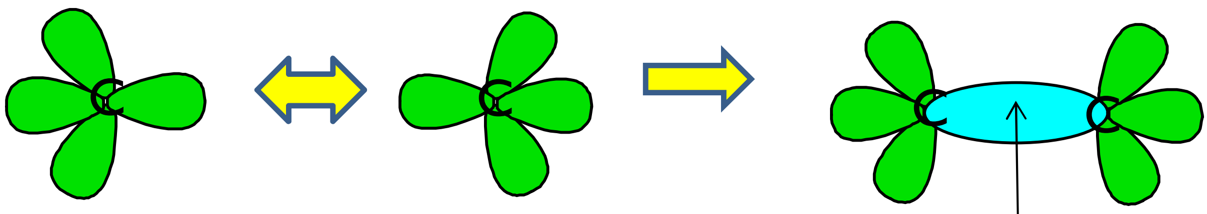
4.1.2 Alkanes

Alkanes and cycloalkanes are saturated hydrocarbons

Formation of σ bond in alkanes

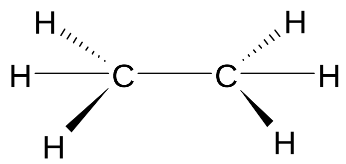


In alkanes one sp^3 orbital from each carbon overlap to form a single C-C bond called a sigma **σ** bond

Rotation can occur around a sigma bond

Remember that the shape around the carbon atom in saturated hydrocarbons is tetrahedral and the bond angle is 109.5^{O}

The shape is tetrahedral as a result of the four bond pairs of electrons equally repelling.



Boiling Point

The increasing boiling points of the alkane homologous series can be explained by the increasing number of electrons in the bigger molecules causing an increase in the size of the induced dipole–dipole interactions (London forces) between molecules.

The shape of the molecule can also have an effect on the size of the induced dipole–dipole interactions (London forces) . Long chain alkanes have a larger surface area of contact between molecules for London force to form than compared to spherical shaped branched alkanes and so have stronger induced dipole–dipole interactions and higher boiling points.

Reactivity
The low reactivity of alkanes with many reagents can be explained by the high bond enthalpies of the C-C and C-H bonds and the very low polarity of the σ-bonds present.

Hydrocarbons 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 $O_2(g)$ → $8CO_2(g)$ + 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)

$CH_4(g)$ + $^3/_2$ $O_2(g)$ → CO(g) + 2 $H_2O(l)$

$CH_4(g)$ + $O_2(g)$ → C(s) + 2 $H_2O(l)$

Incomplete combustion produces less energy per mole than complete combustion

Carbon (soot) 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.

Cracking

Cracking: conversion of large hydrocarbons to smaller molecules of 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 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.

Catalytic Cracking

Conditions:
Low pressure
High Temperature (450°C)
Zeolite Catalyst

Turns straight chain alkanes into 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

Substitution reactions of alkanes

Synthesis of chloroalkanes

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

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**

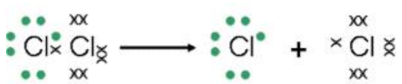
STEP ONE Initiation

Essential condition: UV light

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

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 •

DEFINITION

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

STEP TWO Propagation

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

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

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

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

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

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

$\mathbf{Br_2 \rightarrow 2Br^{\cdot}}$

Br_2 splits in the same way as Cl_2

STEP TWO Propagation

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

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

STEP THREE Termination

$\mathbf{CH_3CH_2CH_2^{\cdot} + Br^{\cdot} \rightarrow CH_3CH_2CH_2Br}$

$\mathbf{CH_3CH_2CH_2^{\cdot} + CH_3CH_2CH_2^{\cdot} \rightarrow CH_3CH_2CH_2CH_2CH_2CH_3}$

Further substitution

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

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

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

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

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 $CH_4 + Cl_2$

$$\mathbf{CH_4 + 4\ Cl_2 \rightarrow CCl_4 + 4\ HCl}$$

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

$$\mathbf{CH_3F + 3\ Cl_2 \rightarrow CFCl_3 + 3\ HCl}$$

Note HCl is always the side product – never H_2