and Alkanes

Hazards and Risks

A **hazard** is a substance or procedure that can has the potential to do harm.
Typical hazards are toxic/flammable /harmful/ irritant /corrosive /oxidizing/ carcinogenic

RISK: This is the probability or chance that harm will result from the use of a hazardous substance or a procedure

In the laboratory we try to minimise the risk

Irritant - dilute acid and alkalis- wear googles
Corrosive- stronger acids and alkalis wear goggles
Flammable – keep away from naked flames
Toxic – wear gloves- avoid skin contact- wash hands after use
Oxidising- Keep away from flammable / easily oxidised materials

Risks can be reduced by
- working on a smaller scale
- taking precautions specific to the hazard
- using an alternative method that involves less hazardous substances

Hazardous substances in low concentrations or amounts will not pose the same risks as the pure substance.

Basic definitions to know

Hydrocarbon is a compound consisting of hydrogen and carbon **only**

Saturated: Contain single carbon-carbon bonds only

Unsaturated : Contains a C=C double bond

Molecular formula: The formula which shows the actual **number** of **each type** of **atom**

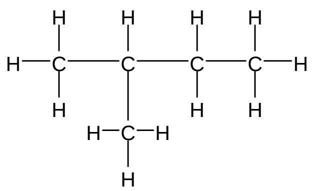
Empirical formula: shows the simplest whole number ratio of atoms of each element in the compound

General formula: algebraic formula for a homologous series e.g. C_nH_{2n}

Structural formula shows the minimal detail that shows the arrangement of atoms in a molecule, eg for butane: $CH_3CH_2CH_2CH_3$ or $CH_3(CH_2)_2CH_3$,

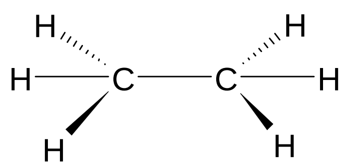
Displayed formula: show all the covalent bonds present in a molecule

Drawing Displayed formulae

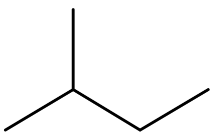


When drawing organic compounds add the hydrogen atoms so that each carbon has 4 bonds

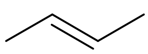
Remember that the shape around the carbon atom in saturated hydrocarbons is tetrahedral and the bond angle is 109.5°



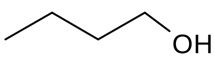
Skeletal formula shows the simplified organic formula, shown by removing hydrogen atoms from alkyl chains, leaving just a carbon skeleton and associated functional Groups.



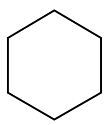
2-methylbutane



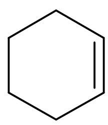
But-2-ene



Butan-1-ol



cyclohexane

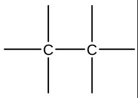
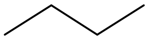
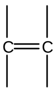
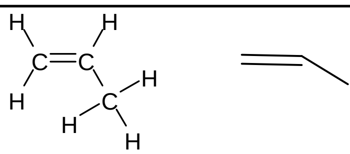
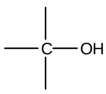
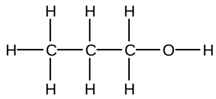
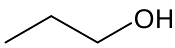
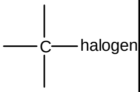
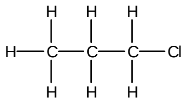
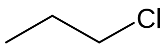
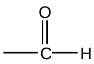
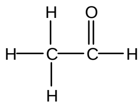
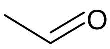
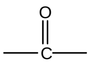
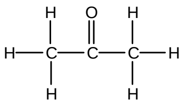
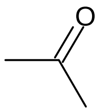
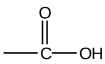
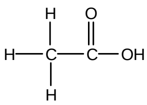
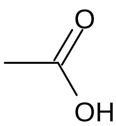
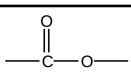
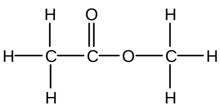
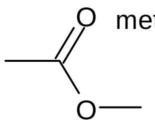


cyclohexene

Homologous series are families of organic compounds with the **same functional group** and **same general formula.**

- They show a gradual change in physical properties (e.g. boiling point).
- Each member differs by CH_2 from the last.
- same chemical properties.

Functional group is an atom or group of atoms which when present in different molecules causes them to have similar chemical properties

homologous series	functional group	prefix / suffix (* = usual use)	example
Alkane		*-ane*	$CH_3CH_2CH_2CH_3$  Butane
Alkenes		*suffix* **-ene**	 propene
Alcohols		*suffix** **-ol** *prefix* **hydroxy-**	 Propan-1-ol 
Halogenoalkanes		*prefix* **chloro-** **bromo-** **iodo-**	 1-chloropropane 
Aldehydes		*suffix* **-al** *prefix* **formyl-**	  ethanal
Ketones		*suffix** -o**ne** *prefix* **oxo-**	  Propanone
carboxylic acids		*suffix* **-oic acid**	  Ethanoic acid
Esters		*-yl –oate*	  methylethanoate

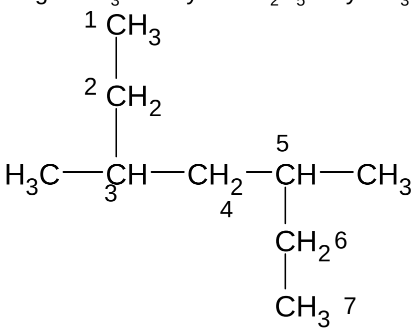
When compounds contain more than one functional group, the order of precedence determines which groups are named with prefix or suffix forms. The highest precedence group takes the suffix (and the lowest number on the carbon chain), with all others taking the prefix form. However, double and triple C-C bonds only take suffix form.
Order of priority highest first:
Carboxylic acids >aldehydes>ketones>alcohols>alkenes>halogenoalkanes

code	no of carbons
meth	1
eth	2
prop	3
but	4
pent	5
hex	6
hept	7
oct	8
non	9
dec	10

General rules for naming carbon chains

- Count the longest carbon chain and name appropriately
- Find any branched chains and count how many carbons they contain
- Add the appropriate prefix for each branch chain

Eg $-CH_3$ methyl or $-C_2H_5$ ethyl $–C_3H_7$ propyl



3,5-dimethylheptane

Basic rules for naming functional groups

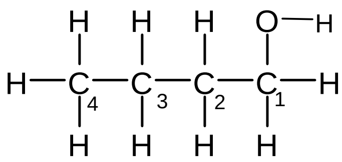
The functional group is named by a prefix or suffix. e.g. **bromo**ethane, ethan**ol**, prop**ene**

- When using a suffix, add in the following way :

  If the suffix starts with a vowel- remove the –e from the stem alkane name
  e.g. Propan-1-ol, butan-1-amine, ethanoic acid, ethanoylchloride, butanamide

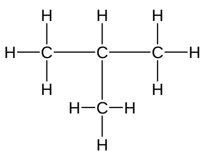
  If the suffix starts with a consonant or there are two or more of a functional group meaning di, or tri needs to be used then **do not remove the the –e** from the stem alkane name
  e.g. Propan**e**nitrile, ethan**e**-1,2-diol, propan**e**dioic acid, propan**e**-1,2,3-triol, Pentan**e**-2,4-dione.

- The position of the functional group on the carbon chain is given by a number – counting from the end of the molecule that gives the functional group the lowest number. For aldehydes, carboxylic acids & nitriles, the functional group is always on carbon 1.



Butan-1-ol

- We only include numbers, however, if they are needed to avoid ambiguity.



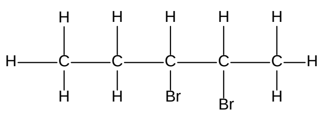
methylpropane

$CHCl_3$ trichloromethane

- The functional groups take precedence over branched chains in giving the lowest number

3-methylbut-1-ene is correct and not 2-methylbut-3-ene

- Where there are two or more of the same groups, ***di-*, *tri-* , *tetra-*, *penta-* or *hexa-*** are used. Note the point made above about the addition of 'e' to the stem



2,3-dibromopentane.

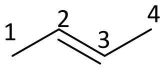
- Words are separated by numbers with dashes
- numbers are separated by commas
- If there is more than one functional group or side chain, the groups are listed in alphabetical order (ignoring any *di*, *tri*).

$CH_2FCCl_2CH_2CH_3$ 2,2-dichloro-1-fluorobutane.

$CH_2FCH_2CHBrCH_2CH_3$ 3-bromo-1-fluoropentane

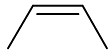
Alkenes

The double bond will be between two carbons. Use the lower number of the two to show the position of the double bond



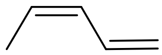
Double bond between C^2 and C^3 so But-2-ene

The name for alkenes may include E or Z at start to show the type of stereoisomer



Z-but-2-ene

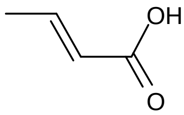
If more than one double bond is present then suffix ends **di**ene or **tri**ene. The stem ends in **a**



Pent**a**-1,3-diene

The suffix **-en** for alkenes can go in front of other suffixes. The alcohol and carboxylic acid groups have higher priority than the alkene group so take precedence with numbering

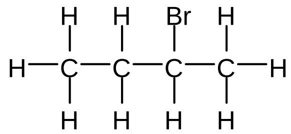
$CH_2OHCHBrCH=CH_2$ 2-bromobut-3-**en**-1-ol



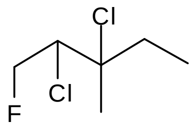
E-but-2-**en**oic acid

Halogenoalkanes

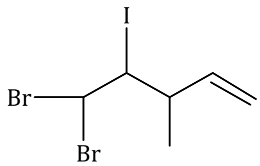
Class the halogen as a substituent on the C chain and use the prefix **-fluoro**, **-chloro**, **-bromo**, or **–iodo**. (Give the position number if necessary)



2-bromobutane



2,3-dichloro-1-fluoro-3-methylpentane



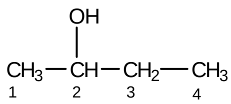
5,5-dibromo-4-iodo-3-methylpent-1-ene

Multiple functional group and side chains are listed in alphabetical order (ignoring any *di*, *tri*).

The alkene group has higher priority than the halogenoalkane group so it takes the lowest number on the carbon chain

Alcohols

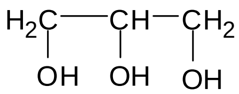
These have the ending **-ol** and if necessary the position number for the OH group is added between the name stem and the –ol



Butan-2-ol

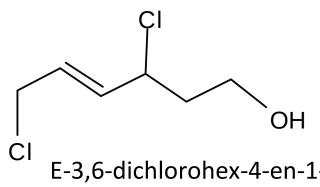
If there are two or more -OH groups then di, tri are used.
Add the **'e'** on to the stem name though.

$HO-CH_2CH_2-OH$ Ethan**e**-1,2-diol



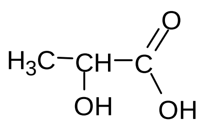
propan**e**-1,2,3-triol

The OH group has a higher priority than the halogenoalkane group and alkene so takes precedence in numbering. The OH is on carbon 1



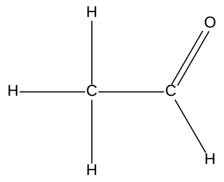
E-3,6-dichlorohex-4-en-1-ol

If the compound has an –OH group in addition to another functional group with a higher priority. The priority group gets the suffix ending and the OH can be named with the prefix **hydroxy-**:



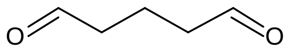
2-hydroxypropanoic acid

Aldehydes
An aldehyde's name ends in **–al**
It always has the C=O bond on the first carbon of the chain so it does not need an extra number. It is by default number one on the chain.



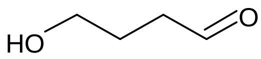
Ethan**al**

If two aldehyde groups then **di** is put before **–al** and an **e** is added to the stem.



pentanedial

Aldehydes have a higher priority than alcohol so the –OH group uses the hydoxy prefix.

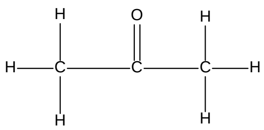


4-hydroxybutanal

Ketones

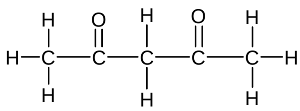
Ketones end in **-one**

When ketones have 5C's or more in a chain then it needs a number to show the position of the double bond. E.g. pentan-2-one



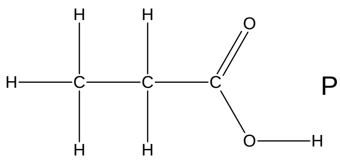
Propan**one**

If two ketone groups then **di** is put before **–one** and an **e** is added to the stem.



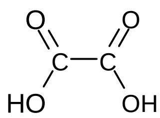
Pentan**e**-2,4-dione

Carboxylic acids
These have the ending **-oic acid** but no number is necessary for the acid group as it must always be at the end of the chain. The numbering always starts from the carboxylic acid end.



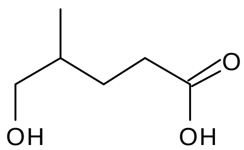
Propan**oic acid**

If there are carboxylic acid groups on both ends of the chain then it is called a - dioic acid



Ethan**edioic acid**

Note the **e** in this name



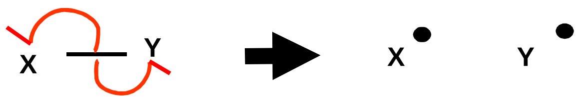
5-hydroxy-4-methylpentanoic acid

Introduction to Mechanisms

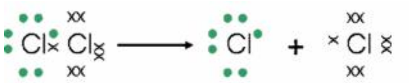
To understand how the reaction proceeds we must first understand how bonds are broken in organic mechanisms
There are two ways to break a covalent bond:

1.Homolytic fission:

each atom gets **one** electron from the covalent bond



one headed arrow shows movement of one electron



The bond has broken in a process called **homolytic** fission.

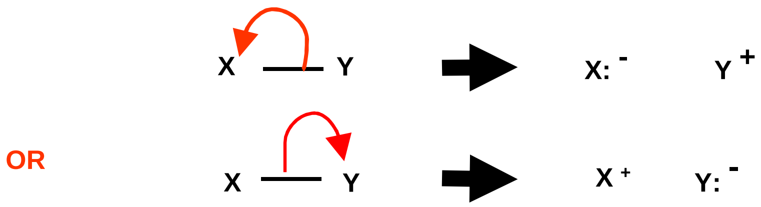
When a bond breaks by homolytic fission it forms two **Free Radicals.**

Free Radicals do not have a charge and are represented by a ●

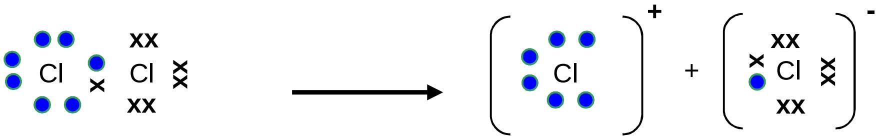
DEFINITION

A **Free Radical** is a reactive species which possess an **unpaired electron**

2. Heterolytic fission: (**one** atom gets **both** electrons)



two headed arrow shows movement of pair of electrons

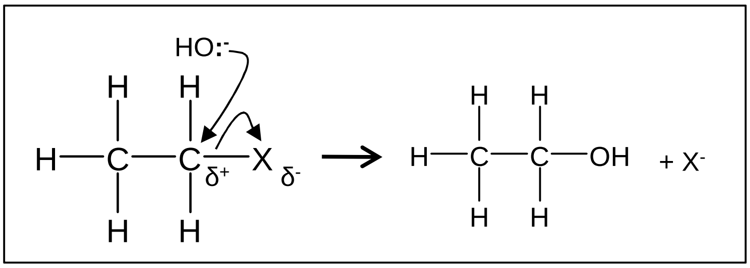


Heterolytic fission produces **IONS**

Most organic reactions occur via heterolytic fission, producing ions

The Mechanism:

To understand a reaction fully we must look in detail at how it proceeds step by step. This is called its **mechanism**



The carbon has a small positive charge because of the electronegativity difference between the carbon and the halogen

We use curly arrows in mechanisms to show the movement of an electron pair showing either breaking or formation of a covalent bond;

A curly arrow will always **start** from a **lone pair** of electrons or the **centre of a bond**

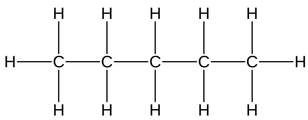
Isomers

Structural isomers: same molecular formula different structures (or structural formulae)

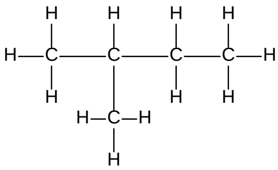
Structural isomerism can arise from
- Chain isomerism
- Position isomerism
- Functional group isomerism

EDEXCEL does not split structural isomers into the different categories. They are all classed as structural isomers.

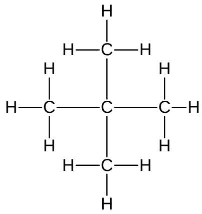
Chain isomers: Compounds with the same molecular formula but different structures of the carbon skeleton



pentane

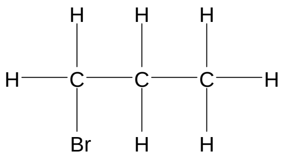


2-methylbutane

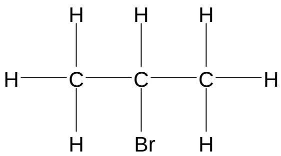


2,2-dimethylpropane

Position isomers: Compounds with the same molecular formula but different structures due to different positions of the same functional group on the same carbon skeleton

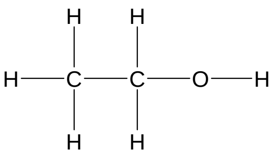


1-bromopropane

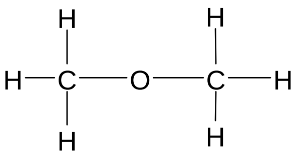


2-bromopropane

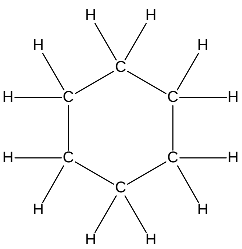
Functional group isomers: Compounds with the same molecular formula but with atoms arranged to give different functional groups



ethanol: an alcohol



Methoxymethane: an ether



Cyclohexane- cyclo alkane

$CH_3CH_2CH_2CH_2CH{=}CH_2$ **hexene- alkene**

Note: alkene and cyclo alkanes have the same general formula. Hexene and cyclohexane have the same molecular formula but have a different functional group

4B Alkanes

Alkanes are saturated hydrocarbons

Saturated: Contain single carbon-carbon bonds only

General formula alkane C_nH_{2n+2}

Hydrocarbon is a compound consisting of hydrogen and carbon **only**

Fuels from crude oil

They are obtained from the crude oil in the order of fractional distillation, cracking and reformation of crude oil

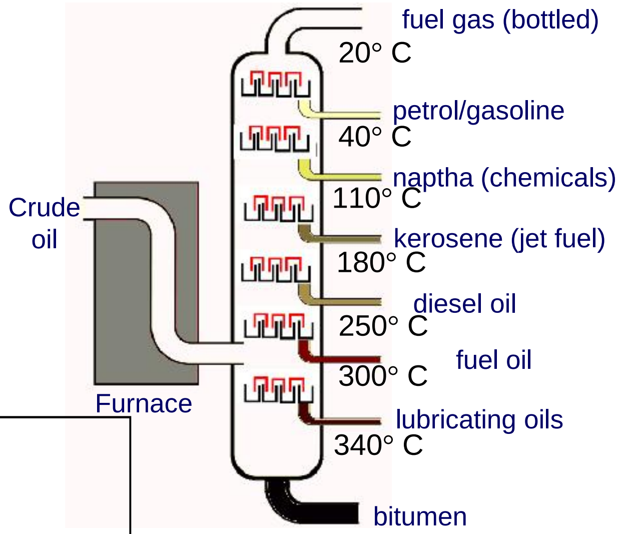
Alkanes are used as fuels

Refining crude oil

Fractional Distillation:

Petroleum is a mixture consisting mainly of alkane hydrocarbons

Petroleum fraction: mixture of hydrocarbons with a similar chain length and boiling point range



- Oil is pre-heated
- then passed into column.
- The fractions condense at different heights
- The temperature of column decreases upwards
- The separation depends on boiling point.
- Boiling point depends on size of molecules.
- The larger the molecule the larger the London forces
- Similar molecules (size, bp, mass) condense together
- Small molecules condense at the top at lower temperatures
- and big molecules condense at the bottom at higher temperatures.

This is a physical process involving the splitting of weak London forces between molecules

Cracking

Cracking: conversion of large hydrocarbons to smaller molecules by breakage of C-C bonds

High Mr alkanes → smaller Mr alkanes+ alkenes + (hydrogen)

Economic reasons for catalytic cracking

- The petroleum fractions with shorter C chains (e.g. petrol and naphtha) are in **more demand** than larger fractions.
- To make use of excess larger hydrocarbons and to supply demand for shorter ones, longer hydrocarbons are cracked.
- The products of cracking are **more useful and valuable** than the starting materials (e.g. ethene used to make poly(ethene) and ethane-1,2-diol, and ethanol) The smaller alkanes are used for motor fuels which burn more efficiently.

This is a chemical process involving the splitting of strong covalent bonds so requires high temperatures.

Reforming

Turns straight chain alkanes into branched and cyclic alkanes and Aromatic hydrocarbons

Branched and cyclic hydrocarbons burn more cleanly and are used to give fuels a higher octane number.

Used for making motor fuels

Alkanes as Fuels

Fuel : releases heat energy when burnt

Alkanes readily burn in the presence of oxygen. This combustion of alkanes is highly exothermic, explaining their use as **fuels**.

Complete Combustion

In excess oxygen alkanes will burn with complete combustion

The products of *complete* combustion are CO_2 and H_2O.

$$C_8H_{18}(g) + 12.5\ O_2(g) \rightarrow 8CO_2(g) + 9\ H_2O(l)$$

Incomplete Combustion

If there is **a limited amount of oxygen** then *incomplete* combustion occurs, producing CO (which is very toxic) and/or C (producing a sooty flame)

$$CH_4(g) + {}^{3}/_{2}\ O_2(g) \rightarrow CO(g) + 2\ H_2O(l)$$
$$CH_4(g) + O_2(g) \rightarrow C(s) + 2\ H_2O(l)$$

Incomplete combustion produces less energy per mole than complete combustion.

Carbon (soot)/particulates can cause global dimming- reflection of the sun's light

Carbon monoxide is an highly toxic but odourless gas. It can cause death if it builds up in a enclosed space due to faulty heating appliances.

CO is toxic to humans as CO can from a strong bond with haemoglobin in red blood cells. This is a stronger bond than that made with oxygen and so it prevents the oxygen attaching to the haemoglobin.

Pollution from Combustion

Sulfur containing impurities are found in petroleum fractions which produce SO_2 when they are burned.

$S + O_2 \rightarrow SO_2$ $\qquad CH_3SH + 3O_2 \rightarrow SO_2 + CO_2 + 2H_2O$

Coal is high in sulfur content, and large amounts of sulfur oxides are emitted from power stations.

SO_2 is acidic and will dissolve in atmospheric water and can produce **acid rain**.

Nitrogen Oxides NO_x

Nitrogen oxides form from the reaction between N_2 and O_2 inside the car engine.
The **high temperature** and **spark** in the engine provides sufficient energy to break strong N_2 bond

$N_2 + O_2 \rightarrow 2NO$ $\qquad N_2 + 2O_2 \rightarrow 2NO_2$

Pollutant	**Environmental consequence**
Nitrogen oxides (formed when N_2 in the air reacts at the **high temperatures and spark** in the engine)	NO is toxic and can form smog NO_2 is toxic and acidic and forms acid rain
Carbon monoxide	toxic
Carbon dioxide	Contributes towards global warming
Unburnt hydrocarbons (not all fuel burns in the engine)	Contributes towards formation of smog
Soot/particulates	Global dimming and respiratory problems

Catalytic converters

These remove CO, NO_x and unburned hydrocarbons (e.g. octane, C_8H_{18}) from the exhaust gases, turning them into 'harmless' CO_2, N_2 and H_2O.

$$2\ CO + 2\ NO \rightarrow 2\ CO_2 + N_2$$
$$C_8H_{18} + 25\ NO \rightarrow 8\ CO_2 + 12\tfrac{1}{2}\ N_2 + 9\ H_2O$$

Converters have a ceramic honeycomb coated with a thin layer of catalyst metals **Platinum, Palladium, Rhodium** – to give a large surface area.

Biofuels

Most fossil fuels come from crude oil, which is a non-renewable resource. Fossil fuel reserves will eventually run out
Alternative fuels have been developed from renewable resources. Alcohols and biodiesel, which can both be made from plants, are two examples of renewable plant-based fuels

Alcohols such as ethanol can be produced from the fermentation of sugars from plants.
Biodiesel is produced by reacting vegetable oils with a mixture of alkali and methanol

Advantages of using Biofuels
Reduction of use of fossil fuels which are finite resources
biofuels are renewable
Use of biodiesel is more carbon-neutral
Allows fossil fuels to be used as a feedstock for organic compounds
No risk of large scale pollution from exploitation of fossil fuels

Disadvantages of Biofuels
Less food crops may be grown
Land not used to grow food crops
Rain forests have to be cut down to provide land
Shortage of fertile soils

Free Radical Substitution Reactions of Alkanes

Reaction of alkanes with bromine / chlorine in UV light

In the presence of **UV light** alkanes react with chlorine to form a mixture of products with the halogens substituting hydrogen atoms.

In general, alkanes do not react with many reagents.
This is because the C-C bond and the C-H bond are relatively strong.

Overall Reaction

$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$

methane **chloromethane**

This is the overall reaction, but a more complex mixture of products is actually formed

The **mechanism** for this reaction is called a **free radical substitution**

It proceeds via a series of steps:
Step one: **Initiation**
Step two: **Propagation**
Step three: **Termination**

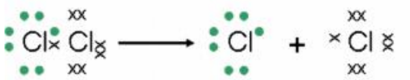
Step one Initiation

Essential condition: UV light

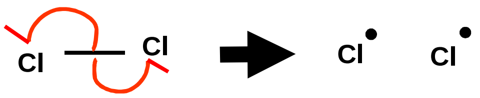
$Cl_2 \rightarrow 2Cl^{\bullet}$

The UV light supplies the energy to break the Cl-Cl bond. It is broken in preference to the others as it is the weakest.

UV light does not have enough energy to break the C-H bond



The bond has broken in a process called **homolytic** fission.



***each** atom gets **one** electron from the covalent bond*

When a bond breaks by homolytic fission it forms **Free Radicals.**

Free Radicals do not have a charge and are represented by a •

DEFINITION

A **Free Radical** is a reactive species which possess an **unpaired electron**

Step two Propagation

$CH_4 + Cl^{\bullet} \rightarrow HCl + {}^{\bullet}CH_3$

${}^{\bullet}CH_3 + Cl_2 \rightarrow CH_3Cl + Cl^{\bullet}$

The chlorine free radicals are very reactive and remove an H from the methane leaving a methyl free radical

The methyl free radical reacts with a Cl_2 molecule to produce the main product and another Cl free radical

All propagation steps have a **free radical** in the ***reactants*** and in the ***products***.

As the Cl free radical is regenerated, it can react with several more alkane molecules in a ***CHAIN REACTION***

Step three Termination

${}^{\bullet}CH_3 + Cl^{\bullet} \rightarrow CH_3Cl$

${}^{\bullet}CH_3 + {}^{\bullet}CH_3 \rightarrow CH_3CH_3$

$Cl^{\bullet} + Cl^{\bullet} \rightarrow Cl_2$

Collision of two free radicals *does not generate* further free radicals: the chain is **TERMINATED**.

Minor step leading to impurities of ethane in product.
Write this step using structural formulae and don't use molecular formulae

Applying the mechanism to other alkanes

The same mechanism is used: Learn the patterns in the mechanism

Example: Write mechanism of Br_2 and Propane

STEP ONE Initiation

Essential condition: UV light

$Br_2 \rightarrow 2Br^{\bullet}$

Br_2 splits in the same way as Cl_2

STEP TWO Propagation

$CH_3CH_2CH_3 + Br^{\bullet} \rightarrow HBr + CH_3CH_2CH_2^{\bullet}$ ← Remove one H from the alkane to produce a radical

$CH_3CH_2CH_2^{\bullet} + Br_2 \rightarrow CH_3CH_2CH_2Br + Br^{\bullet}$ ← To the radical produced in the previous step add a Br

STEP THREE Termination

$CH_3CH_2CH_2^{\bullet} + Br^{\bullet} \rightarrow CH_3CH_2CH_2Br$

$CH_3CH_2CH_2^{\bullet} + CH_3CH_2CH_2^{\bullet} \rightarrow CH_3CH_2CH_2CH_2CH_2CH_3$

Propagation steps for substituting a halogen on a 'middle' carbon

$CH_3CH_2CH_3 + Br^{\bullet} \rightarrow HBr + CH_3CH^{\bullet}CH_3$

$CH_3CH^{\bullet}CH_3 + Br_2 \rightarrow CH_3CH_2BrCH_3 + Br^{\bullet}$

If the question asks for the halogen to be substituted onto a middle carbon in the chain, it is important to put the free radical **'dot'** on the correct carbon in the propagation stages.

Further substitution reactions

Excess Cl_2 present will promote further substitution and could produce **CH_2Cl_2, $CHCl_3$ and CCl_4**

These reactions could occur

$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl$
$CH_2Cl_2 + Cl_2 \rightarrow CHCl_3 + HCl$
$CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$

Example propagation steps that would lead to further substitution

$CH_3Cl + Cl^{\bullet} \rightarrow HCl + {}^{\bullet}CH_2Cl$

${}^{\bullet}CH_2Cl + Cl_2 \rightarrow CH_2Cl_2 + Cl^{\bullet}$

Overall reaction equations

You should be able to write overall reaction equations for various reactions

Example 1. Write the overall reaction equation for the formation of CCl_4 from $CH_4 + Cl_2$

$$CH_4 + 4\,Cl_2 \rightarrow CCl_4 + 4\,HCl$$

Example 2. Write the overall reaction equation for the formation of $CFCl_3$ from $CH_3F + Cl_2$

$$CH_3F + 3\,Cl_2 \rightarrow CFCl_3 + 3\,HCl$$

Note HCl is always the side product – never H_2