3.2 The alkanes

Prior knowledge:

- Types of formula – general, empirical, molecular, structural, displayed and skeletal.
- Nomenclature
- Structural isomers – chain and position isomers
- Free radicals

Aliphatic Alkanes

- General formula: C_nH_{2n+2}
- Saturated hydrocarbons
- Can have unbranched or branched chains
- All carbon- carbon bonds are single bonds
- All bond angles are 109.5^o

Saturated: Contains C – C single bonds only

Hydrocarbon: Only contains the elements hydrogen and carbon

Isomerism:

Alkanes with 4 or more carbons show a type of ***structural isomerism*** called ***chain isomerism***

Structural isomerism: Same molecular formula but different structural formula

Chain Isomerism: Same molecular formula but different arrangement of the carbon skeleton

Chain isomers of C_4H_{10}

	butane	**Methylpropane**
displayed formula		
structural formula		
skeletal formula		

Draw the chain isomers of C_5H_{12}

Cyclic alkanes have the general formula C_nH_{2n}, **2 less hydrogen than a straight chain alkane**

e.g **C_6H_{12}**

1. cyclohexane
2. methylcyclopentane

Physical properties of the alkanes:

Polarity:

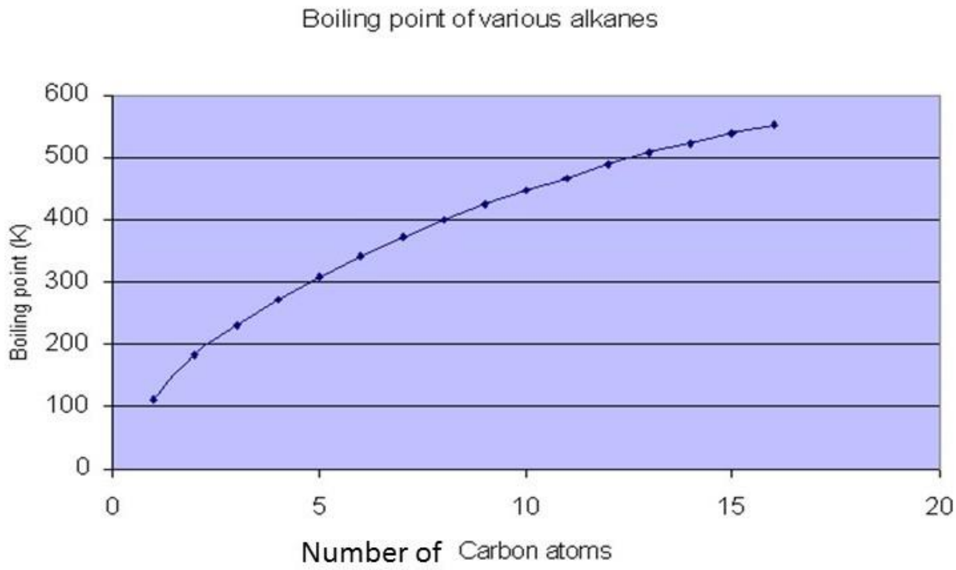
- C and H have very similar electronegativities so the bonds are non – polar.
- This means that all alkane molecules will also be non – polar.
- The only intermolecular force (IMF) holding the alkanes together will therefore be Van Der Waals (VDW) forces of attraction.

Solubility:

- Water molecules are held together by hydrogen bonds and these are much stronger that VDW so the alkanes are not soluble in water.

Boiling points:

A) Chain length effect



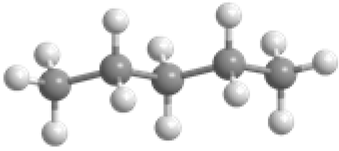
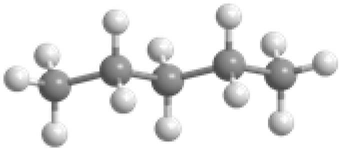
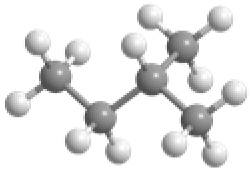
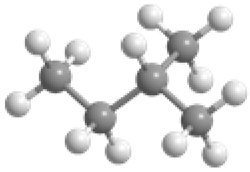
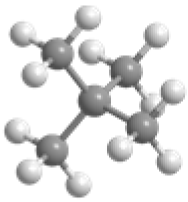
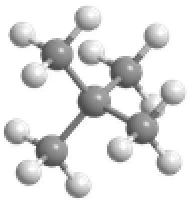
Trend:

- As the carbon chain **increases**, the boiling point of the alkanes also **increases**.

Explanation

- This is because there are **more electrons** in the molecule (due to the extra CH_2) so the **Van der Waals** forces of attraction become **stronger**.
- This means **more energy** is required to overcome this **increased attraction**.

B) Branching effect

Chain Isomer	Shape	Boiling point
Pentane	 	309K
2-methylbutane	 	301K
2,2-dimethylpropane	 	283K

Trend:

- As the amount of **branching increases**, the **boiling point** of the alkane **decreases**.

Explanation:

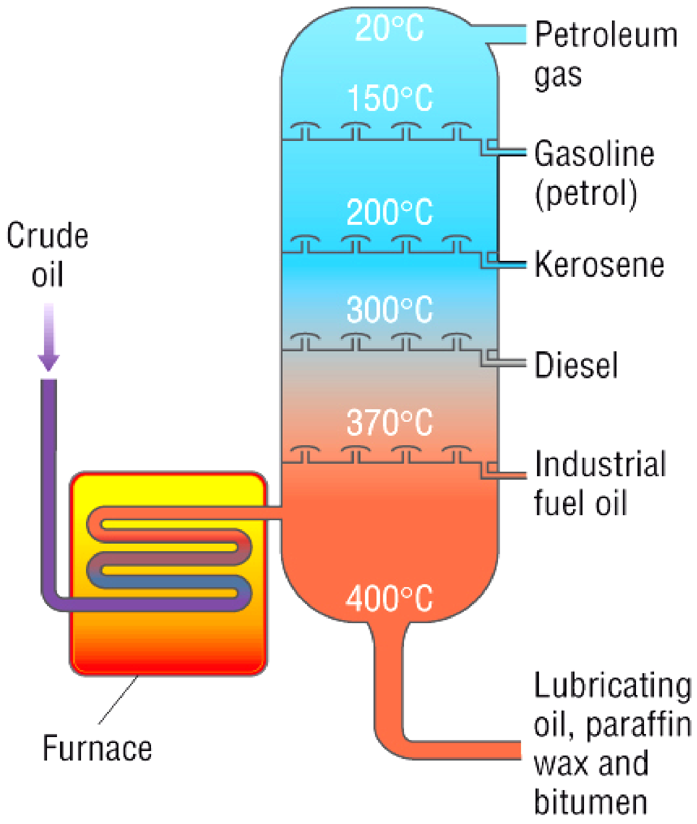
- This is because there are **less points of contact / smaller surface area** between the molecules.
- This means the **Van der Waals** forces of attraction become **weaker** so **less energy** is required to overcome **attraction**.

Fractional distillation of crude oil

Crude oil is a mixture of hydrocarbons and is our main source of fuels and petrochemicals

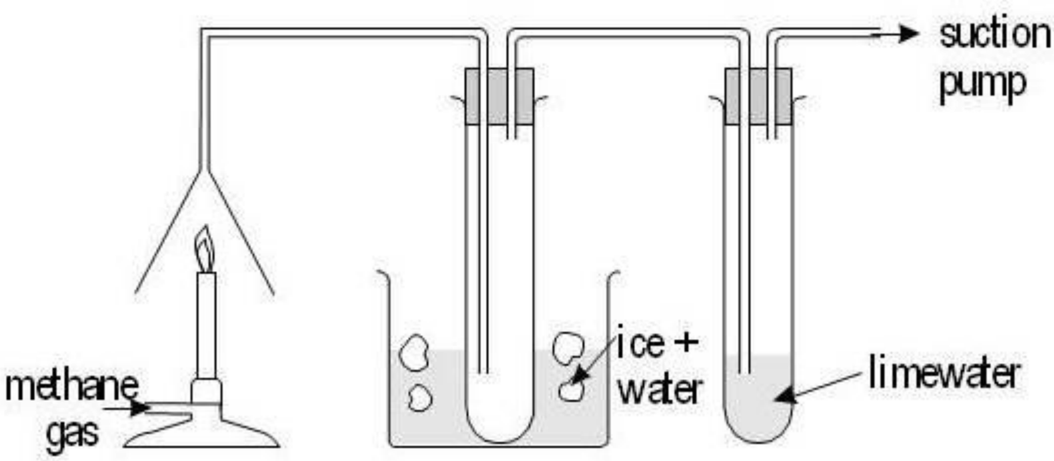
Fractional Distillation is the continual evaporation and condensation of a mixture causing components to separate due to a difference in their boiling points.

Fraction is a group of compounds that have similar boiling points and are removed at the same level in of a fractionating column

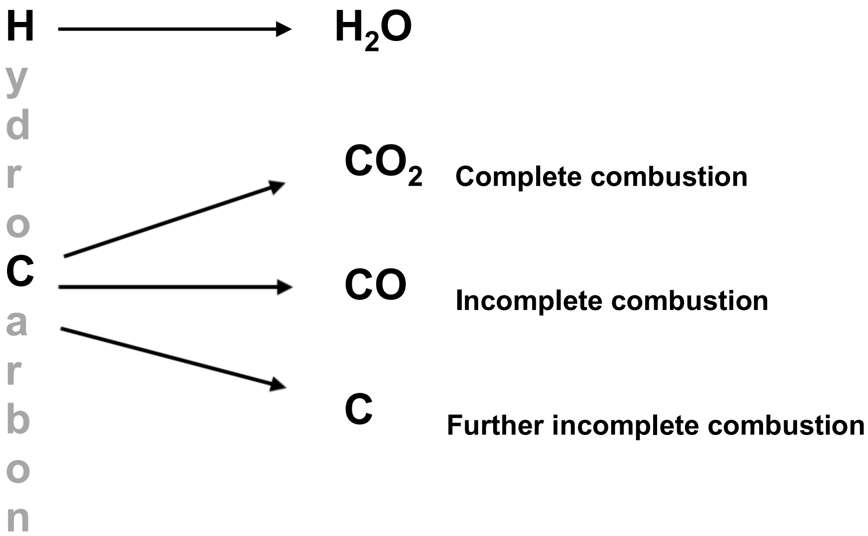


- Crude oil vapour is introduced near the bottom of the column.
- The vapour rises causing a temperature gradient.
- The temperature at the bottom is high and the top is low.
- Fractions with low boiling points (low numbers of carbons) rise to the top of the column and condense.
- Fractions with high boiling points (high numbers of carbons) condense in the lower chambers
- The largest hydrocarbons will not vaporise and are tapped off at the bottom of the column.
- Each fraction contains a mixture of hydrocarbons with similar boiling points and similar numbers of carbon atoms in the molecules.

Combustion of Alkanes



- The yellow colour of the flame is due to incomplete combustion.
- The yellow colour is due to particles of carbon glowing in the heat.
- More oxygen (air) increases oxidation of the carbon.
- The products of complete combustion are water and carbon dioxide.
- The **C** in the hydrocarbon reacts with oxygen in the air forming **CO_2**
- The **H** in the hydrocarbon reacts with oxygen in the air forming **H_2O**



Complete combustion – plentiful supply of oxygen

$CH_{4(g)} \quad + \quad 2O_{2(g)} \quad \rightarrow \quad CO_{2(g)} \quad + \quad 2H_2O_{(g)}$

Incomplete combustion – limited supply of oxygen

$CH_{4(g)} \quad + \quad 1\,^1/_2O_{2(g)} \quad \rightarrow \quad CO_{(g)} \quad + \quad 2H_2O_{(g)}$

- Carbon monoxide is a poisonous gas. It has no colour or odour so is not noticed.
- Deaths occur from faulty gas fires or boilers in poor ventilated rooms.
- Landlords are now required to have gas appliances serviced annually.

Further Incomplete combustion – further limited supply of oxygen

$CH_{4(g)} \quad + \quad O_{2(g)} \quad \rightarrow \quad C_{(s)} \quad + \quad 2H_2O_{(g)}$

Examples:

Complete combustion producing carbon dioxide and water

1. ethane

2. octane

Incomplete combustion producing carbon monoxide and water

3. ethane

4. octane

Further incomplete combustion producing **solid** carbon and water

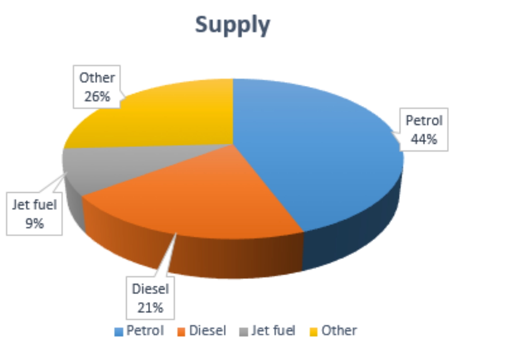
5. ethane

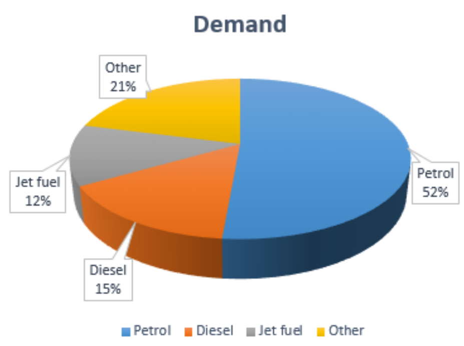
6. octane

Combustion and the internal combustion engine:

- Most of a barrel of crude oil is used as a fuel in engines.
- The issue is that the demand for petrol, diesel and jet fuel does not match the natural abundancies in a barrel of crude oil:

Supply and demand abundance per barrel of oil:





Cracking:

- Where long less useful alkanes are broken into shorter more useful molecules by breaking C-C bonds.

1) **Thermal Cracking:**
    - 1000K 70 atm approximately 1s
    - If these conditions occur for too long, decomposition to C and H may occur
    - Produces alkanes and alkenes
    - Any C-C bond can break which gives a mixture of alkanes and
    - **High % of alkenes made**

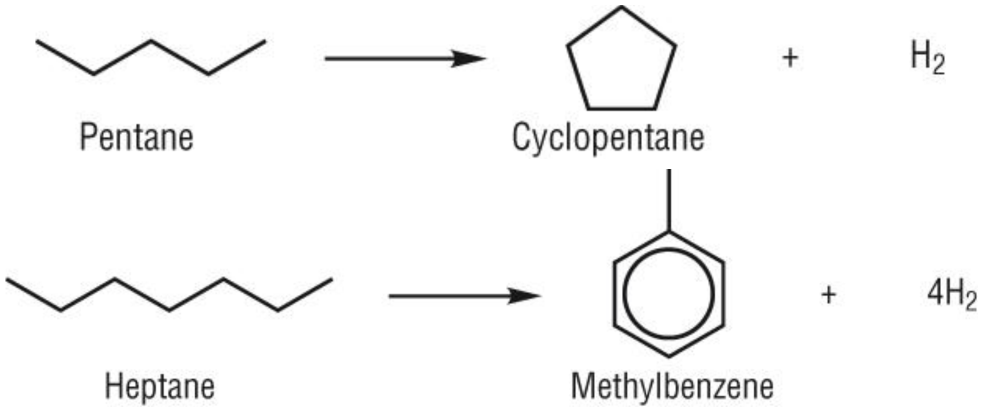
$$C_{12}H_{26} \rightarrow C_{10}H_{22} + C_2H_4$$

$$C_{12}H_{26} \rightarrow C_8H_{18} + C_4H_8$$

$$C_{12}H_{26} \rightarrow C_8H_{18} + 2C_2H_4$$

2) **Catalytic cracking:**

- 800K   2atm   approximately 4s   zeolite catalyst
- Zeolite catalyst consists of Al_2O_3 and SiO_2
- Produces branched, cyclic alkanes and aromatic compounds which are **good fuels in the motor industry**.



Examples:

- Show how these molecules can undergo thermal cracking and break up in different ways:

  $C_{14}H_{30} \rightarrow$

  $C_{14}H_{30} \rightarrow$

- Show how these molecules can undergo catalytic cracking producing molecules that would be good as fuels:

  $C_6H_{14} \rightarrow$

  $C_6H_{14} \rightarrow$

Pollution from combustion:

1) **Nitrogen Oxides, NO_x**

- Under the high temperatures and pressures in a car engine, the triple bond in nitrogen, N_2 can break.
- This will react with oxygen producing several oxides of nitrogen, NO_x

Nitrogen	+	Oxygen	→	Nitrogen (II) oxide
$N_{2(g)}$	+	$O_{2(g)}$	→	$NO_{(g)}$

Nitrogen	+	Oxygen	→	Nitrogen (IV) oxide
$N_{2(g)}$	+	$O_{2(g)}$	→	$NO_{2(g)}$

2) **Sulphur dioxide, SO_2**

- Sulphur compounds can also be present in fuels as impurities.
- These also react with oxygen forming sulphur dioxide, SO_2

Sulphur compound	+	Oxygen	→	Sulphur dioxide

3) **Unburnt hydrocarbons**

- Some of the fuel can pass through the combustion engine without being combusted.
- These can go straight through the system and out through the exhaust.

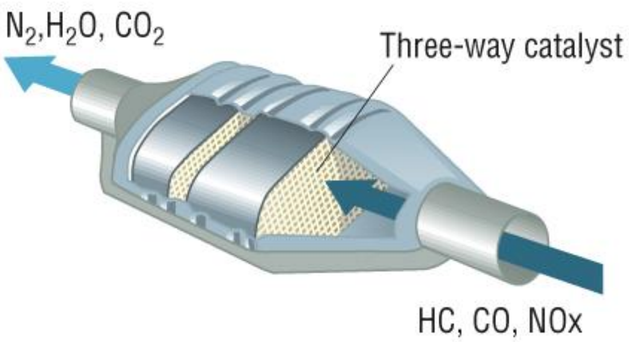
The effects from pollution:

Carbon	**- May cause breathing problems**
Carbon monoxide	**- toxic gas**
Carbon dioxide	**- global warming**
Nitrogen oxides	**- acid rain**
Sulphur dioxide	**- acid rain**
Hydrocarbons	**- photochemical smog**

Dealing with pollution:

1) **The catalytic converter:**

- These are made from **Pt Rh Pd** metals in a honeycombed structure to increase surface area forming the catalyst.



Removal of NO and CO:

$2NO_{(g)} + 2CO_{(g)} \rightarrow N_{2(g)} + 2CO_{2(g)}$

$2NO_{(g)} \rightarrow N_{2(g)} + O_{2(g)}$

Removal of unburnt hydrocarbons:

Hydrocarbon + Nitrogen monoxide → nitrogen + Carbon dioxide + Water

$C_8H_{18(g)} + 25NO_{(g)} \rightarrow 12\frac{1}{2}\ N_{2(g)} + 8CO_{2(g)} + 9H_2O_{(g)}$

Hydrocarbon + Oxygen → Carbon dioxide + Water

$C_8H_{18(g)} + 12\frac{1}{2}\ O_{2(g)} \rightarrow 8CO_{2(g)} + 9H_2O_{(g)}$

2) **Flue gas desulphurisation:**

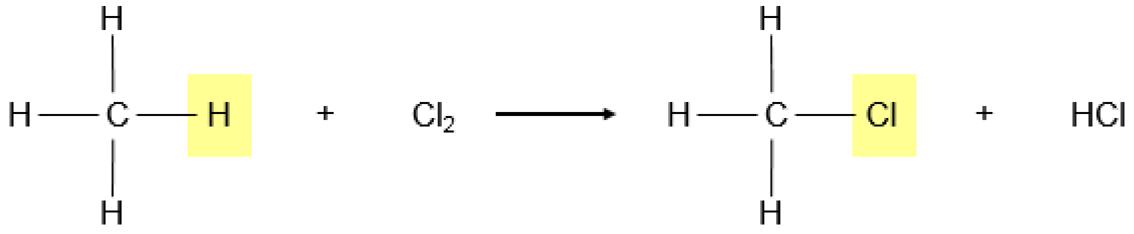
- SO_2 can be removed using either CaO or $CaCO_3$
- A spray of water and CaO or $CaCO_3$ reacts with the SO_2:

$CaO_{(aq)} + SO_{2(g)} \rightarrow CaSO_{3(s)}$

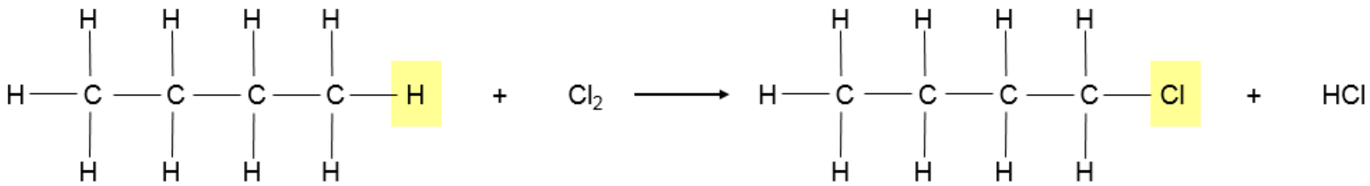
$CaCO_{3(aq)} + SO_{2(g)} \rightarrow CaSO_{3(s)} + CO_{2(g)}$

Halogenation of alkanes - Substitution reactions

- Alkanes are unreactive due to the **lack of polarity**.
- In the presence of **ultraviolet light a halogen** will substitute a hydrogen in an alkane, a halogenoalkane and hydrogen halide is produced:



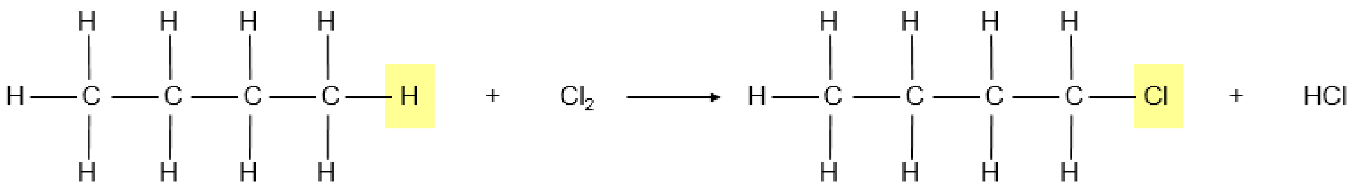
- For the reaction with butane:



- Reactions that occur in light are called photochemical reactions.
- These are all **substitution** reactions

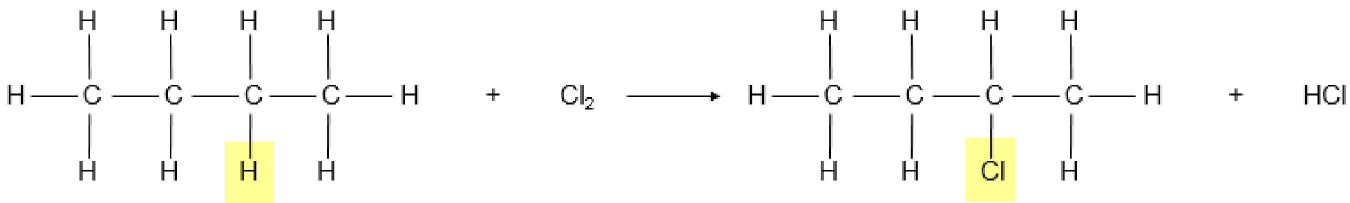
Formation of position isomers:

- Alkanes with 3 or more carbons can form **position isomers**:



Hydrogen on Carbon 1 substituted

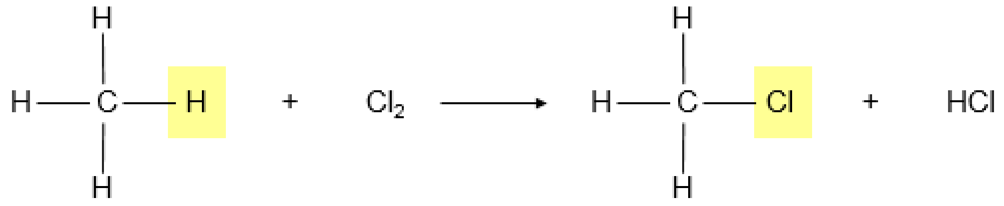
1 - bromo – butane formed



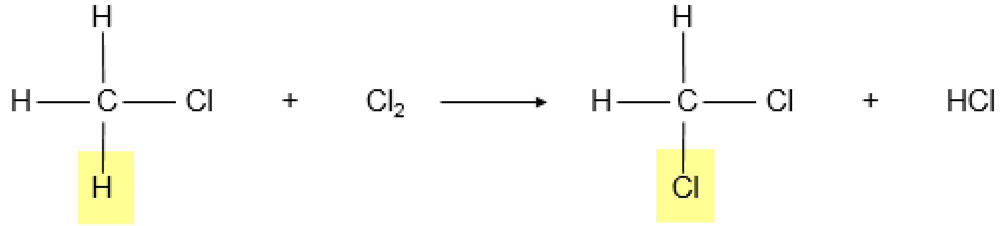
Hydrogen on Carbon 2 substituted

2 - bromo – butane formed

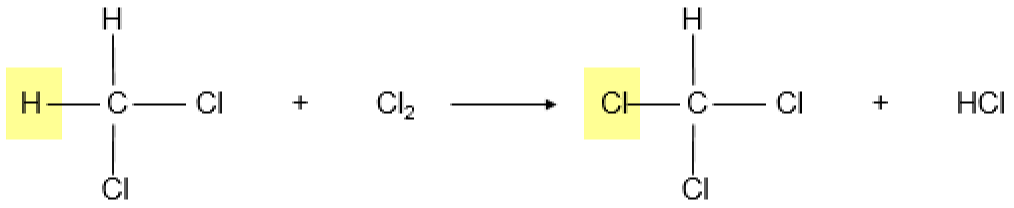
Further substitution reactions:



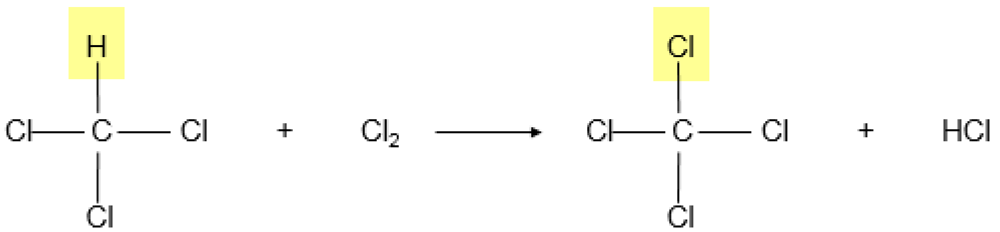
This has H's that can also be substituted



This still has H's that can also be substituted

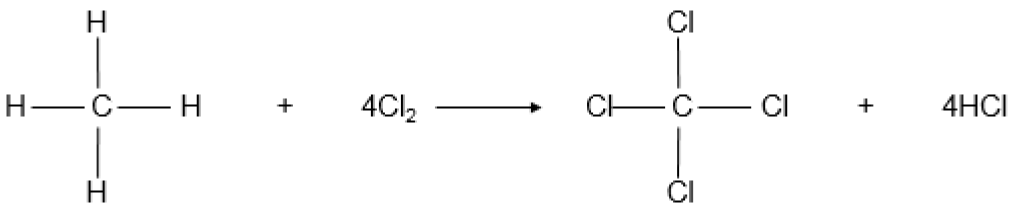


This still has H's that can also be substituted



No further substitution can occur

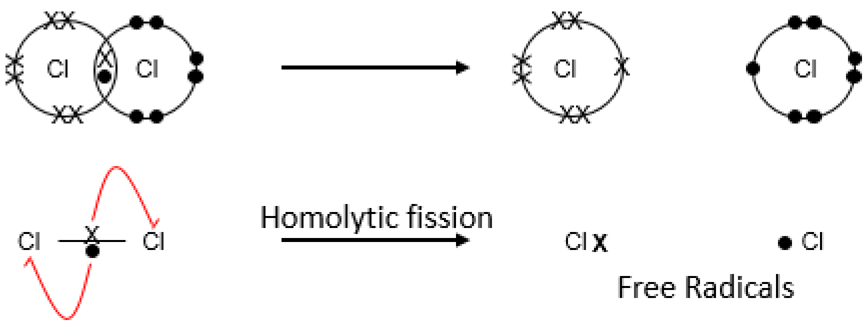
Overall



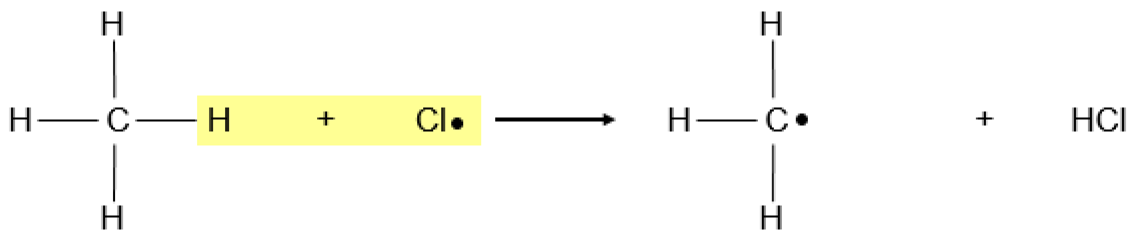
Free radical substitution mechanism for the chlorination of methane

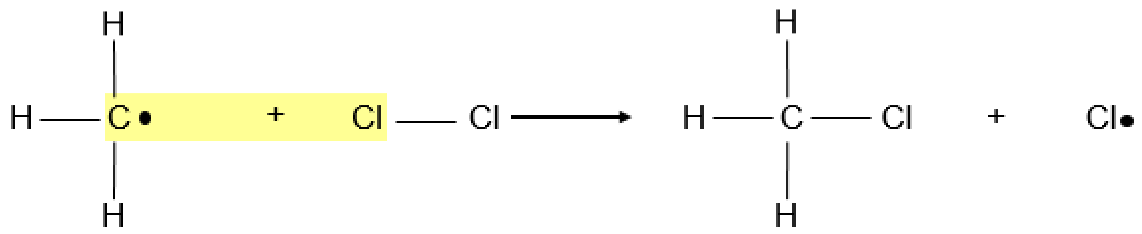
Initiation – Free radicals are made

$$Cl_2 \xrightarrow[\text{Light}]{\text{Uv}} 2Cl\bullet$$



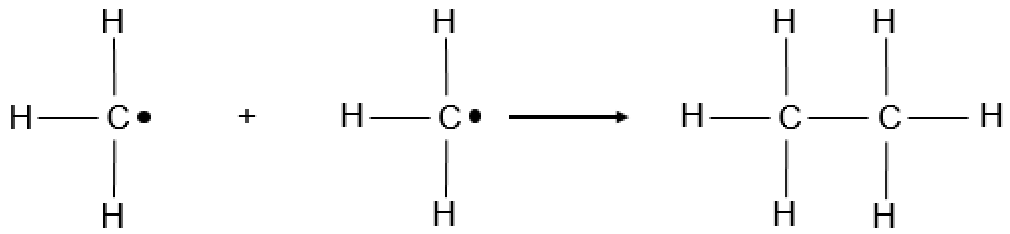
Propagation – Free radicals are used up and made

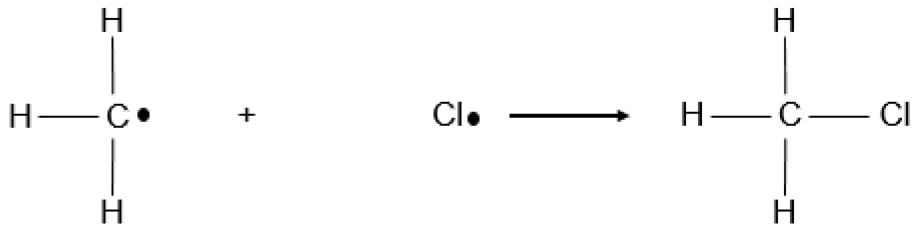




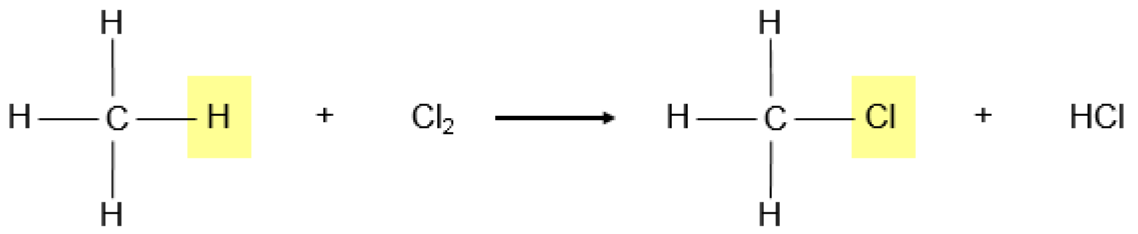
Termination – Free radicals are used up

$$Cl\bullet + Cl\bullet \longrightarrow Cl—Cl$$





Overall



Summary:

Initiation:

$$Cl_2 \xrightarrow[\text{Light}]{\text{Uv}} 2Cl\bullet$$

Propagation:

$$CH_4 + Cl\bullet \longrightarrow \bullet CH_3 + HCl$$

$$\bullet CH_3 + Cl_2 \longrightarrow CH_3Cl + Cl\bullet$$

Termination:

$$2Cl\bullet \longrightarrow Cl_2$$

$$2\bullet CH_3 \longrightarrow CH_3CH_3$$

$$\bullet CH_3 + Cl\bullet \longrightarrow CH_3Cl$$

Overall:

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$

Example: Have a go for the reaction between bromine and butane:

Initiation:

Propagation:

Termination:

Overall:

Example: Have a go for the reaction between Iodine and cyclohexane:

Initiation:

Propagation:

Termination:

Overall: