## **ALKANES**

### General

- a homologous series with general formula  $C_nH_{2n+2}$  non-cyclic only
- saturated hydrocarbons all carbon-carbon bonding is single
- aliphatic C atoms are in straight chains, branches or non-aromatic rings
- C-C and C-H bonds are called sigma (σ) bonds; formed by overlap of orbitals
- σ bonds can rotate freely
- bonds are spaced tetrahedrally about carbon atoms.

- **Isomerism** the first example of structural isomerism occurs with C<sub>4</sub>H<sub>10</sub>
  - two structural isomers exist

$$\begin{array}{ccc} & & & \text{CH}_3 \\ \text{CH}_3 - \text{CH}_2 - \text{CH}_3 & & \text{CH}_3 - \text{CH} - \text{CH}_3 \\ \\ \textit{butane} & & \textit{2-methylpropane} \end{array}$$

Draw out and name the structural isomers of  $C_5H_{12}$  and  $C_6H_{14}$ .

# Physical properties of alkanes

- Boiling point increases as they get more carbon atoms in their formula
  - the more atoms there are the greater the induced dipole-dipole interactions
  - greater intermolecular force = more energy needed to separate the molecules
  - the more energy required, the higher the boiling point

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

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

- straight chains have larger surface areas giving greater molecular interaction
- branched molecules are more compact and have less intermolecular attraction
- the lower the intermolecular forces, the lower the boiling point

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

$$CH_3$$
 $CH_3$ 
 $CH_3$ 

Arrange the isomers of  $C_5H_{12}$  in ascending boiling point order.

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

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### 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, every carbon in the original hydrocarbon gives a carbon dioxide and every two hydrogens give a water molecule. Put these numbers into the equation, count up the O and H atoms on the RHS of the equation then balance the oxygen molecules on the LHS.

<i>Q.3</i>	• Write out the equation for the complete combustion of		
	butane		
	hexane		
	decane		
	• List uses of	methane propane butane	

0.4

- Discuss the dangers of being over reliant on fossil fuels for providing energy.
- What alternative fuels are available?
- List any problems associated with an increase of  $CO_2$  in the atmosphere.

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**Pollution** 

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

power stations

**SO<sub>2</sub>** emissions produce acid rain

internal combustion engines

CO, NO<sub>x</sub> and unburnt hydrocarbons

Q.5

What does the formula  $NO_x$  stand for ?

0.6

Why are the following classed as pollutants?

• CO

•  $NO_x$ 

• unburnt hydrocarbons

AQA

Removal

SO<sub>2</sub>

react effluent gases with a suitable basic compound (e.g. CaO)

CO and NO<sub>x</sub>

pass exhaust gases through a catalytic converter

Catalytic

converters

In the catalytic converter ... CO is converted to CO<sub>2</sub>

NO<sub>x</sub> are converted to N<sub>2</sub>

Unburnt hydrocarbons to CO<sub>2</sub> and H<sub>2</sub>O

e.g. **2NO** + 2CO

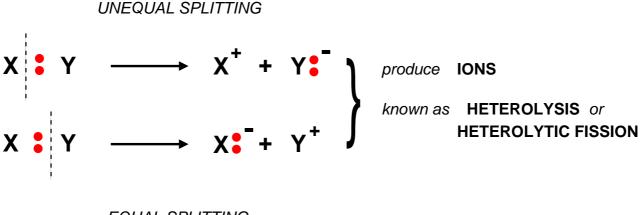
- catalysts are made of finely divided rare metals
- leaded petrol must not pass through the catalyst as the lead deposits on the catalyst's surface and "poisons" it, thus blocking sites for reactions to take place.

*Q*.7

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

## **Breaking covalent bonds**

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



**EQUAL SPLITTING** 



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.

### 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  $CH_3Cl(g) + Cl_2(g)$   $\longrightarrow$   $HCl(g) + CH_2Cl_2(g)$  dichloromethane  $CH_2Cl_2(g) + Cl_2(g)$   $\longrightarrow$   $HCl(g) + CHCl_3(g)$  trichloromethane  $CHCl_3(g) + Cl_2(g)$   $\longrightarrow$   $HCl(g) + CCl_4(g)$  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. 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 
$$Cl_2$$
 —>  $2Cl^{\bullet}$  radicals created

Propagation  $Cl^{\bullet} + CH_4$  —>  $CH_3^{\bullet} + HCl$  radicals used and  $Cl_2 + CH_3^{\bullet}$  —>  $CH_3Cl + Cl^{\bullet}$  then re-generated

Termination  $Cl^{\bullet} + Cl^{\bullet}$  —>  $Cl_2$  radicals removed  $Cl^{\bullet} + CH_3^{\bullet}$  —>  $CH_3Cl$   $CH_3^{\bullet} + CH_3^{\bullet}$  —>  $C_2H_6$ 

0.9 Write out the two **propagation** steps involved in the conversion of CH<sub>3</sub>Cl into CH<sub>2</sub>Cl<sub>2</sub>.

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

(i) ethane (ii) propane

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### 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

THERMAL Free radical mechanism two types

> **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 / ethanol
  - PRODUCES HYDROGEN used in the Haber Process / margarine manufacture

## AQA

### Examples

Bonds can be broken anywhere 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.

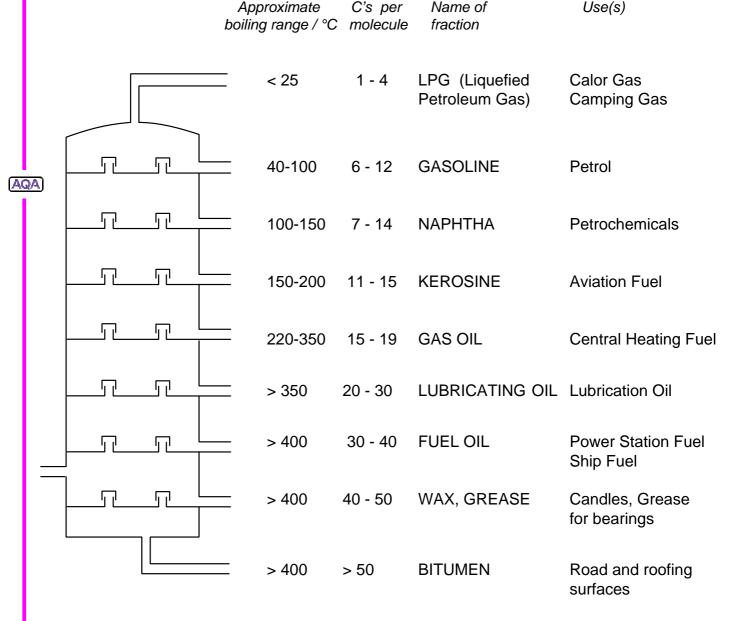
an alkene and an alkane are formed

- **CATALYTIC SLIGHT PRESSURE** 
  - HIGH TEMPERATURE ... 450°C
  - ZEOLITE (Crystalline aluminosilicates; clay like substances) CATALYST
  - CARBOCATION (carbonium ion) MECHANISM
  - HETEROLYTIC FISSION
  - MAKES BRANCHED / CYCLIC ALKANES & AROMATIC HYDROCARBONS
  - MOTOR FUELS ARE A PRODUCT

## 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 +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 ones CRACKING



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**Q.10** Not all fractions are of equal importance. Why is this? What is done to get a greater amount of the more useful products?