ALKANES

General

- members of a homologous series with general formula $\mathbf{C_nH_{2n+2}}$ - *non-cyclic only*
- **saturated hydrocarbons** - *all carbon-carbon bonding is single*
- bonds are **spaced tetrahedrally** about carbon atoms.

Isomerism The first example of structural isomerism occurs with C_4H_{10}. Two structural isomers exist

butane *2-methylpropane*

Structural isomers have different physical properties *e.g. boiling and melting pt*

Q.1 *Draw out and name the structural isomers of C_5H_{12} and C_6H_{14}.*

Physical properties of alkanes

Boiling point

- boiling point of alkanes increases as they get more carbon atoms in their formula
- the more atoms there are the greater the Van der Waals' forces holding them together
- the greater the intermolecular force, the more energy needed to separate the molecules
- the more energy required, the higher the boiling point

$\mathbf{CH_4}$ (-161°C) $\mathbf{C_2H_6}$ (-88°C) $\mathbf{C_3H_8}$ (-42°C) $\mathbf{C_4H_{10}}$ (-0.5°C)

difference gets less because mass is increasing by a smaller percentage each time

- straight chains have a larger surface area giving greater interaction between molecules
- branching makes molecules more compact and lowers the attraction between them
- the lower the intermolecular forces, the lower the boiling point

"The greater the branching, the lower the boiling point "

b.p. - 0.5°C b.p. ______ °C

Q.2 *Arrange the isomers of C_5H_{12} in ascending boiling point order .*

Melting point A general increase with molecular mass - not as regular as that for boiling point.

Solubility Are **non-polar** so are **immiscible with water** but soluble in most organic solvents.

CHEMICAL PROPERTIES OF ALKANES

Introduction
- **fairly unreactive** - *their old family name, paraffin, means little reactivity*
- consist of relatively strong, almost **non-polar** covalent bonds
- have no real sites that will encourage substances to attack them

Combustion
- alkanes make useful fuels - *especially the lower members of the series*
- combine with oxygen in an **exothermic reaction**

complete combustion $CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(l)}$

incomplete combustion $CH_{4(g)} + 1\frac{1}{2}O_{2(g)} \longrightarrow CO_{(g)} + 2H_2O_{(l)}$

- the **greater the number of carbon atoms, the more energy produced** but...
- the greater the amount of oxygen needed for complete combustion.

Handy tip *When balancing equations involving complete combustion, remember that for every carbon in the original hydrocarbon you get a carbon dioxide and for every two hydrogens you get a water. Put these numbers into the equation, count up the oxygen and hydrogen atoms on the RHS of the equation then balance the oxygen molecules on the LHS.*

Q.3
- *Write out the equation for the complete combustion of*

butane

hexane

decane

- *List uses of* *methane* ....
propane ....
butane ....

Pollution Processes involving combustion give rise to a variety of pollutants ...

power stations	**SO_2** emissions produce acid rain
internal combustion engines	**CO**, **NO_x** and **unburnt hydrocarbons**

Q.4 *What does the formula NO_x stand for ?*

Q.5 *Why are the following classed as pollutants ?*

- *CO*
- *NO_x*
- *unburnt hydrocarbons*

Removal

SO_2	react effluent gases with a suitable basic compound (e.g. CaO)
CO and NO_x	pass exhaust gases through a catalytic converter

Catalytic converters

In the catalytic converter ...
CO is converted to CO_2
NO_x are converted to N_2
Unburnt hydrocarbons to CO_2 and H_2O

e.g. $$2NO + 2CO \longrightarrow N_2 + 2CO_2$$

- catalysts are made of finely divided rare metals
- leaded petrol must not pass through the catalyst as the lead deposits on the catalyst's surface and "poisons" it, thus blocking sites for reactions to take place.

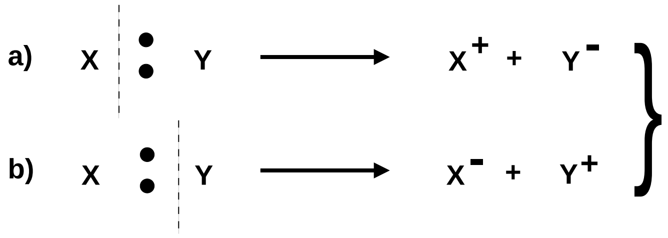
Q.6

- *Which metals are used in catalytic converters ?*
- *Why is the catalyst used in a finely divided form ?*

Breaking covalent bonds

There are three different ways to split the shared pair of electrons in an unsymmetrical covalent bond.

UNEQUAL SPLITTING



produce **IONS**

known as **HETEROLYSIS** *or* **HETEROLYTIC FISSION**

EQUAL SPLITTING

produces **RADICALS**

known as **HOMOLYSIS** *or* **HOMOLYTIC FISSION**

If several bonds are present the **weakest bond is usually broken first**.

- energy to break bonds can come from a variety of sources such as heat and light
- In the reaction between methane and chlorine either can be used but in the laboratory a source of UV light (or sunlight) is favoured.

Q.7 *Look up the strengths of the following bonds (in kJ mol $^{-1}$)*

C-C 348 .... *C-H* 412 .... *Cl-Cl* 242 ....

Which of the bonds is most likely to break first ? Cl-Cl ....

Free Radicals

- reactive species (atoms or groups) possessing an **unpaired electron**
- formed by homolytic fission (homolysis) of covalent bonds
- formed during the reaction between chlorine and methane
- formed during thermal cracking

Chlorination of methane

Reagents chlorine and methane

Conditions UV light or sunlight - *heat could be used as an alternative energy source*

Equation(s)

$CH_{4(g)} + Cl_{2(g)} \longrightarrow HCl_{(g)} + CH_3Cl_{(g)}$ *chloromethane*

$CH_3Cl_{(g)} + Cl_{2(g)} \longrightarrow HCl_{(g)} + CH_2Cl_{2(l)}$ *dichloromethane*

$CH_2Cl_{2(l)} + Cl_{2(g)} \longrightarrow HCl_{(g)} + CHCl_{3(l)}$ *trichloromethane*

$CHCl_{3(l)} + Cl_{2(g)} \longrightarrow HCl_{(g)} + CCl_{4(l)}$ *tetrachloromethane*

Mixture

- free radicals are very reactive as they are trying to pair up their unpaired electron
- if there is sufficient chlorine, every hydrogen will eventually be replaced.

Mechanism Mechanisms portray what chemists think is actually going on in the reaction, whereas an equation tells you the ratio of products and reactants. The chlorination of methane proceeds via a mechanism known as **FREE RADICAL SUBSTITUTION**. It gets its name because the methane is attacked by free radicals resulting in a hydrogen atom being substituted by a chlorine atom.

The process is an example of a **chain reaction**. Notice how, in the propagation step, one chlorine radical is produced for every one used up.

Steps

Initiation $Cl_2 \longrightarrow 2Cl\bullet$ *radicals created*

Propagation
$Cl\bullet + CH_4 \longrightarrow CH_3\bullet + HCl$
$Cl_2 + CH_3\bullet \longrightarrow CH_3Cl + Cl\bullet$
radicals used and then re-generated

Termination
$Cl\bullet + Cl\bullet \longrightarrow Cl_2$
$Cl\bullet + CH_3\bullet \longrightarrow CH_3Cl$
$CH_3\bullet + CH_3\bullet \longrightarrow C_2H_6$
radicals removed

Q.8 *Write out the two* ***propagation*** *steps involved in the conversion of CH_3Cl into CH_2Cl_2.*

Four chlorinated compounds can be produced from chlorine. How many different chlorinated compounds can be made from...

(i) ethane *(ii) propane*

CRACKING

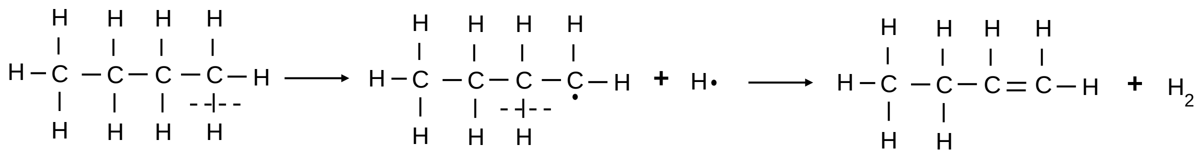
Process
- involves the breaking of C-C (and C-H) bonds in alkanes
- converts heavy fractions into smaller, higher value products such as alkenes

- two types THERMAL **Free radical** mechanism
  CATALYTIC **Carbocation** (carbonium ion) mechanism

THERMAL
- HIGH PRESSURE ... 7000 kPa
- HIGH TEMPERATURE ... 400°C to 900°C
- FREE RADICAL MECHANISM
- HOMOLYTIC FISSION
- PRODUCES MOSTLY ALKENES ... *e.g. ETHENE for making polymers and ethanol*
- PRODUCES HYDROGEN ... *used in the Haber Process and in margarine manufacture*

Examples *Bonds can be broken anywhere in the molecule by C-C bond fission or C-H bond fission*

C-H fission

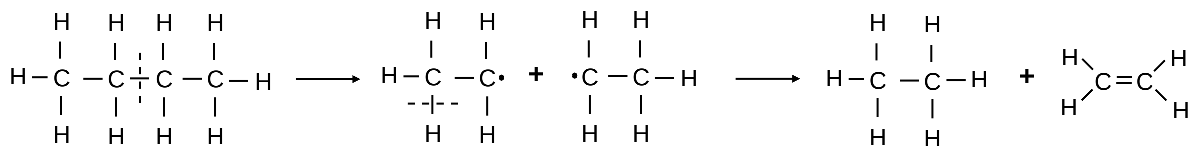


A C-H bond breaks to give a hydrogen radical and a butyl radical.

The hydrogen radical abstracts another hydrogen leaving two unpaired electrons on adjacent carbon atoms. These join together to form a second bond between the atoms.

an alkene and hydrogen are formed

C-C fission



C-C bond breaks to give two ethyl radicals.

One ethyl radical abstracts a hydrogen from the other, thus forming ethane. The unpaired electrons on adjacent carbons join together to form a second bond.

an alkene and an alkane are formed

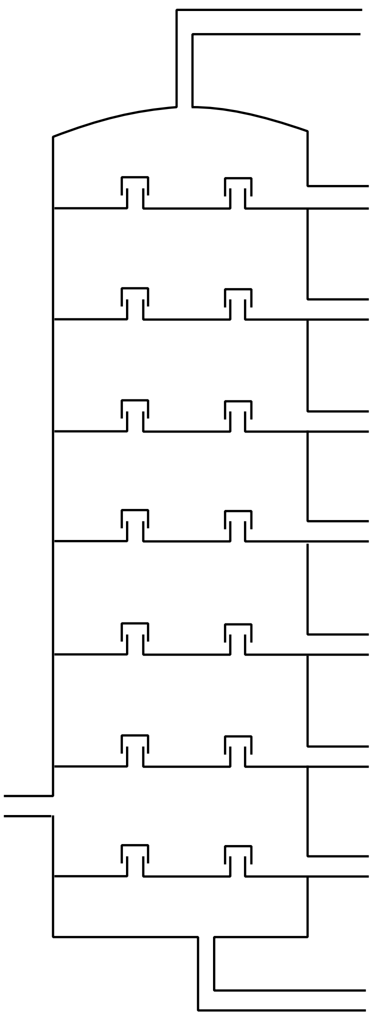
CATALYTIC
- SLIGHT PRESSURE
- HIGH TEMPERATURE ... 450°C
- ZEOLITE CATALYST
- CARBOCATION (carbonium ion) MECHANISM
- HETEROLYTIC FISSION
- PRODUCES BRANCHED or CYCLIC ALKANES & AROMATIC HYDROCARBONS
- MOTOR FUELS ARE A PRODUCT

Zeolites Crystalline aluminosilicates; clay like substances

The Petrochemical Industry

Crude Oil In the past, most important organic chemicals were derived from coal. Nowadays, natural gas and crude petroleum provide an alternative source.

- the composition of crude petroleum varies according to its source
- it is a dark coloured, viscous liquid
- consists mostly of alkanes with up to 40 carbon atoms, plus water, sulphur and sand
- can be split up into fractions by fractional distillation
- distillation separates the compounds according to their boiling point
- at each level a mixture of compounds in a similar boiling range is taken off
- rough fractions can then be distilled further to obtain narrower boiling ranges
- some fractions are more important - *usually the lower boiling point ones*
- high boiling fractions may be broken down into useful lower boiling ones - **CRACKING**



Approximate boiling range / °C	*C's per molecule*	*Name of fraction*	*Use(s)*
< 25	1 - 4	LPG (Liquefied Petroleum Gas)	Calor Gas Gamping Gas
40-100	6 - 12	GASOLINE	Petrol
100-150	7 - 14	NAPHTHA	Petrochemicals
150-200	11 - 15	KEROSINE	Aviation Fuel
220-350	15 - 19	GAS OIL	Central Heating Fuel
> 350	20 - 30	LUBRICATING OIL	Lubrication Oil
> 400	30 - 40	FUEL OIL	Power Station Fuel Ship Fuel
> 400	40 - 50	WAX, GREASE	Candles Grease for bearings
> 400	> 50	BITUMEN	Road surfaces Roofing

Q.9 *Not all fractions are of equal importance. Why is this? What is done to get a greater amount of the more useful products?*