

# CHAPTER 15: Hydrocarbons

## 15.1 Introduction to Alkanes

## 15.2 Reactions of Alkanes

## 15.3 Introduction to Alkenes

## 15.4 Reactions of Alkenes

## 15.5 Uses of Hydrocarbons

### Learning outcomes:

- (a) *show awareness of the general unreactivity of alkanes, including towards polar reagents.*
- (b) *describe the chemistry of alkanes as exemplified by the following reactions of ethane:*
  - (i) *combustion.*
  - (ii) *substitution by chlorine and by bromine.*
- (c) *describe the mechanism of free-radical substitution at methyl groups with particular reference to the initiation, propagation and termination reactions.*
- (d) *describe the chemistry of alkenes as exemplified, where relevant, by the following reactions of ethene and propene (including the Markovnikov addition of asymmetric electrophiles to propene):*
  - (i) *addition of hydrogen, steam, hydrogen halides and halogens.*
  - (ii) *oxidation by cold, dilute, acidified manganate(VII) ions to form the diol.*
  - (iii) *oxidation by hot, concentrated, acidified manganate(VII) ions leading to the rupture of the carbon-to-carbon double bond in order to determine the position of alkene linkages in larger molecules.*
  - (iv) *polymerisation.*
- (e) *describe the mechanism of electrophilic addition in alkenes, using bromine/ethene and hydrogen bromide/propene as examples.*
- (f) *explain the use of crude oil as a source of both aliphatic and aromatic hydrocarbons.*
- (g) *suggest how 'cracking' can be used to obtain more useful alkanes and alkenes of lower Mr from larger hydrocarbon molecules.*
- (h) *describe and explain how the combustion reactions of alkanes led to their use as fuels in industry, in the home and in transport.*
- (i) *recognise the environmental consequences of:*
  - (i) *carbon monoxide, oxides of nitrogen and unburnt hydrocarbons arising from the internal combustion engine and of their catalytic removal.*
  - (ii) *gases that contribute to the enhanced greenhouse effect.*

## 15.1 Introduction to Alkanes

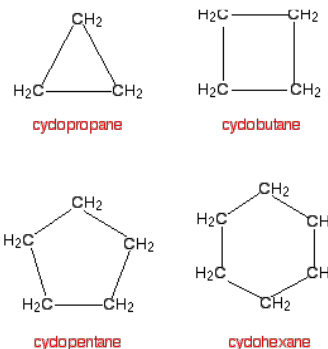
### What is an alkane?

- 1) A *hydrocarbon* is a compound containing carbon and hydrogen atoms only. Examples of hydrocarbons are alkanes, alkenes, alkynes and arenes.
- 2) Alkanes are **saturated hydrocarbons**, the carbon atoms are joined to each other via single covalent bond only. They form the homologous series with a general formula  $C_nH_{2n+2}$ .

Name	Molecular formula	Structural formula	State	m.p. / °C	b.p. / °C	density / g cm <sup>-3</sup>
methane	CH <sub>4</sub>	CH <sub>4</sub>	gas	-182	-164	0.424
ethane	C <sub>2</sub> H <sub>6</sub>	CH <sub>3</sub> CH <sub>3</sub>	gas	-183	-88	0.546
propane	C <sub>3</sub> H <sub>8</sub>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	gas	-190	-42	0.582
butane	C <sub>4</sub> H <sub>10</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub>	gas	-138	-0.5	0.579
pentane	C <sub>5</sub> H <sub>12</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	liquid	-130	36	0.626
hexane	C <sub>6</sub> H <sub>14</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH <sub>3</sub>	liquid	-95	69	0.657
heptane	C <sub>7</sub> H <sub>16</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub>	liquid	-90	98	0.684
octane	C <sub>8</sub> H <sub>18</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> CH <sub>3</sub>	liquid	-57	126	0.703
nonane	C <sub>9</sub> H <sub>20</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> CH <sub>3</sub>	liquid	-51	151	0.718
decane	C <sub>10</sub> H <sub>22</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> CH <sub>3</sub>	liquid	-30	174	0.730
⋮						
eicosane	C <sub>20</sub> H <sub>42</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>18</sub> CH <sub>3</sub>	solid	37	344	0.785

- 3) Physical properties of alkanes:
  - i. Alkanes are **non-polar**, thus they are soluble in non-polar solvents like CCl<sub>4</sub>. They are, in general, insoluble and less dense than water.
  - ii. The boiling point of straight-chain alkanes **increases** with the size of molecule. This is because the number of electrons in each molecule increases, resulting in the increased strength of van der Waals'. Thus more energy is required to break these forces.
  - iii. For a branched alkane, it is **more volatile** and its boiling point is **lower** than its counterpart with the same number of carbon atoms. This is because they are more spherical and have a lower surface area. Thus less temporary dipoles can be set up and the van der Waals' forces are weaker, less energy is required to overcome it.
  - iv. The density of liquid alkanes **increases slightly**. The mass of each succeeding molecule increases but due to the increased strength of van der Waals' forces, the molecules are more closer together. This results in higher ratio of mass/volume.

- 4) Cycloalkanes are alkanes that joined up as a **ring**. The smallest possible cycloalkane is cyclopropane. Cycloalkanes have two hydrogen less than the corresponding straight-chain alkanes.



## 15.2 Reactions of Alkanes

### Reactivity of alkanes

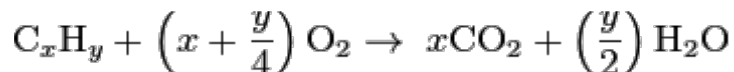
- 1) Alkanes are saturated and generally **unreactive** because they are non-polar, hence they are unattractive towards nucleophiles and electrophiles.
- 2) Alkanes will only react with non-polar reagents in the presence of heat or ultraviolet light.

### Combustion

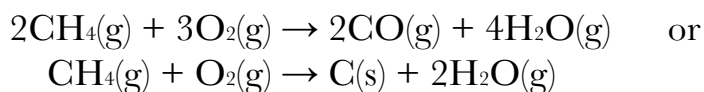
- 1) Alkanes undergo **complete combustion** under **excess oxygen** gas to give carbon dioxide and water. For example:



- 2) In general,



- 3) Larger alkanes are more difficult to ignite. This is because alkanes only burn in the gaseous state and larger alkanes have stronger van der Waals' forces that hold them together. Therefore more energy is required to vaporise it.
- 4) When the supply of oxygen is limited, alkanes undergo **incomplete combustion**. The possible products are carbon monoxide, carbon and water. For example,



## Halogenation

1) Alkanes undergo halogenation via **free-radical substitution** to give a range of products. In free-radical substitution, hydrogen atoms in the molecule are **gradually substituted** by halogen atoms.

2) **Reagent** : Chlorine gas,  $\text{Cl}_2$  or bromine gas,  $\text{Br}_2$

**Condition** : The presence of ultraviolet(UV) light or sunlight

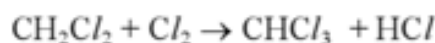
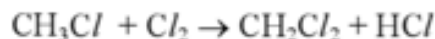
**Product** : Halogenoalkanes (alkanes with halogens)

3) Free-radical substitution proceeds via a **chain reaction**. During a chain reaction, for every reactive species you start off with, a new one is generated at the end, and this keeps the process going.

4) i. When methane reacts with chlorine in sunlight, the greenish-yellow colour fades and steamy acidic fumes of hydrogen chloride can be observed.



ii. However, this is a chain reaction and does not end here. More hydrogen atoms will be substituted as long as there are sufficient chlorine atoms.



5) The mechanism of free-radical substitution:

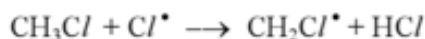
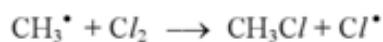
i. *Step 1: Initiation step*

The reaction is initiated by the **homolytic fission** of chlorine molecule in the **presence of UV light**, forming chlorine free radicals.



ii. *Step 2: Propagation step*

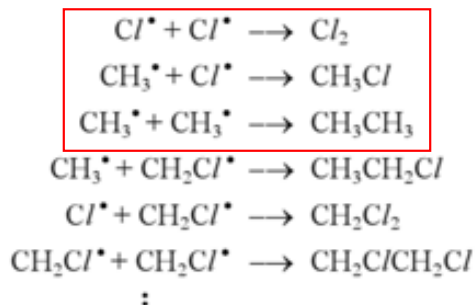
The free radicals then **attack** the methane molecules, leading to a chain reaction.



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iii. *Step 3: Termination step*

The reaction ends with the free radicals joining up with each other.



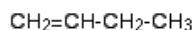
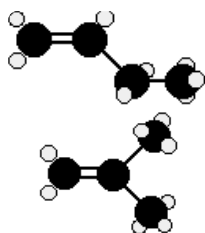
[ Note: All other alkanes react in a similar manner but the reactions involved are getting more and more complicated. ]

- 6) To produce mainly tetrachloromethane, an excess of chlorine gas is used so that all the hydrogen atoms eventually get substituted.
- 7) Bromine gas reacts in a similar manner but the reaction is slower.

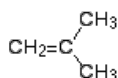
## 15.3 Introduction to Alkenes

What is an alkene?

- 1) Alkenes are **unsaturated hydrocarbons** which contain **at least one carbon-carbon double bond (C=C) bond**. They form the homologous series with the general formula of  $\text{C}_n\text{H}_{2n}$ .
- 2) The physical properties of alkenes are similar to that of alkanes.
- 3) Alkenes can exhibit **both structural and stereoisomerism**. This is due to the rotation-restricting double bond. The isomers of  $\text{C}_4\text{H}_8$  are:

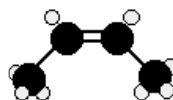


but-1-ene

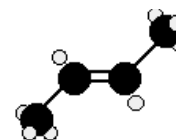


2-methylpropene

The structural isomers



cis-but-2-ene



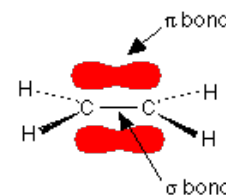
trans-but-2-ene

The geometrical isomers

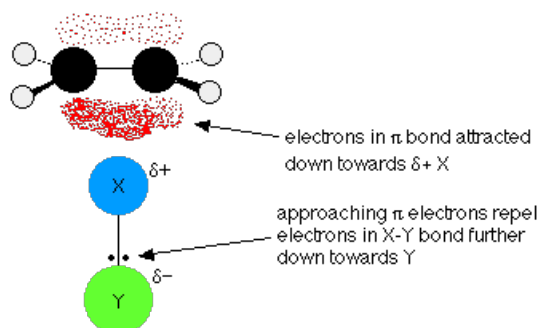
## 15.4 Reactions of Alkenes

### Electrophilic addition

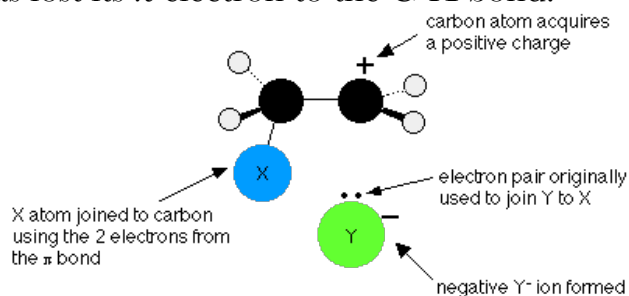
- 1) Unlike alkanes, alkenes are **more reactive** because they are unsaturated and contain a C=C bond. A C=C bond contains a  $\sigma$  bond and a  $\pi$  bond. A  $\pi$  bond is a **region of high density of electron** which is **open to attack** by something that carries an amount of positive charge, electrophiles.



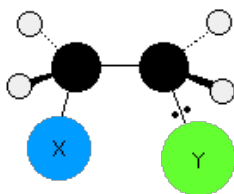
- 2) Alkenes mainly undergo **electrophilic addition**. An electrophilic addition reaction is **the addition of an electrophile across the C=C bond**.
- 3) The general mechanism of electrophilic addition:
- The electronegativity difference in an electrophile, say, XY causes the molecule to be polar. Therefore it carries a  $\delta^+$  and  $\delta^-$  end. The  **$\delta^+$  end** of the molecule behaves as an electrophile.
  - The  $\delta^+$  end is **attracted to the  $\pi$  bond**, a region with high electron density. As it approaches the  $\pi$  bond, the electrons in the X-Y bond are repelled further and further to the Y atom.



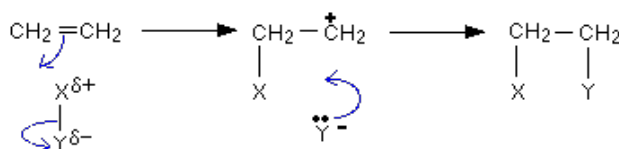
- Eventually the electrons are donated to Y, forming  $Y^-$  ion. The X atom forms a single bond with carbon. The electrons needed for this bonding come from the  $\pi$  bond. As a result, the adjacent carbon atom will carry a positive charge because it has lost its  $\pi$  electron to the C-X bond.



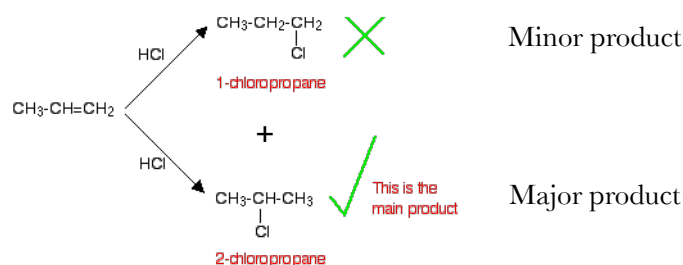
- iv. The carbon-containing species which carries a positive charge is called **carbocation**. The carbocation is attracted to the negative  $Y^-$  ion. These two particles eventually bond together via a co-ordinate bond.



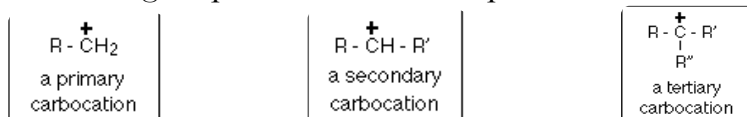
- 4) In the examination, the mechanism can be written like this. The curly arrows show the movement of electrons.



- 5) The addition of unsymmetrical alkenes follows **Markovnikov's rule**:  
**" In the addition of H-X to a C=C bond of an unsymmetrical alkene, the hydrogen atom attaches itself to the carbon atom that holds the greatest number of hydrogen atoms. "**

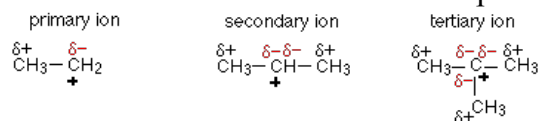


- 6) Hydrocarbons can be classified as primary, secondary or tertiary depending on the number of R groups attached to the positive carbon.

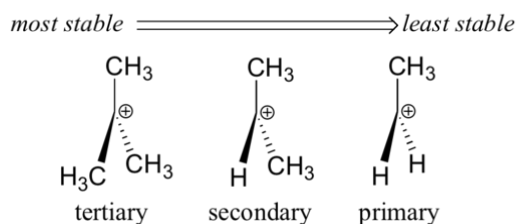


The Rs are alkyl groups, they can be the same or different. Carbocation is formed as an **intermediate** when the electrophile bonds with the carbon atom.

- 7) The alkyl groups have an **electron-pushing effect**, they tend to push the electrons towards the carbon atom which carries a positive charge.



- 8) It follows that **tertiary carbocation is the most stable** because the positive charge is neutralised by the negative charges. The charge density on the carbon atom is the least.



- 9) Therefore, if the electrophile is bonded in such a way that a tertiary carbocation is produced, the stability of the intermediate formed can be increased. This can only happen if the hydrogen attaches itself with the carbon with most hydrogen atom (normally at the ends of the molecule). Therefore Markovnikov's rule is obeyed.
- 10) Reactions that alkenes undergo:
- Addition of hydrogen,  $\text{H}_2$  (Hydrogenation)
  - Addition of steam,  $\text{H}_2\text{O}$  (Hydration)
  - Addition of halogen,  $\text{X}_2$  (Halogenation) where  $\text{X}$  = A halogen
  - Addition of hydrogen halide,  $\text{HX}$  where  $\text{X}$  = A halogen
  - Oxidation by cold and hot potassium manganate(VII),  $\text{KMnO}_4$
  - Addition polymerisation

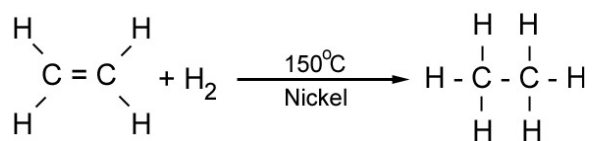
### Addition of hydrogen, $\text{H}_2$ (Hydrogenation)

- 1) **Reagent : Hydrogen gas,  $\text{H}_2$**

**Condition : Heat in the presence of nickel, Ni catalyst at  $150^\circ\text{C}$**

**Product : Alkanes**

- 2) In hydrogenation of ethene, two hydrogen atoms are added across the  $\text{C}=\text{C}$  double bond. Ethane is produced.



- 3) In this case, although hydrogen molecule has no polarity, it is still able to behave as an electrophile. This is because as the hydrogen molecule approaches the double bond, **a dipole is induced** due to the repulsion between the two bond pair of electrons (one from the  $\text{C}=\text{C}$  bond, another from the  $\text{H}-\text{H}$  bond).



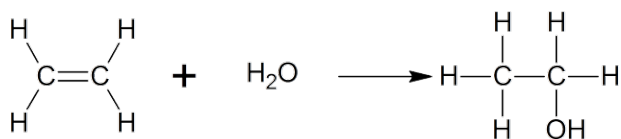
## Addition of steam, H<sub>2</sub>O (Hydration)

1) **Reagent : Steam, H<sub>2</sub>O**

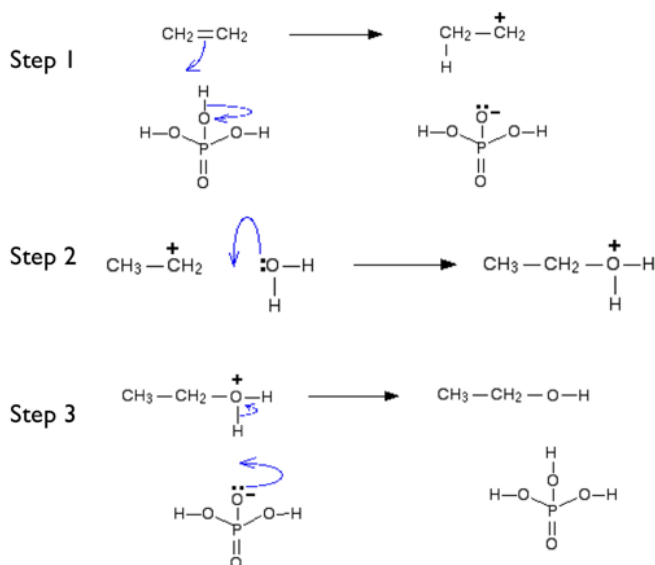
**Condition : Heat the gaseous alkene at 330 °C and 60 atm in the presence of phosphoric(V) acid, H<sub>3</sub>PO<sub>4</sub> as catalyst**

**Product : Alcohols (compounds that -OH group)**

2) In the hydration of alkene, steam, H-OH is added across the double bond. Ethanol is produced.

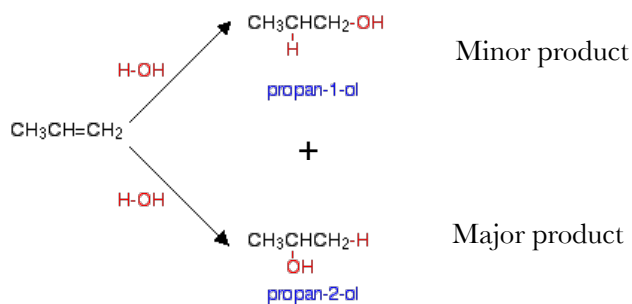


3) The detailed mechanism of the reaction is as follow:



The only way oxygen can have 3 bonds is by having a positive charge.

4) The addition of unsymmetrical alkene is as follow. Take propene as an example:



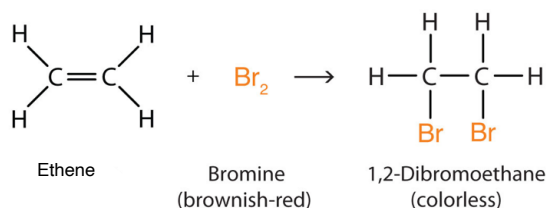
## Addition of halogen, $X_2$ (Halogenation)

1) **Reagent : Halogen,  $X_2$  (in tetrachloromethane or aqueous)**

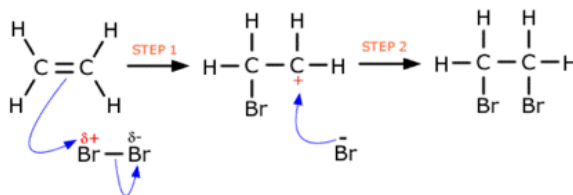
**Condition : Room temperature in dark**

**Product : Halogenoalkanes (alkanes with halogens)**

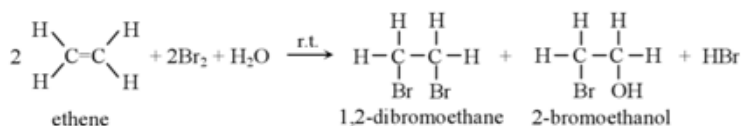
2) When ethene is bubbled into  **$Br_2$  in  $CCl_4$**  at room temperature in dark,  $Br-Br$  is added across the  $C=C$  bond. The brown colour of bromine is decolourised. 1,2-dibromoethane is produced.



3) The mechanism of this reaction is as follow:



4) When ethene is bubbled into **aqueous  $Br_2$**  at room temperature in dark, two products are obtained:



5)  $Br_2$  in  $CCl_4$  is used as **a test to differentiate alkanes and alkenes** as they both are colourless. **Alkene will decolourise the brown colour of bromine** whereas alkane will not.

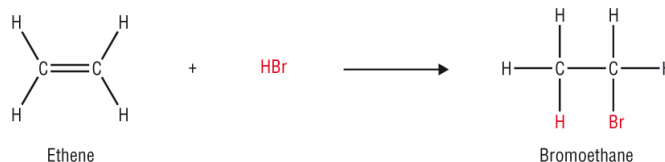
## Addition of hydrogen halide, $HX$

1) **Reagent : Hydrogen halide,  $HX(g)$**

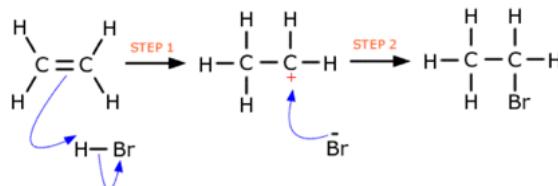
**Condition : Room temperature**

**Product : Halogenoalkanes (alkanes with halogens)**

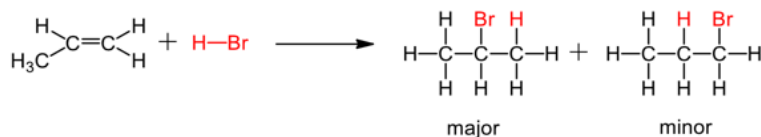
2) When ethene reacts with hydrogen bromide, 1-bromoethane, a halogenoalkane is produced.



3) The mechanism of this reaction is as follow:



4) The addition of unsymmetrical alkene is as follow. Take propene as an example:



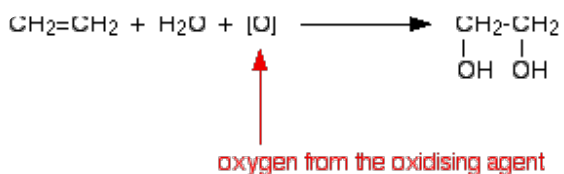
### Oxidation by cold and dilute potassium manganate(VII) solution, $\text{KMnO}_4$

1) **Reagent : Cold and dilute potassium manganate(VII) solution,  $\text{KMnO}_4$**

**Condition : Room temperature**

**Product : Alcohols(diols)**

2) When ethene is reacted with cold, dilute acidified  $\text{KMnO}_4$  solution, the purple colour of  $\text{KMnO}_4$  is decolourised. Ethane-1,2-diol is produced.



3) This is a redox reaction, the carbon species is oxidised while the oxidising agent is reduced.

4) This is **another test used to differentiate alkanes and alkenes. Only alkene will decolourise the purple colour of  $\text{KMnO}_4$**  whereas alkane will not.

Oxidation by hot and concentrated potassium manganate(VII) solution,  $\text{KMnO}_4$

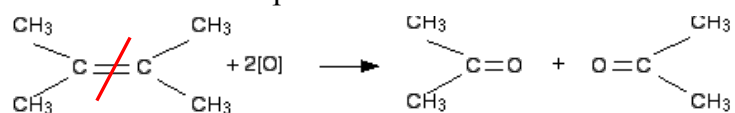
1) **Reagent : Hot and concentrated acidified potassium manganate(VII) solution,  $\text{KMnO}_4$**

**Condition : Room temperature**

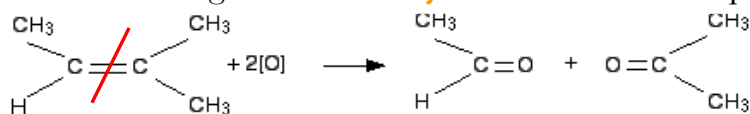
**Product : Carbon dioxide/carboxylic acids/ketones**

2) When an alkene is reacted with hot and concentrated acidified  $\text{KMnO}_4$  solution, the **C=C bond in the alkene ruptures**. The purple colour of  $\text{KMnO}_4$  is also decolourised. The product formed will differ according to the position of the C=C bond.

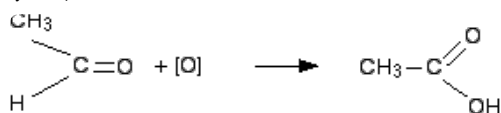
3) i. If there are two alkyl groups at one end of the bond, that part of the molecule will give a **ketone**. For example:



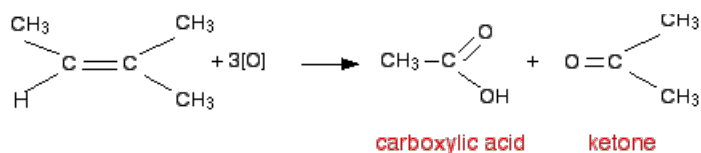
ii. If there are one alkyl group and one hydrogen at one end of the bond, that part of the molecule will give a **carboxylic acid**. For example:



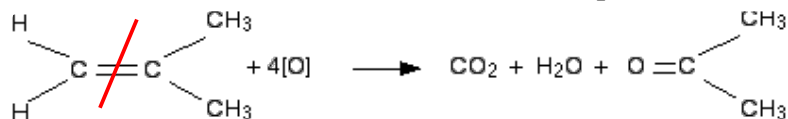
Ethanal(an aldehyde) is further oxidised to ethanoic acid(a carboxylic acid)



The net effect is as such:



iii. If there are two hydrogens at one end of the bond, that part of the molecule will give **carbon dioxide and water**. For example:

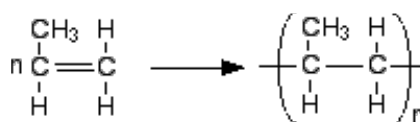
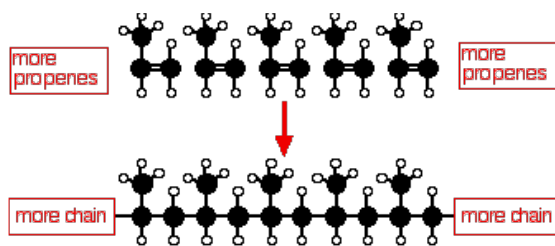


4) This reaction is useful in determining the position of C=C bond in an alkene molecule. This can be done by examining the product(s) formed.

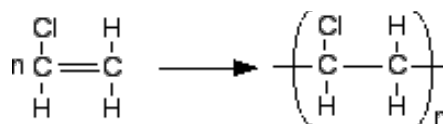
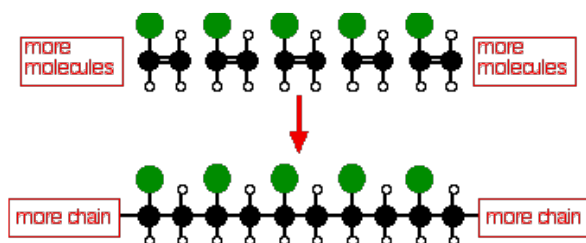
## Addition polymerisation

1) Alkenes can open up its C=C bond and join with each other in a long chain to form a polymer. A *polymer* is a long-chain molecule made of repeating units called monomers.

2) i. Polymer : Poly(propene)  
Monomer : Propene



ii. Polymer : Poly(chloroethene) (polyvinyl chloride or PVC)  
Monomer : Chloroethane



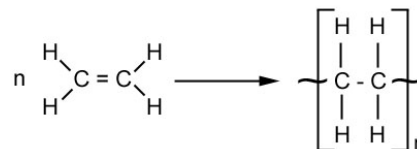
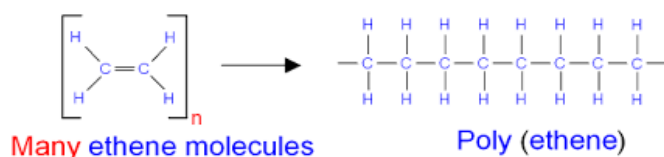
iii. Polymer : Poly(ethene) (polythene or polyethylene)  
Monomer : Ethene

The conditions required for this to happen are as follow:

**Temperature - about 60°C**

**Pressure - a few atmospheres**

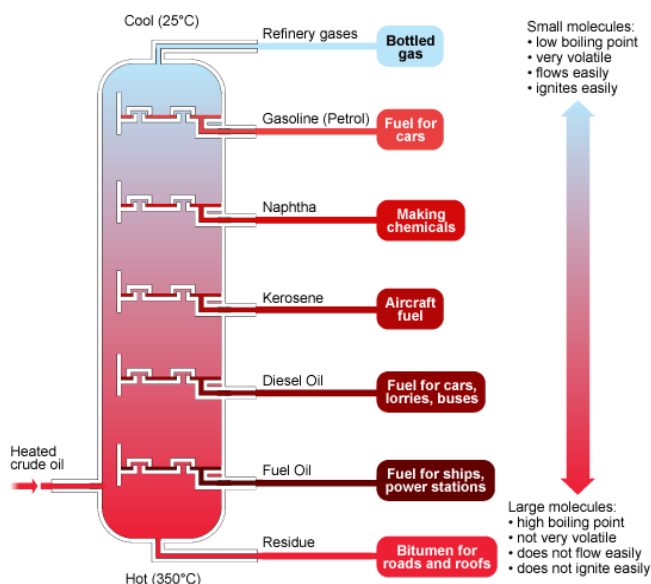
**Catalyst - Ziegler-Natta catalysts or other metal compounds**



## 15.5 Uses of Hydrocarbons

### Sources of hydrocarbons

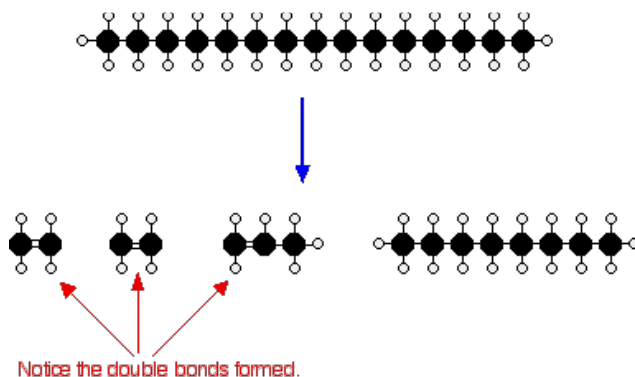
- 1) **Crude oil** is the main source of hydrocarbons, it is found trapped in layers beneath the surface of the earth. Crude oil is a **complex mixture of hydrocarbons - alkanes, cycloalkanes and aromatic compounds**.  
[ Note: Aromatic compounds are compounds which have a benzene ring attached to it ]
- 2) These substances can be separated by a technique called **fractional distillation**. *Fractional distillation* is the separation of compounds by their boiling points.
- 3) Different hydrocarbons have different molar masses, and so they have different boiling points.



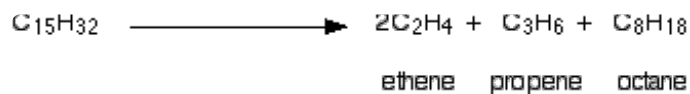
- 4) Crude oil enters the bottom of the fractionating column as liquid and vapour. The liquids (less volatile hydrocarbons) are drawn off at the bottom while less volatile ones rise up the column. They condense at different levels as the temperature gradually falls and are collected as liquids.
- 5) The most volatile short-chain hydrocarbons, which are methane and butane, leave the top as gases.

## Catalytic cracking

- 1) After the hydrocarbons are separated, oil companies found that hydrocarbons from lighter fractions (such as gasoline) are in higher demand compared to the ones from heavier fractions.
- 2) Therefore something must be done to convert those heavier hydrocarbons into the more useful, lighter ones. This is done by **cracking**.
- 3) Cracking breaks less useful hydrocarbons (normally long-chain) into smaller and more useful ones. Alkenes are normally produced as they are more industrially useful. This is because starting from alkenes, a wide range of organic compounds can be produced.



- 4) The larger hydrocarbons are fed into a chamber which contains no oxygen, so combustion does not take place. The larger hydrocarbons are heated at **high temperature (about 500 °C)** and passed over **zeolite catalyst**.
- 5) Cracking of a hydrocarbon is **not unique**, different molecules of hydrocarbons can be broken in different ways, giving rise to different products. One possible reaction of involving  $C_{15}H_{32}$  is as follow:



## Environmental consequences of using hydrocarbons

- 1) Alkanes are often used as **fuels**. This is because the combustion of alkanes is an exothermic process and produces a lot heat energy. Alkanes are also readily available and relatively cheap. The main uses of alkanes as fuels are:

- To generate electricity.
- To heat domestic houses and cook foods.
- To provide energy needed in industrial processes.
- To provide power for ships, aeroplanes, trains, lorries, buses, cars and motorbikes.

- 2) However, the combustion of alkanes can produce some poisonous gases which can act as pollutants.
- 3) One such example is **carbon monoxide, CO** which arises from the incomplete combustion of alkane. Carbon monoxide is a toxic gas that will bind readily to the haemoglobin molecules in the blood. This causes oxygen cannot be transported to cells and the victim will die.
- 4) The **carbon dioxide, CO<sub>2</sub>** produced from the complete combustion of alkane can also act as a **greenhouse gas**. The increasing amount of these greenhouse gases enhances **global warming**.
- 5) Burning fuels in car engines will also oxidise the nitrogen gas in air to produce **oxides of nitrogen (nitrogen monoxide, NO or nitrogen dioxide, NO<sub>2</sub>)**. These oxides of nitrogen is believed to contribute in the formation of acid rain. (For more details, refer Chapter 13)
- 6) Catalytic converters can be installed to remove carbon monoxide and the oxides of nitrogen. More details about catalytic converters can be found in Chapter 13.