

15 Hydrocarbons

Alkanes

Chemical Reactivity

Alkanes do not react with many reagents.

This is because the C-C bond and the C-H bond are relatively strong and so cannot form stronger bonds with other elements that easily and there are no polar side groups .

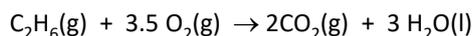
There main reactions are combustion reactions in air although they can react with halogens in the presence of UV light

Combustion

Complete Combustion

In excess oxygen alkanes will burn with complete combustion

The products of *complete* combustion are CO₂ and H₂O.



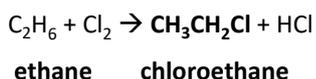
Alkanes readily burn in the presence of oxygen. This combustion of alkanes is highly exothermic, explaining their use as **fuels**.

Reaction of alkanes with bromine / chlorine in UV light

Synthesis of chloroalkanes

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

Overall Reaction



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

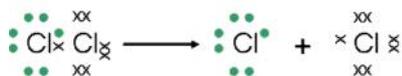
*To understand this reaction fully we must look in detail at how it proceeds step by step. This is called its **mechanism***

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



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.

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 \bullet

DEFINITION

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

STEP TWO Propagation



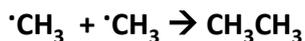
The chlorine free radicals are very reactive and remove an H from the methane leaving a methyl free radical

The methyl free radical reacts with a Cl₂ 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



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

Example: Write mechanism of Br₂ and Propane

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

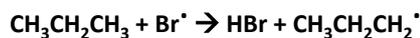
STEP ONE Initiation

Essential condition: UV light



Br₂ splits in the same way as Cl₂

STEP TWO Propagation

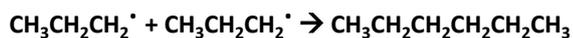
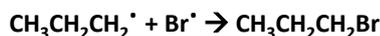


← Remove one H from the alkane to produce a radical



← To the radical produced in the previous step add a Br

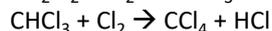
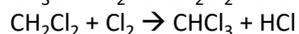
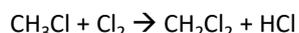
STEP THREE Termination



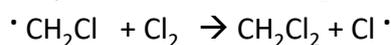
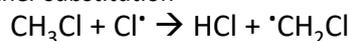
Further substitution

Excess Cl₂ present will promote further substitution and could produce **CH₂Cl₂, CHCl₃ and CCl₄**

These reactions could occur



Example propagation steps that would lead to further substitution

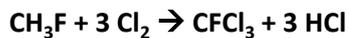


You should be able to write **overall reaction** equations for various reactions

Example 1. Write the overall reaction equation for the formation of CCl₄ from CH₄ + Cl₂



Example 2. Write the overall reaction equation for the formation of CFCl₃ from CH₃F + Cl₂



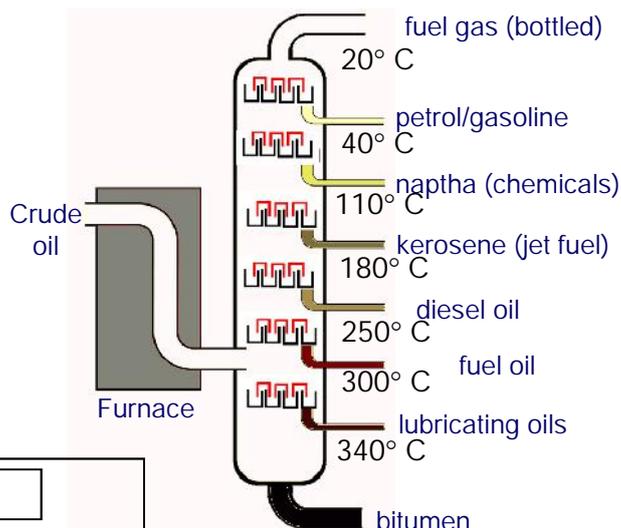
Note HCl is always the side product – never H₂

Refining crude oil

Fractional Distillation: Industrially

Petroleum is a mixture consisting mainly of alkane hydrocarbons

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



- Key points to learn
- 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 van der waals 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 van der waals forces between molecules

Vacuum distillation unit

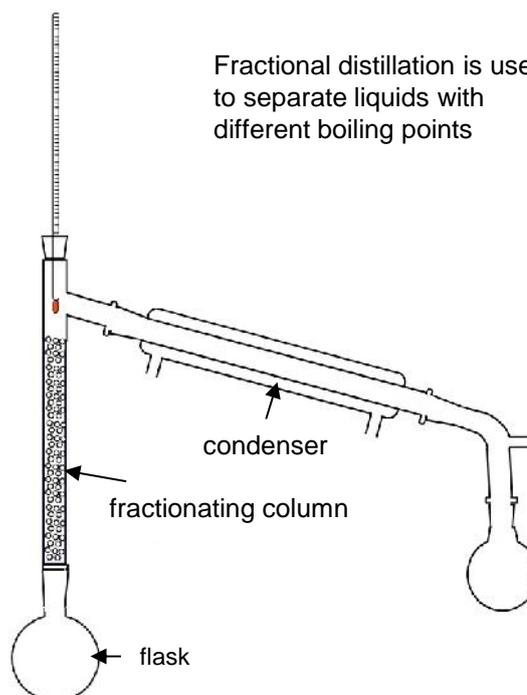
- Heavy residues from the fractionating column are distilled again under a vacuum.
- Lowering the pressure over a liquid will lower its boiling point.

Vacuum distillation allows heavier fractions to be further separated without high temperatures which could break them down.

Fractional Distillation: In the laboratory

- Heat the flask, with a Bunsen burner or electric mantle
- This causes vapours of all the components in the mixture to be produced.
- Vapours pass up the fractionating column.
- The vapour of the substance with the lower boiling point reaches the top of the fractionating column first.
- The thermometer should be at or below the boiling point of the most volatile substance.
- The vapours with higher boiling points condense back into the flask.
- Only the most volatile vapour passes into the condenser.
- The condenser cools the vapours and condenses to a liquid and is collected.

Fractional distillation is used to separate liquids with different boiling points



Cracking

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

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

Economic reasons for 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 valuable** than the starting materials (e.g. ethene used to make poly(ethene), branched alkanes for motor fuels, etc.)

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

There are two main types of cracking: **thermal** and **catalytic**. They need different conditions and are used to produce different products

Thermal Cracking

Conditions:

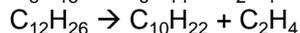
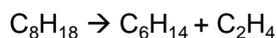
High Pressure (7000 kPa)

High Temperature (400°C to 900°C)

produces mostly alkenes e.g. ethene used for making polymers and ethanol

sometimes produces hydrogen used in the Haber Process and in margarine manufacture

Example Equations



Bonds can be broken anywhere in the molecule by C-C bond fission and C-H bond fission.

Catalytic Cracking

Conditions:

Low pressure

High Temperature (450°C)

Zeolite Catalyst

Produces branched and cyclic alkanes and Aromatic hydrocarbons

Used for making motor fuels

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

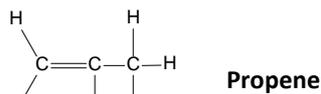
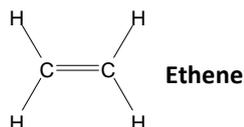
Cheaper than thermal cracking because it saves energy as lower temperatures and pressures are used

Alkenes

Alkenes are unsaturated hydrocarbons

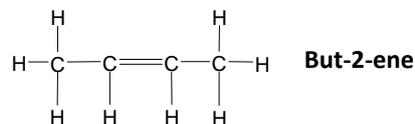
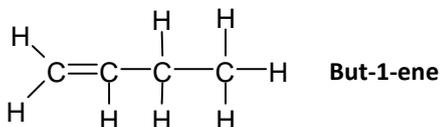
General formula is C_nH_{2n}

Alkenes contain a carbon-carbon double bond somewhere in their structure.

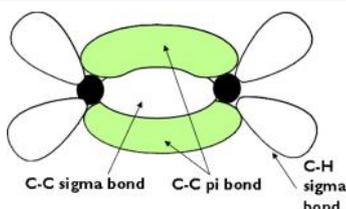


The arrangement of bonds around the $>C=C<$ is planar and has the bond angle 120°

Numbers need to be added to the name when positional isomers can occur.



$C=C$ double covalent bond consists of **one sigma (σ) bond and one pi (π) bond.**



π bonds are **exposed** and have **high electron density**.

They are therefore vulnerable to attack by species which 'like' electrons: these species are called **electrophiles**.

Addition reactions of alkenes

The alkenes are relatively reactive because of the relatively low bond enthalpy of the π -bond.

Addition reaction: a reaction where two molecules react together to produce one

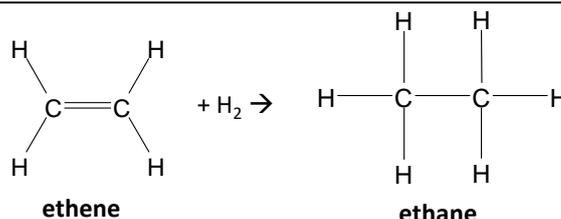
1. Reaction of Alkenes with Hydrogen

Change in functional group: alkene \rightarrow alkane

Reagent: hydrogen

Conditions: Nickel Catalyst

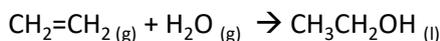
Type of reaction: Addition/Reduction



2. Reaction of alkenes with steam to form alcohols

Industrially alkenes are converted to alcohols in one step. They are reacted with steam in the presence of an acid catalyst.

This reaction can be called **hydration**: a reaction where water is **added** to a molecule



The high pressures needed mean this cannot be done in the laboratory. It is preferred industrially, however, as there are no waste products and so has a high atom economy. It would also mean separation of products is easier (and cheaper) to carry out.

Reagent : steam

Essential Conditions

High temperature 300 to 600°C

High pressure 60 atm

Catalyst of **concentrated H_3PO_4** or **concentrated H_2SO_4**

Electrophilic Addition Reactions of Alkenes

The double bonds in alkenes are areas with high electron density. This attracts electrophiles and the alkenes undergo addition reactions.

Definition Electrophile: an **electron pair acceptor**

3. Reaction of Bromine with Alkenes

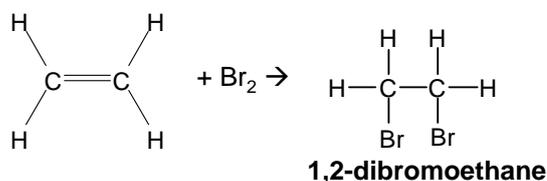
Change in functional group: alkene \rightarrow dihalogenoalkane

Reagent: Bromine

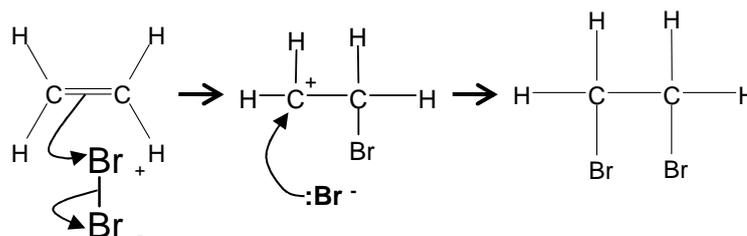
Conditions: Room temperature (not in UV light)

Mechanism: Electrophilic Addition

Type of reagent: Electrophile, $\text{Br}^{\delta+}$



As the Br_2 molecule approaches the alkene, the pi bond electrons repel the electron pair in the Br-Br bond. This **INDUCES** a **DIPOLE**. Br_2 becomes **polar** and **ELECTROPHILIC** ($\text{Br}^{\delta+}$).



The **INTERMEDIATE** formed, which has a positive charge on a carbon atom is called a **CARBICATION**

4. Reaction of Hydrogen Bromide with Alkenes

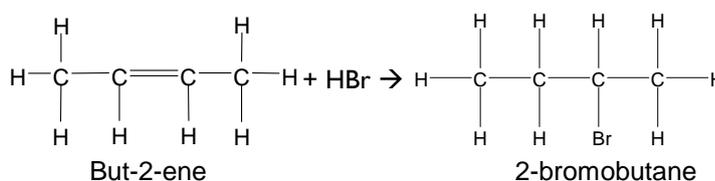
Change in functional group: alkene \rightarrow halogenoalkane

Reagent: HCl or HBr

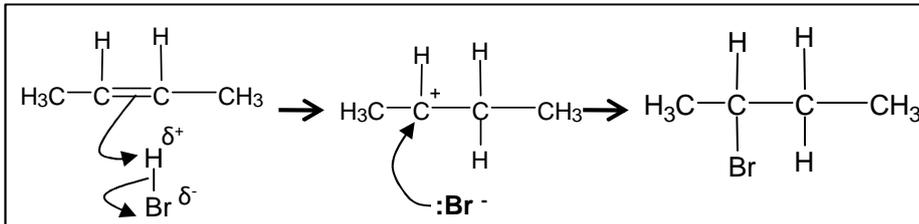
Conditions: Room temperature

Mechanism: Electrophilic Addition

Type of reagent: Electrophile, $\text{H}^{\delta+}$



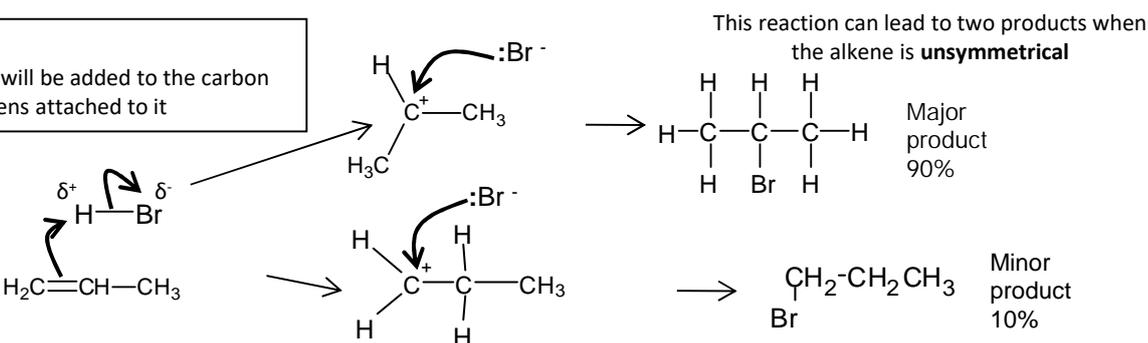
HBr is a polar molecule because Br is more electronegative than H. The $\text{H}^{\delta+}$ is attracted to the electron-rich pi bond.



'Markownikoff's Rule'

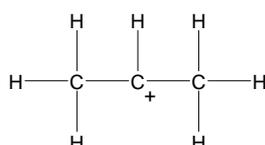
In most cases, bromine will be added to the carbon with the fewest hydrogens attached to it

If the alkene is unsymmetrical, addition of hydrogen bromide can lead to two isomeric products.



WHY?

This carbocation intermediate is more stable because the methyl groups on either side of the positive carbon are electron releasing and reduce the charge on the ion which stabilises it.



In **electrophilic addition** to alkenes, the **major product** is formed **via the more stable carbocation** intermediate.

In exam answers

- Draw out both carbocations and identify as primary, secondary and tertiary
- State which is the more stable carbocation e.g. secondary more stable than primary
- State that the more stable carbocation is stabilised because the methyl groups on either (or one) side of the positive carbon are electron releasing and reduce the charge on the ion.
- (If both carbocations are secondary then both will be equally stable and a 50/50 split will be achieved)

The order of stability for carbocations is
tertiary > secondary > primary

5. Reaction of cold dilute Potassium Manganate(VII) with Alkenes

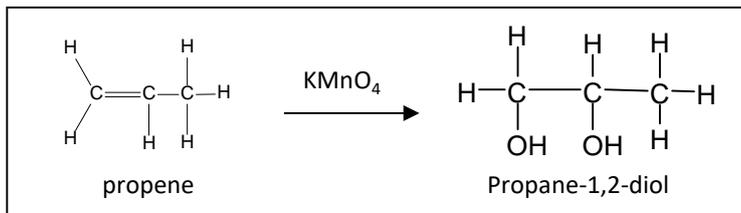
Change in functional group: alkene → diol

Reagent: KMnO_4 in an acidified solution

Conditions: cold dilute

Type of reaction: Oxidation

Observation: purple colour of MnO_4^- ion will decolourise to colourless



This reaction with its colour change can be used as a test for the alkene functional group. It would not change colour with alkanes

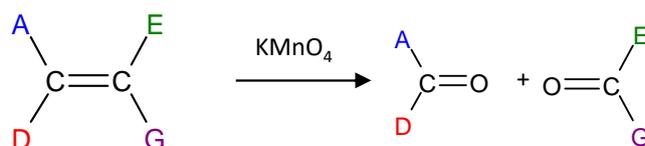
5. Reaction of hot concentrated Potassium Manganate(VII) with Alkenes

Change in functional group: alkene → carbonyls (mostly)

Reagent: KMnO_4 in an acidified solution

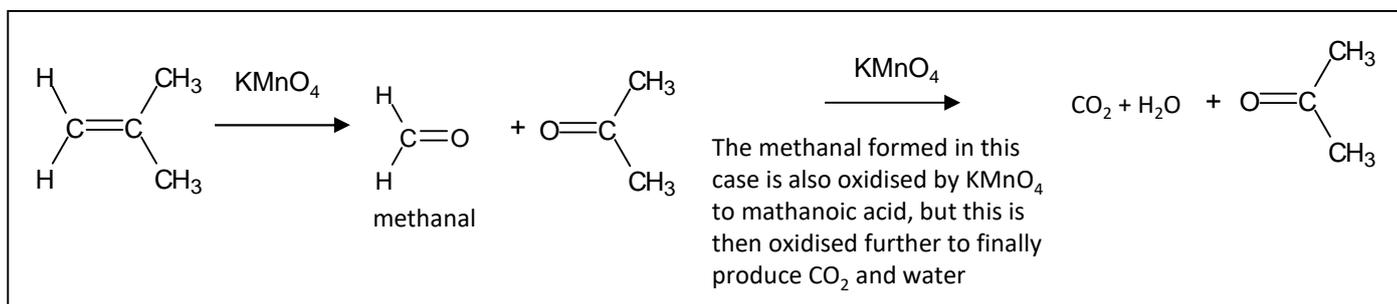
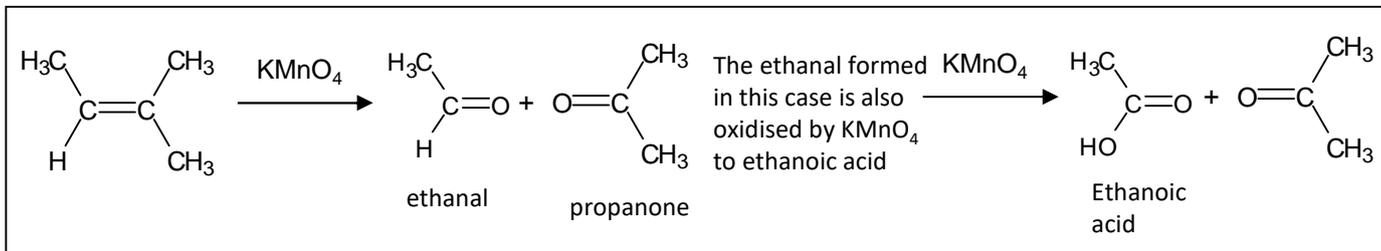
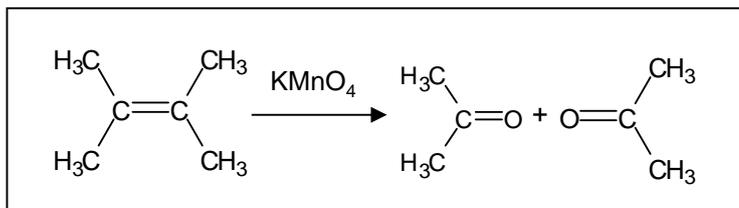
Conditions: hot concentrated

Type of reaction: Oxidation



General reaction – double bond breaks and two carbonyls are formed. The products formed can be used to work out which alkene was the reactant

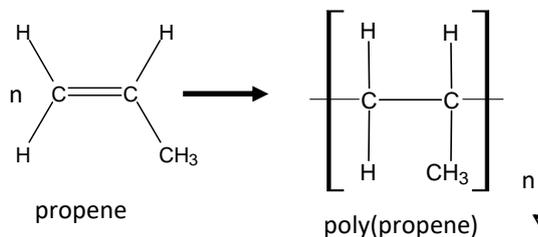
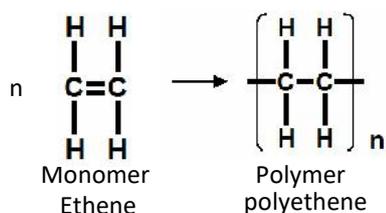
Different alkenes will lead to different types of products.



Addition Polymers

Addition polymers are formed from alkenes

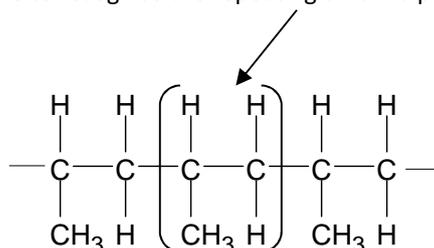
This is called **addition polymerisation**



Poly(propene) is recycled

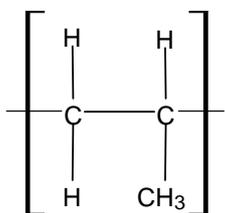
Poly(alkenes) like alkanes are unreactive due to the strong C-C and C-H bonds

be able to recognise the repeating unit in a poly(alkene)

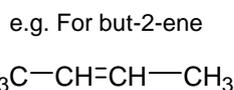


Add the **n's** if writing an equation showing the reaction where 'n' monomers become 'n' repeating units

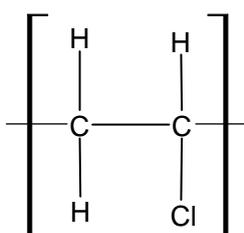
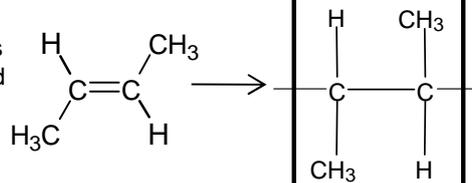
If asked to draw **one repeating unit**, don't add the **n** on to your diagram, because **n** represents a large number



You should be able to draw the polymer repeating unit for any alkene



It is best to first draw out the monomer with groups of atoms arranged around the double bond



Poly(chloroethene) is a polymer that is water proof, an electrical insulator and doesn't react with acids.

In its pure form it is a rigid plastic due to the strong intermolecular bonding between polymer chains prevents them moving over each other. In this un-plasticised form it is used to make uPVC window frame coverings and guttering.

Dealing with waste polymers

Most polymers (polyalkenes) are non-biodegradable and take many years to break down.

Combustion for energy production

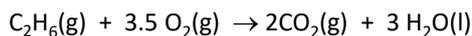
Waste polymers can be incinerated and the heat released can be used to generate electricity.

Combustion of halogenated plastics (ie PVC) can lead to the formation of toxic, acidic waste products such as HCl.

Chemists can minimise the environmental damage of this by removing the HCl fumes formed from the combustion process.

Hydrocarbons as fuels

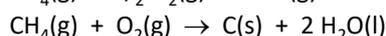
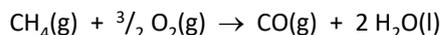
Alkanes are good fuels. They burn cleanly, have high enthalpies of combustion and are easy to transport.



Pollution from Combustion

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)



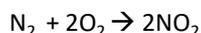
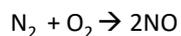
Incomplete combustion produces less energy per mole than complete combustion

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

Nitrogen Oxides NO_x

Nitrogen oxides form from the reaction between N₂ and O₂ inside the car engine.

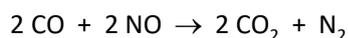
The **high temperature** and **spark** in the engine provides sufficient energy to break strong N₂ bond



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 acidic gas NO ₂ NO ₂ is toxic and acidic and forms acid rain
Carbon monoxide	toxic
Carbon dioxide	Contributes towards global warming
Unburnt hydrocarbons (not all the fuel burns in the engine) Some escapes at petrol filling stations.	Contributes towards formation of smog
soot	Global dimming and respiratory problems

Catalytic converters

These remove CO, NO_x and unburned hydrocarbons (e.g. octane, C₈H₁₈) from the exhaust gases, turning them into 'harmless' CO₂, N₂ and H₂O.



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

Global warming

•Carbon dioxide (CO₂), methane (CH₄) and water vapour (H₂O) are all greenhouse gases. (They trap the Earth's radiated infra red energy in the atmosphere).

•Water is the main greenhouse gas (but is natural), followed by carbon dioxide and methane.

Carbon dioxide levels have risen significantly in recent years due to increasing burning of fossil fuels.
Carbon dioxide is a particularly effective greenhouse gas and its increase is thought to be largely responsible for global warming.

The Earth is thought to be getting warmer, and many scientists believe it is due to increasing amounts of greenhouse gases in the atmosphere.

Infrared spectroscopy

This type of spectroscopy can be used to measure the amounts of greenhouse gases in the atmosphere. The bonds in CO₂, methane and water vapour absorb infra-red radiation. See chapter 22 for more details.

Aromatic Hydrocarbons / Arenes

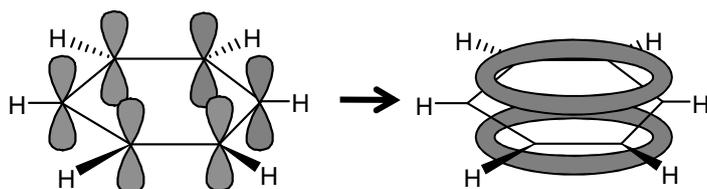
There are two major classes of organic chemicals
aliphatic : straight or branched chain organic substances
aromatic or arene: includes one or more ring of six carbon atoms with delocalised bonding.

All of the organic substances we have looked at so far have been aliphatic.

Benzene belongs to the aromatic class.

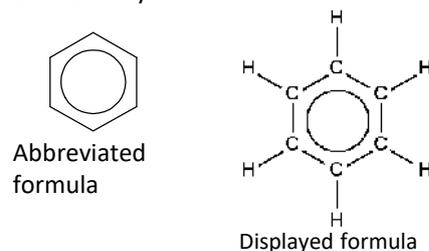
Benzene's Structure

The simplest arene is benzene. It has the molecular formula C_6H_6 . Its basic structure is six C atoms in a hexagonal ring, with one H atom bonded to each C atom.
 Each C atom is bonded to two other C atoms and one H atom by single covalent σ -bonds. This leaves one unused electron on each C atom in a p orbital, perpendicular to the plane of the ring.
 The Six p electrons are delocalised in a ring structure above and below the plane of carbon atoms.



Benzene is a **planar** molecule. The evidence suggests all the C-C bonds are the same and have a length and bond energy between a C-C single and C=C double bond.

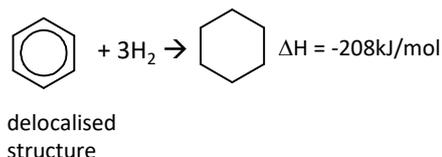
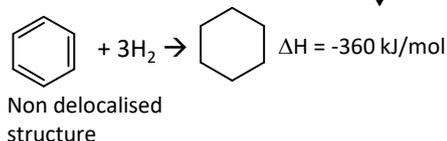
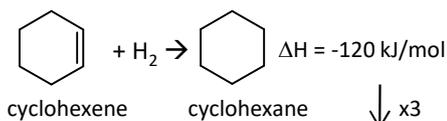
In formulae we draw a circle to show this delocalised system.



The six electrons in the pi bonds are delocalised and spread out over the whole ring. Delocalised means not attached to a particular atom.

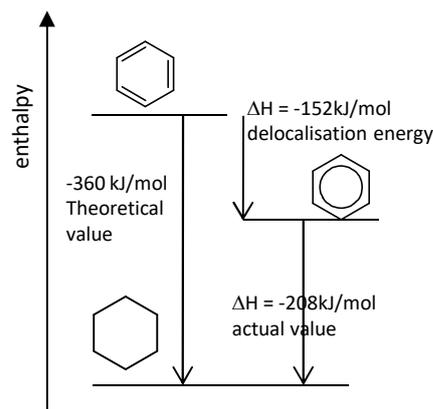
The H-C-C bond angle is 120° in Benzene

Using Enthalpies of Hydrogenation to show Thermodynamic Stability



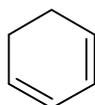
Theoretically because there are 3 double bonds in the theoretical cyclohexa-1,3,5-triene one might expect the amount of energy to be 3 times as much as cyclohexene.

However, in actual benzene the amount of energy is less. The 6 pi electrons are delocalised and not arranged in 3 double bonds

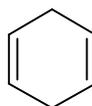


The increase in stability connected to delocalisation is called the **delocalisation energy**.

This when represented on an energy level diagram shows that the delocalised benzene is more thermodynamically stable than the theoretical structure .



In cyclohexa-1,3-diene, there would be some delocalisation and extra stability as the pi electrons are close together, in the same plane and so overlap . The hydrogenation value would be less negative than -240 kJ/mol (showing more stable)



In cyclohexa-1,4-diene, there would not be delocalisation as the pi electrons are too far apart and so don't overlap. The hydrogenation value would be -240 kJ/mol

Halogenation of Benzene

Change in functional group: benzene → Bromobenzene

Reagents: Bromine

Conditions: iron(III) bromide catalyst FeBr_3

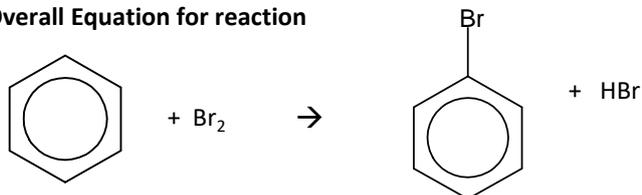
Mechanism: Electrophilic Substitution

This reaction can be done with chlorine.

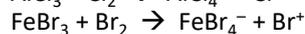
The catalyst can be AlCl_3 or FeCl_3

It is possible to create the iron(III) bromide in situ by reacting iron with bromine

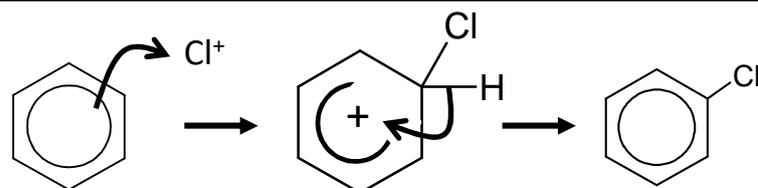
Overall Equation for reaction



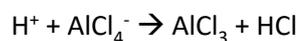
Equation for Formation of electrophiles: (Learn!)



Mechanism



The H^+ ion reacts with the AlCl_4^- to reform AlCl_3 catalyst and HCl .



Nitration of Benzene

Change in functional group: benzene → nitrobenzene

Reagents: conc nitric acid in the presence of concentrated sulphuric acid (catalyst)

Mechanism: Electrophilic Substitution

Electrophile: NO_2^+

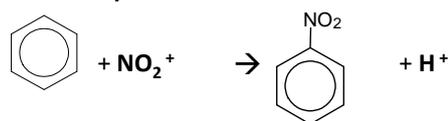
Importance of this reaction

Nitration of benzene and other arenes is an important step in synthesising useful compounds e.g. explosive manufacture (like TNT, trinitrotoluene/ 2,4,6-trinitromethylbenzene) and formation of amines from which dyestuffs are manufactured. (The reaction for this is covered in the amines section.)

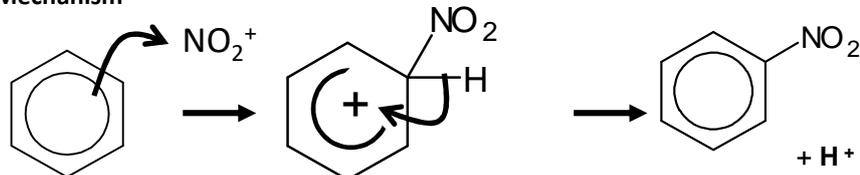
Equation for Formation of electrophile: (Learn!)



Overall Equation for reaction



Mechanism



The horseshoe shape of the intermediate must not extend beyond C's 2 to 6

The H^+ ion rejoins with the HSO_4^- to reform H_2SO_4 catalyst.

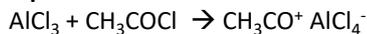
This reaction is done at 60°C . On using higher temperatures a second nitro group can be substituted.

Friedel Crafts Acylation

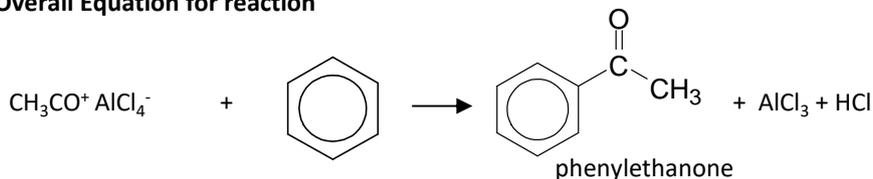
Change in functional group: benzene → phenyl ketone
Reagents: acyl chloride in the presence of anhydrous aluminium chloride catalyst
Conditions: heat under reflux (50°C)
Mechanism: Electrophilic Substitution

Any acyl chloride can be used RCOCl where R is any alkyl group e.g. $-\text{CH}_3$, $-\text{C}_2\text{H}_5$. The electrophile is the RCO^+ .

Equation for Formation of the electrophile.

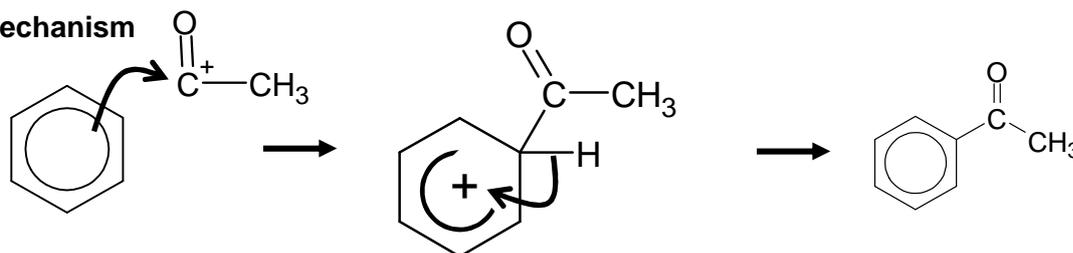


Overall Equation for reaction



These are important reactions in organic synthesis because they introduce a reactive functional group on to the benzene ring

Mechanism



The H^+ ion reacts with the AlCl_4^- to reform AlCl_3 catalyst and HCl .

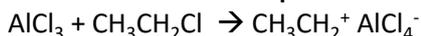


Friedel Crafts Alkylation

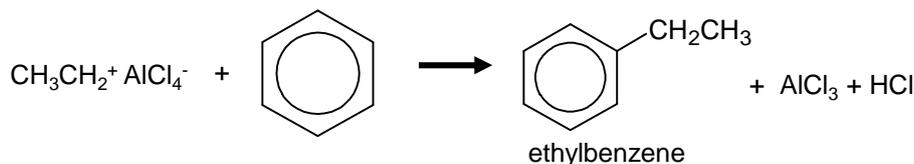
Change in functional group: benzene → alkylbenzene
Reagents: chloroalkane in the presence of anhydrous aluminium chloride catalyst
Conditions: heat under reflux
Mechanism: Electrophilic Substitution

Any chloroalkane can be used RCl where R is any alkyl group Eg $-\text{CH}_3$, $-\text{C}_2\text{H}_5$. The electrophile is the R^+ .

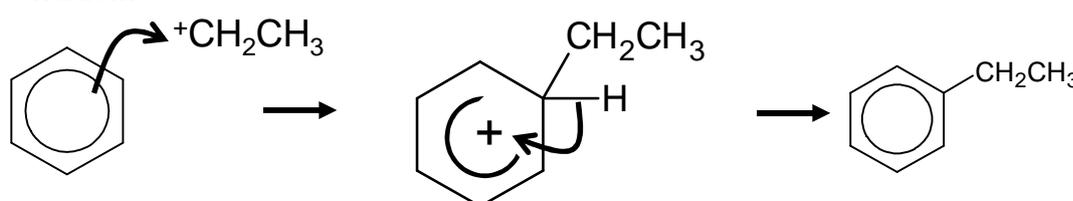
Formation of the electrophile.



Overall Equation for reaction



Mechanism



The H^+ ion reacts with the AlCl_4^- to reform AlCl_3 catalyst and HCl .



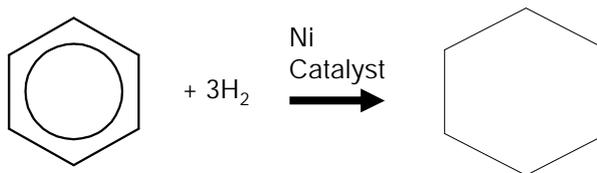
Hydrogenation of Benzene

Reaction: benzene \rightarrow cyclohexane

Reagents: Hydrogen

Conditions: Nickel catalyst at 200C and 30 atm

Type of reaction: Addition and reduction



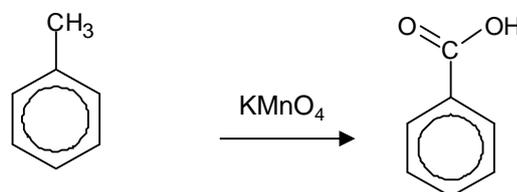
Oxidation of side chains

Reaction: alkylbenzene \rightarrow benzoic acid

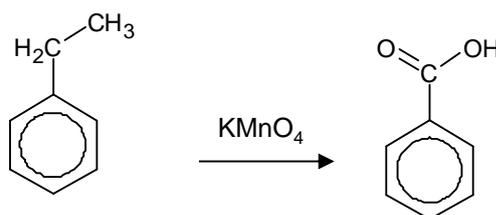
Reagents: alkaline KMnO_4 (followed by H_2SO_4)

Conditions: heat under reflux

Type of reaction: oxidation



Different lengths of alkyl groups all get oxidised to benzoic acid



Reactions of Benzene

Benzene does not readily undergo addition reactions because these would involve permanently breaking up the delocalised system. Most of Benzene's reactions involve substituting one H for another atom or group of atoms. Its reactions are usually **electrophilic substitutions**.

Comparison of Benzene with alkenes: reaction with Bromine

The delocalised electrons above and below the plane of the molecule are attractive for electrophiles to attack. But they do undergo electrophilic reactions more slowly than alkenes

Alkenes react with Bromine easily at room temperature. Benzene does not react with Bromine without additional halogen carrier chemicals.

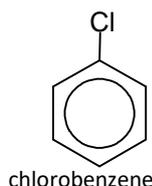
In benzene, electrons in π -bond(s) are delocalised. In alkenes, π -electrons are localised between two carbons.

Benzene therefore has a lower electron density than $\text{C}=\text{C}$. Benzene therefore polarises bromine less and induces a weaker dipole in bromine than an alkene would.

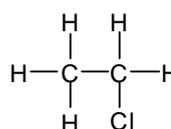
The electrophilic substitution mechanisms involve a temporary breaking of the delocalization to form an intermediate. It takes energy to form this intermediate. The activation energies are therefore high, and substitution reactions of arenes tend to be relatively slow

Effect of delocalisation on side groups with lone pairs

If a $-\text{Cl}$ atom is directly attached to a benzene ring the delocalisation in the benzene ring will extend to include the lone pairs on the Cl. This changes the properties and reactions of the side group.

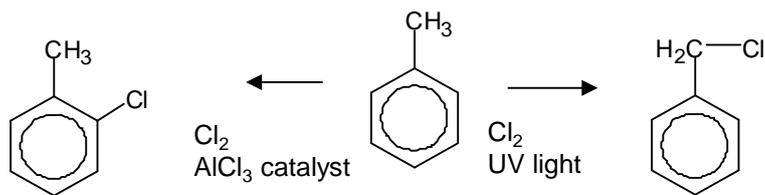


The C-Cl bond is made stronger. Typical halogenoalkane nucleophilic substitution and elimination reactions do not occur. Also the electron rich benzene ring will repel nucleophiles.



Aliphatic halogenoalkanes will undergo nucleophilic substitution reactions to produce alcohols

Halogenation and conditions



Use the AlCl_3 catalyst to substitute directly on the benzene ring

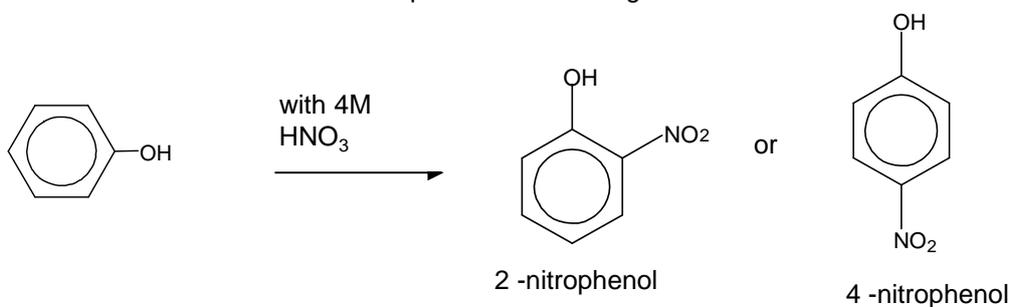
Use UV light to substitute on to the side group

Effect of side groups on substitution

Side groups on a benzene ring can affect the position on the ring of substitution reactions.

Electron-donating groups such as OH , NH_2 , $-\text{Cl}$ will force further substitutions to occur on the 2- and 4- positions of the ring

Table 9 in the data book has this information



Electron-withdrawing groups (such as NO_2 , $-\text{CN}$, $-\text{CO}_2\text{H}$) will have a 3-directing effect in electrophilic substitution of aromatic compounds

