

Alkanes and Alkenes

The Alkanes

Alkanes are **hydrocarbons** (i.e. compounds of carbon and hydrogen **only**). They are called **saturated** hydrocarbons because they contain no double bonds, and so cannot undergo addition reactions.

They have the general formula : C_nH_{2n+2}

Physical Properties

The boiling points of the alkanes increase steadily with the number of C atoms. This is because the van der Waals' forces between the molecules increase with the total number of electrons in the molecule. As the chain length increases, the van der Waals' attractions increase, and the liquid needs to reach a higher temperature before the molecules can acquire enough energy to separate and go into the vapour state. As isomers become more highly branched, boiling points usually fall slightly. This is because the branching means that the molecule has less surface area in contact with its neighbours, thus decreasing the van der Waals attractions.

Isomerism

Isomerism is when two molecules of the same molecular formula have a different arrangement of atoms (structural formula).

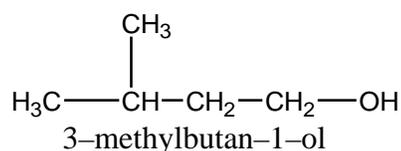
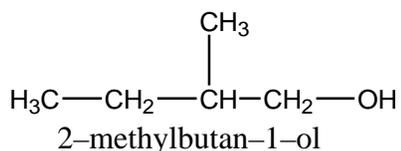
There are two main types of isomerism: **structural isomerism** and **stereoisomerism**.

Structural isomers: these have different structural formulae. i.e. the atoms are joined together in a different order.

At the most extreme, they may have different functional groups: e.g. C_2H_6O may be ethanol, CH_3CH_2OH , or it may be methoxymethane (an ether), CH_3OCH_3 .

Alternatively, they may have similar functional groups, but differ in the position of these in the molecule: e.g. propan-1-ol, $CH_3CH_2CH_2OH$, and propan-2-ol, $CH_3CH(OH)CH_3$.

Or they may differ only in the hydrocarbon chain (see below):



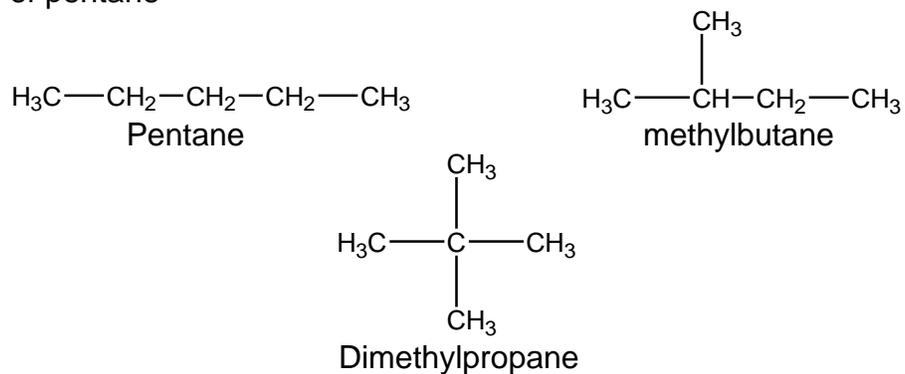
Stereoisomers.

These have the same structural formulae, and differ only by the arrangement of the atoms in space. There are two sorts: cis-trans (or geometrical), and optical. Optical isomerism will be looked at next year.

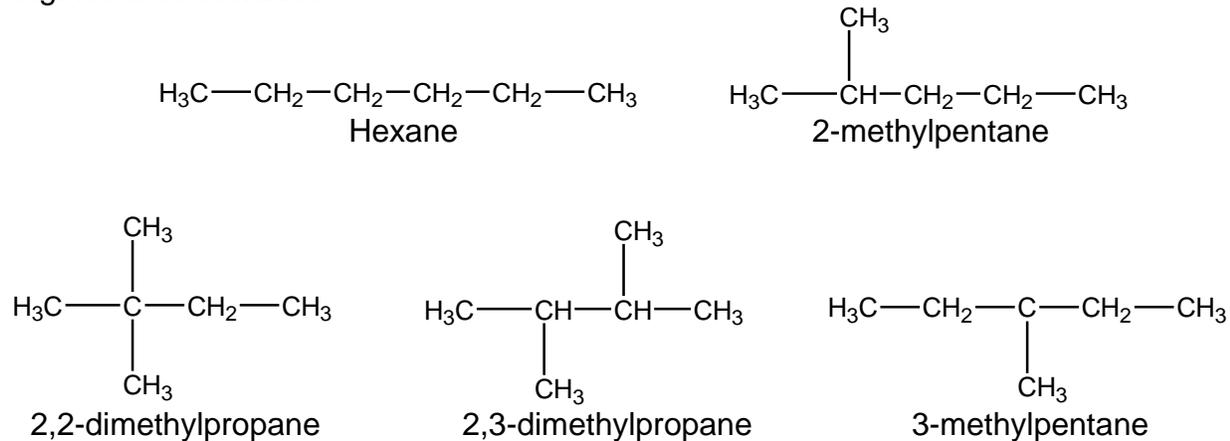
Isomers of alkanes

Alkanes exhibit structural isomerism.

e.g. Isomers of pentane



e.g. Isomers of hexane



Fuels

One of the main uses of alkanes is as fuels.

Crude oil consists of a mixture of a large number of hydrocarbon compounds.

Crude oil undergoes **fractional distillation**, and the fractions obtained by this process consist of mixtures of hydrocarbons that boil within particular ranges.

The more useful fractions are those with the lower boiling ranges, such as that of gasoline which is used for petrol, but they generally occur in smaller proportions.

To convert some of the larger, less useful alkanes into smaller, more useful alkanes the process of **cracking** is used.

Cracking involves passing the alkane vapour through a heated catalyst.

The alkane molecules break up to form a smaller alkane molecule and at the same time an alkene, such as ethene, is formed which can then be used to make polymers.

A typical cracking reaction might be:



The straight chain alkanes do not burn very evenly, and tend to cause “**knocking**” in a car engine. Branched alkanes burn more smoothly and are much more appropriate for modern high-performance engines.

The petrochemical industry carries out the process of **reforming** to convert straight chain alkanes into branched chain alkanes.

Hydrocarbon fuels produce carbon dioxide when they burn.

Carbon dioxide is a “**greenhouse gas**”. When infra red radiation from the sun hits the Earth’s surface, it is absorbed and then re-radiated at a lower frequency.

A greenhouse gas absorbs the re-radiated infra red and converts it to heat energy, so causing a warming of the atmosphere. This means that the production of carbon dioxide by burning fossil fuels increases the concentration of greenhouse gases in the atmosphere and is considered to cause **climate change**.

The problem of climate change means that there is a search for alternative fuels which do not place greenhouse gases in the air.

Chemical properties of alkanes

Alkanes contain carbon-hydrogen bonds, and, from ethane on, carbon-carbon single bonds. These are all non-polar, and the electron density in the σ -bonds is hard to distort (not polarisable), so that alkanes do not react with electrophiles or nucleophiles, or other polar reagents, like acids, alkalis or aqueous oxidising agents.

The bonds can only undergo **homolytic bond fission**, which occurs when a covalent bond breaks in such a way that each atom takes one electron. This leads to formation of two **free radicals**.

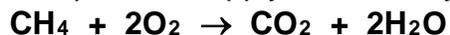
A **free radical** is an atom, or group of atoms, which have an unpaired electron. It is normally highly reactive, and written with a dot (which does not show an extra electron, simply the unpaired one). e.g. $\text{Cl}\cdot$ or $\text{CH}_3\cdot$.

Alkanes therefore undergo very few reactions: **combustion** and **cracking** are the most important.

Reactions of alkanes

(a) Combustion

Alkanes burn in a plentiful supply of air or oxygen, to give carbon dioxide and steam:



If air is restricted, carbon monoxide is likely to be formed:



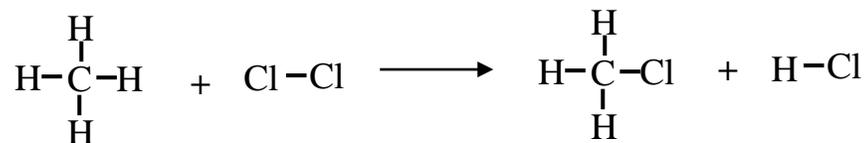
The former reaction gives out much heat, and so alkanes are useful fuels. Methane itself is called **natural gas**, and is used in the home and in modern gas-turbine power stations.

(b) Halogenation

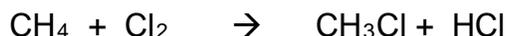
It is possible for the hydrogen atoms in the alkane to be **substituted** by chlorine or bromine.

Alkanes react with chlorine or bromine, in the presence of light, or on heating, to form halogenoalkanes and the hydrogen halide:

For example the reaction between methane and chlorine can be represented as follows:



The reaction does not necessarily stop at one substitution, and the reaction between methane and chlorine produces dichloro-, trichloro- and tetrachloro- methane.



The process of substitution is random, so all possible products result, though if there is excess methane the main one will be CH_3Cl , while a large excess of chlorine will give mainly CCl_4 .

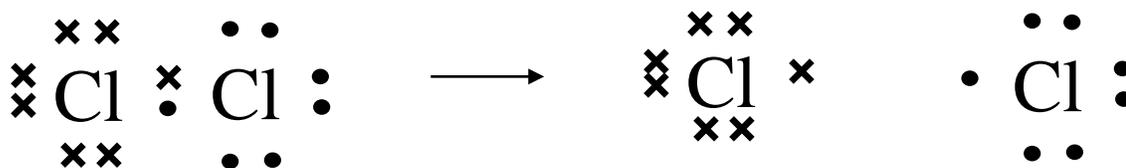
The substitution of a hydrogen atom by a chlorine atom actually takes place in a number of stages. Looking in detail at what happens in each stage of such a reaction is called the **reaction mechanism**.

The halogenation of an alkane takes place by a **free radical** reaction.

The reaction between alkanes and these halogens requires an energy source such as ultra violet (u.v.) light. Considering the reaction between methane and chlorine, looking at the bond enthalpies for the bonds present

Bond	Energy kJ/mol
C-H	413
Cl-Cl	242

It can be seen that the Cl-Cl bond requires less energy to break, so this is the bond which is broken by the u.v. light.

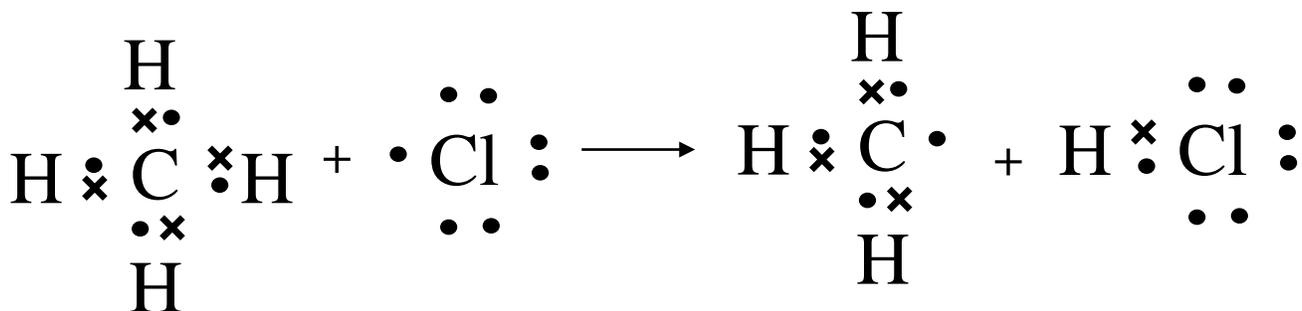


This energy is used to split the halogen molecule to form two chlorine atoms; the chlorine atoms have an unpaired electron – such a species is called **free radical**.

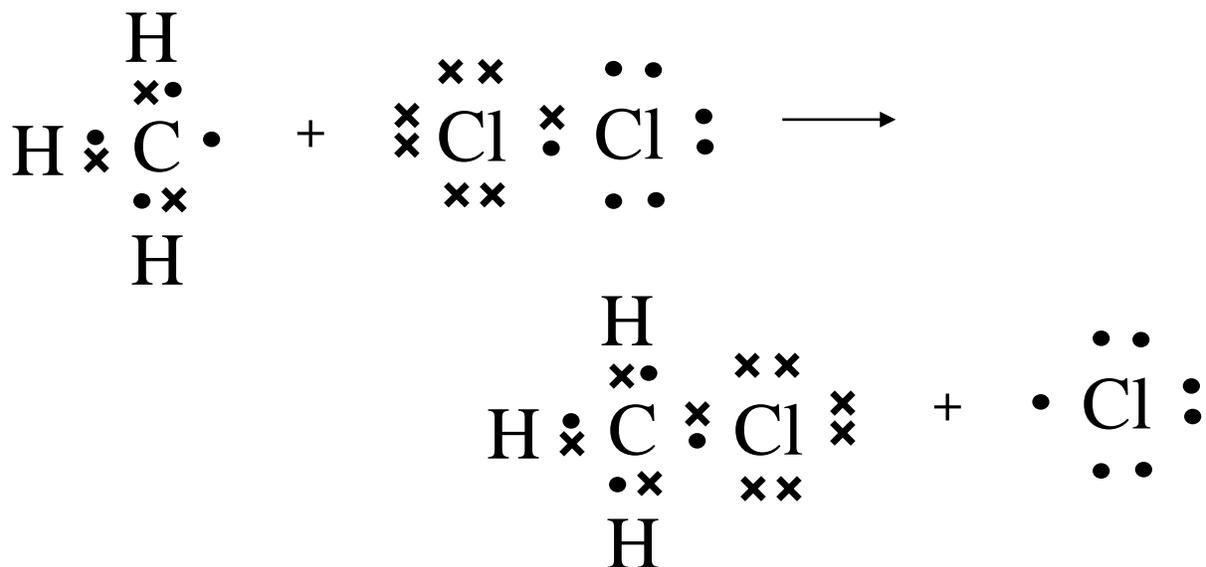
The chlorine radical reacts with a methane molecule. It forms a bond. Looking at the bond enthalpies for the bonds that could be formed;

Bond	Energy kJ/mol
C-Cl	339
H-Cl	431

It can be seen that the H-Cl bond has a higher bond enthalpy, so this is the bond which forms.



This forms a methyl radical. The methyl radical then reacts with a chlorine molecule:



In this reaction a chlorine radical is generated; this then reacts with a methane molecule and the process continues.

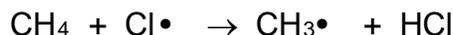
Curly arrow mechanisms

Reaction mechanisms look at the movement of electrons within and between molecules and ions. The movement of electrons are shown by “curly arrows”, using  for a single electron and  for an electron pair.

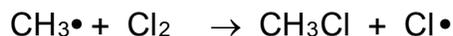
The first step in the reaction between methane and chlorine is the formation of the chlorine radical. This is called the **initiation step**. It is shown as follows.



The chlorine radical then attacks the methane molecule.

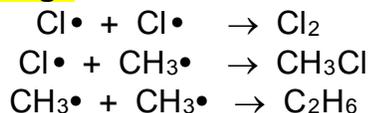


The methyl radical from this reaction reacts with a chlorine molecule to form chloromethane and a new chlorine radical.



The chlorine radical starts the cycle again and the process continues. These two reactions are called the **propagation stage**.

The propagation stage continues until two radicals meet to form a molecule. There are three possibilities for this reaction. Since it ends the sequence it is called the **termination stage**.



The overall mechanism is called **free radical substitution**.

Note that in the propagation stage the $\text{Cl}\cdot$ at the end can go on to attack another CH_4 and so the chain can go on for several thousand reactions from one initiation.

The presence of traces of C_2H_6 in the products shows that $\text{CH}_3\cdot$ radicals must have been formed.

Of course, the $\text{Cl}\cdot$ atoms can remove a hydrogen atom from CH_3Cl , and so the reaction can go on to CH_2Cl_2 , then CHCl_3 and finally CCl_4 .

The Alkenes

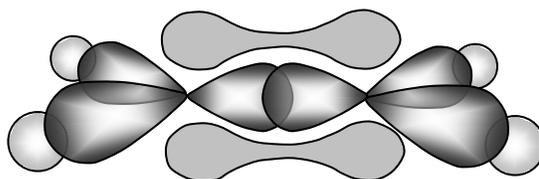
Alkenes are hydrocarbons that contain one double bond.

They are **unsaturated compounds**: compounds which are able to undergo addition reactions.

They have the general formula : C_nH_{2n}

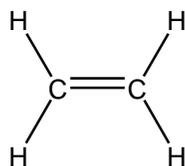
The double bond in alkenes does not consist of two identical bonds. One of the bonds is a normal bond with the electron cloud lying between to two atoms. This is called a **sigma, σ , bond**. The other bond has an electron cloud which is placed above and below the two atoms. This is called the **pi, π , bond**.

The electron clouds in ethene can be represented as shown below.



Isomers of alkenes (E-Z Isomerism)

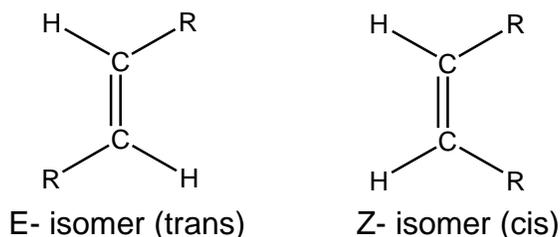
The geometry of the C=C bond is determined by the π -bond, and means that ethene is a rectangular, flat molecule.



The bond angles are at about 120° , and rotation about the C=C axis is restricted, since twisting through 90° would mean the p-orbitals would no longer overlap and the π -bond would be broken.

The restriction of rotation produces isomers called **E-Z isomers** (geometric isomers or cis-trans isomers).

For E-Z isomerism (cis-trans isomerism) to occur there must be a **double bond** and **two different groups** on **each** of the double bonded **carbon** atoms.

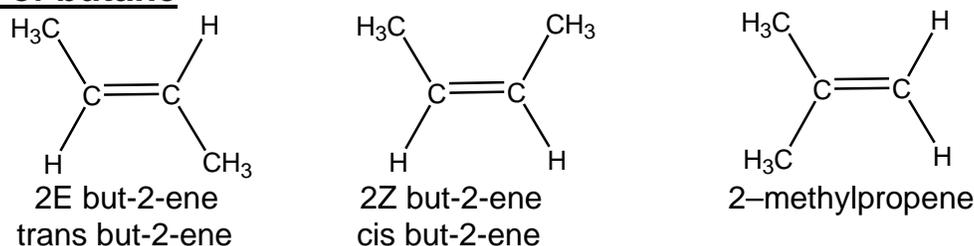


E-Z and cis-trans are different terms for the same type of isomerism.

Trans refers to the isomer where the R groups are on opposite sides of the C=C.

Cis refers to the isomer where the R groups are on the same side of the C=C.

Isomers of butane

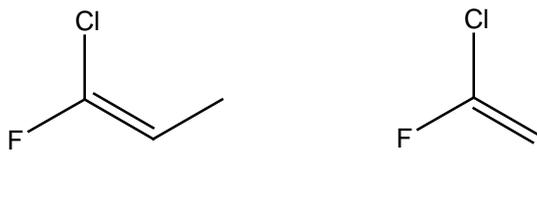


The E-Z (cis / trans) isomers will be chemically very similar, though not quite identical, and will have slightly different melting and boiling points.

[Note that a third isomer, 2-methylpropene, which has two methyl groups attached to the same carbon atom, is a **structural** isomer of these, as is but-1-ene]

E- and Z- vs cis-trans nomenclature

The cis trans system breaks down with examples like;



The E-Z naming system is more useful than the cis-trans system.

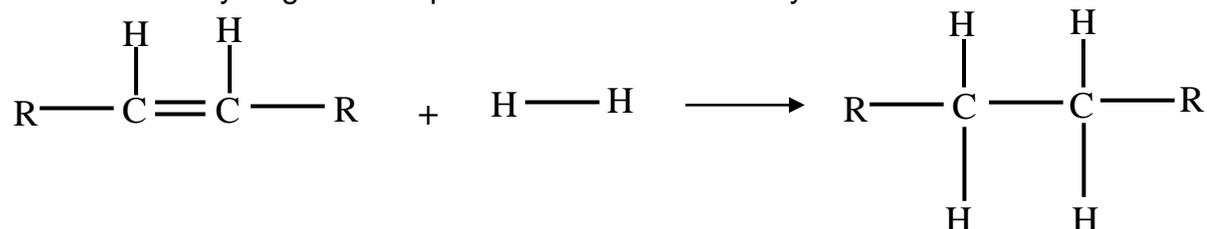
- The naming of the isomer is determined by priorities.
- Each atom on the double bond is given a priority determined by its atomic number.
- The smaller the atomic number the lower the priority – hydrogen in the example above.
- If atoms with the lowest priority are on the same side on each end of the C=C the isomer is called the **Z-isomer**. (Z=Zusammen (together)).
- If atoms with the lowest priority are on the opposite side on each end of the C=C the isomer is called the **E-isomer**. (E=Entgegen (opposite)).

Reactions of alkenes

The alkenes are more reactive than the alkanes because of the C=C bond. It is possible for the double bond to break, allowing each carbon to form a new bond, which is often energetically favourable. Halogens, hydrogen halides, hydrogen and potassium manganate(VII) will produce **addition reactions** with alkenes.

Addition of hydrogen (hydrogenation)

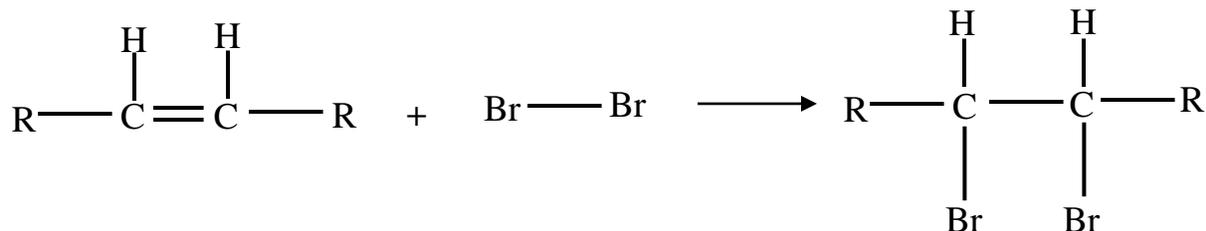
Alkenes react with hydrogen in the presence of a nickel catalyst at 150°C.



This is important in the hydrogenation of vegetable fats to make margarine. An unsaturated vegetable oil is mixed with a nickel catalyst at 50°C, and hydrogen gas bubbled through. The saturated product has a higher melting point, and is less easily oxidised (longer shelf life).

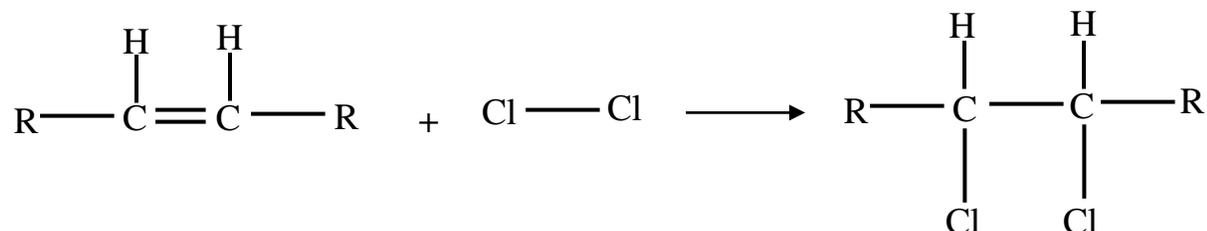
Addition of bromine

Alkenes will decolorise bromine immediately:

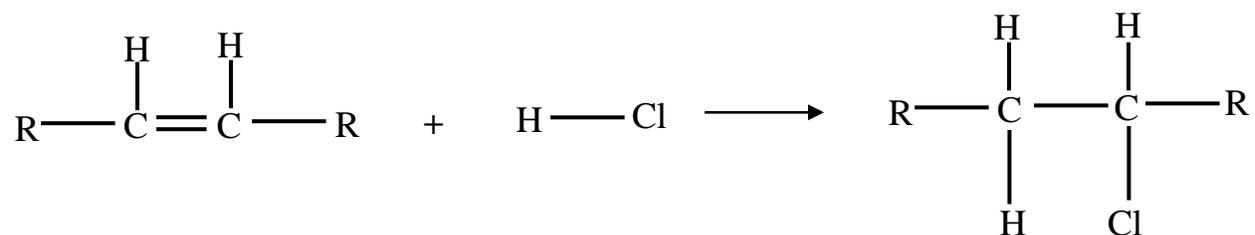


The decolorisation of bromine water is used as a test for the C=C double bond. This reaction occurs in an inert solvent like volasil.

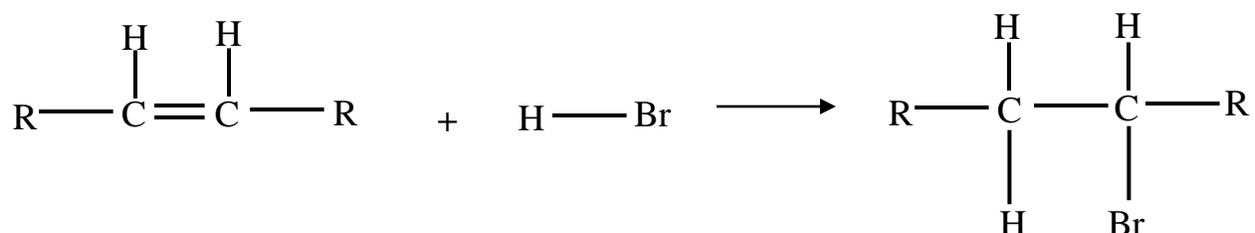
Addition of chlorine



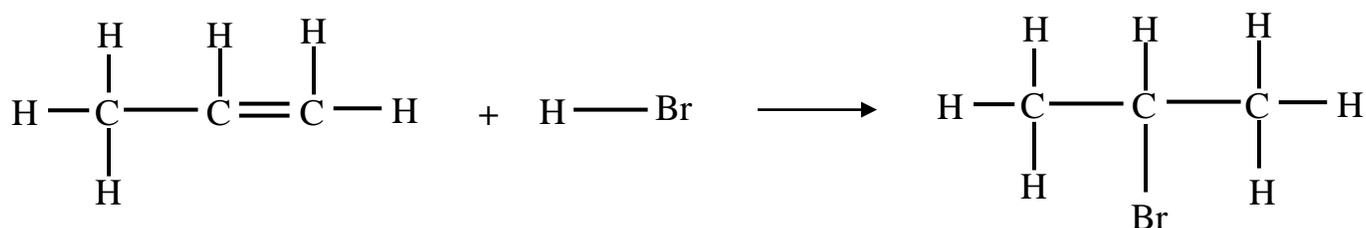
Addition of Hydrogen chloride*



Addition of Hydrogen bromide*

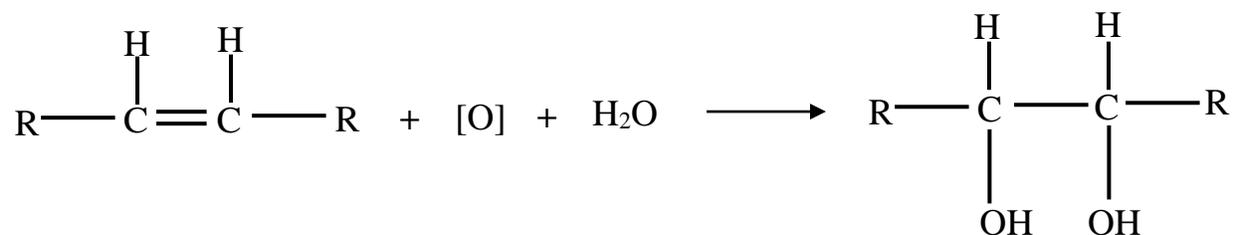


* When addition of a hydrogen halide takes place, if the alkene is not symmetrical, the hydrogen adds to the carbon that already has the most hydrogen. This is called **Markovnikoff's rule**



Reaction with Potassium manganate(VII)

Acidified potassium manganate(VII) is decolourised (from purple to colourless) by an alkene and a **diol** is formed.



[O] is a shorthand for the oxidizing agent potassium manganate(VII).

Addition Reactions of Alkenes

The addition reactions have a mechanism which we need to study. It is the electron rich area in the double bond which causes the initial attack. A molecule attacking such an area is called an **electrophile** (electron loving). This reaction results in addition, so this type of reaction is called **electrophilic addition**.

A definition of the term electrophile is;

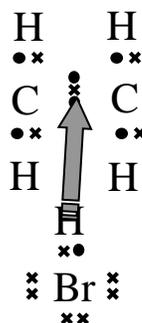
An electrophile is a species attracted to an area of negative charge and is an electron pair acceptor.

Mechanism for the reaction of hydrogen bromide with ethane.

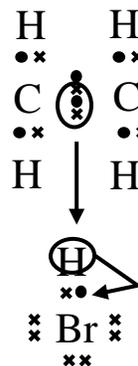
Looking at dot and cross diagram for the reaction.

This is not the way a mechanism is shown.

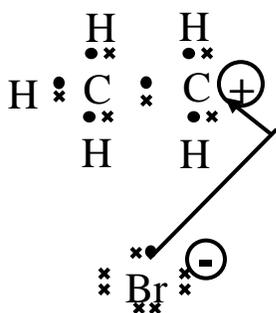
1. The hydrogen in the hydrogen bromide has a partial positive charge. It is attracted to the high electron density in the double bond.



2. The hydrogen draws an electron pair out of the double bond and forms a bond to the hydrogen.



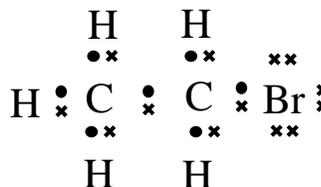
3. The bond between the bromine and the hydrogen weakens and breaks, both the electrons going to the bromine.



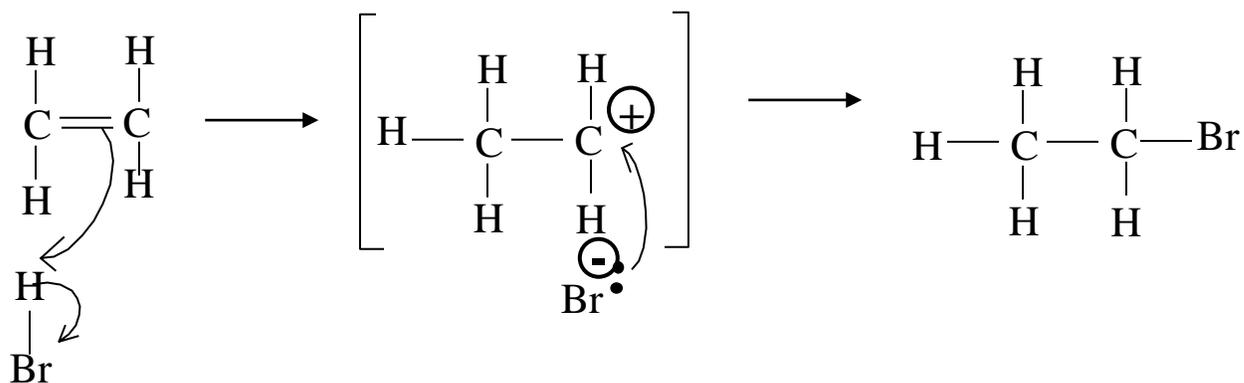
4. The carbon on the right now has only three of its original four electrons, so it has a positive charge. This intermediate is called a **carbocation ion**.

5. The bromine has gained an electron making it a bromide ion with a negative charge.

6. The bromide donates an electron pair to the positively charged carbon forming a bond.

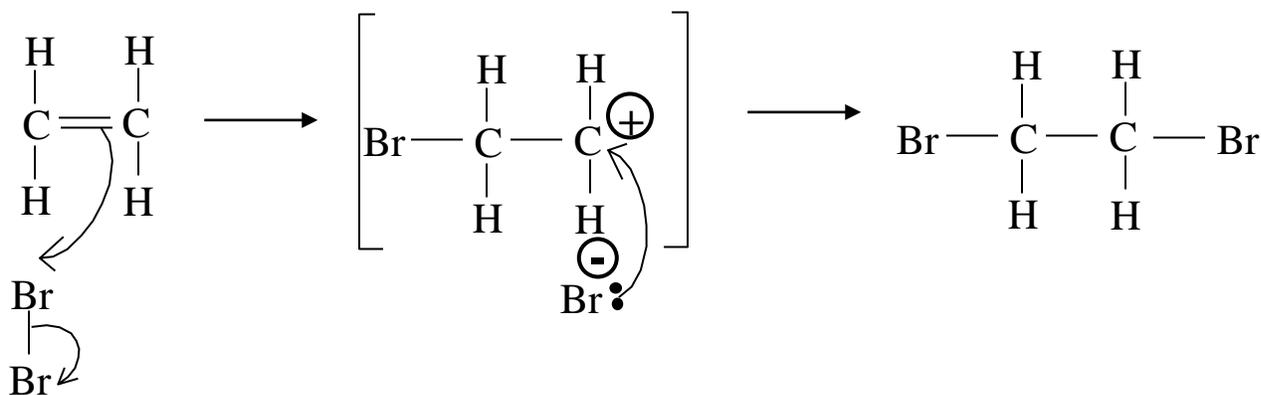


The reaction mechanism for this is shown as follows.



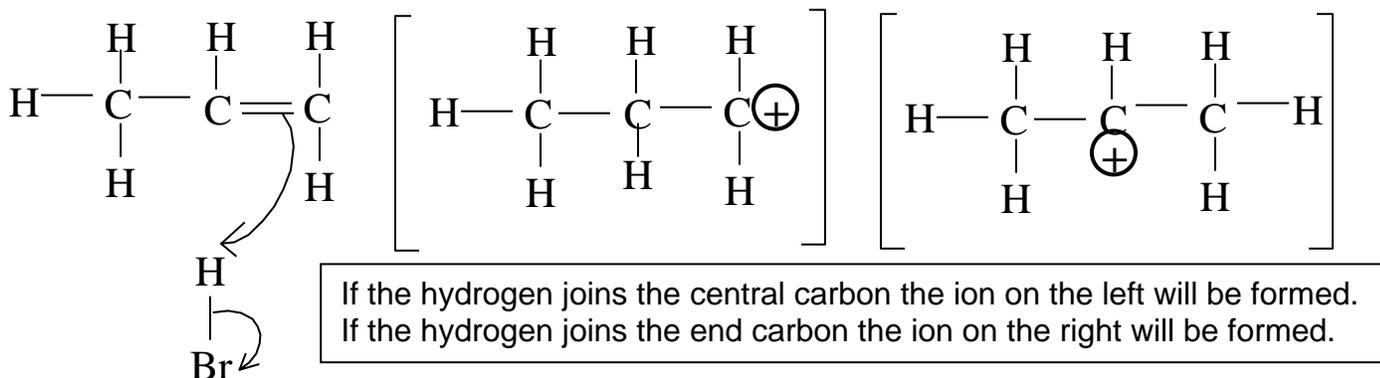
The mechanism for the attack of bromine on ethane is almost identical, but as bromine is not a polar molecule it has no partial charge.

As a bromine molecule approaches the ethane, the high electron density in the double bond repels electrons in the nearest bromine so causing an induced partial positive charge.

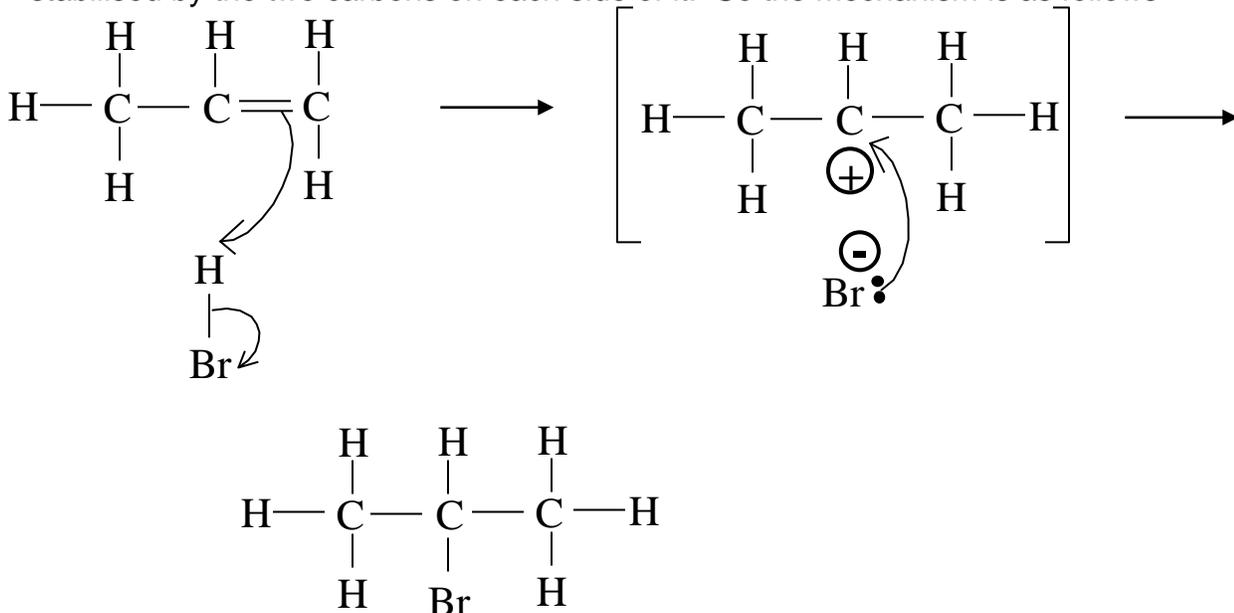


Asymmetric Additions (Markovnikoff's rule)

The addition of hydrogen bromide to propene could lead to two possible intermediates.



The carbocation ion with the charge on the central carbon is formed as the charge is stabilised by the two carbons on each side of it. So the mechanism is as follows



Markovnikoff's rule states that;

When addition of a hydrogen halide takes place, if the alkene is not symmetrical, the hydrogen adds to the carbon that already has the most hydrogen.

Test for alkenes

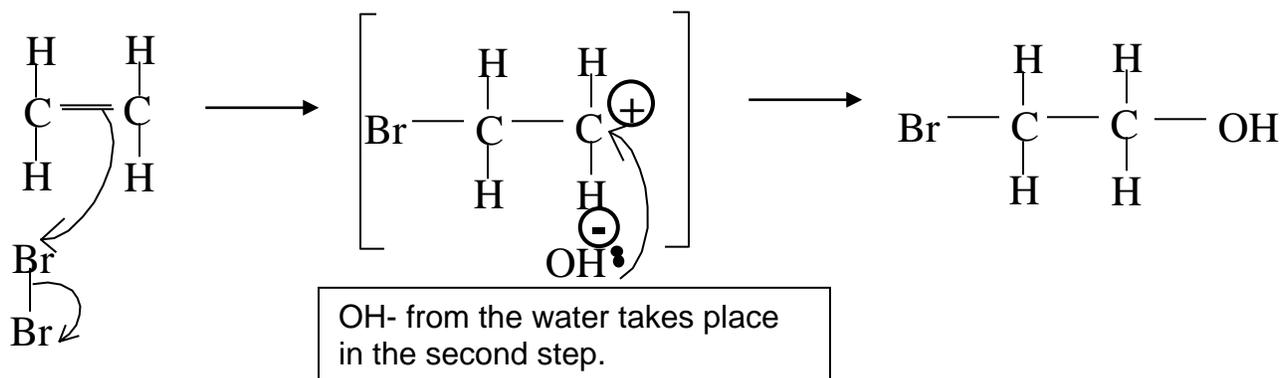
The addition reactions are used to test for the presence of a double bond.

If **bromine water** is added to an unsaturated compound, an addition reaction occurs fairly rapidly and the bromine water changes from orange to colourless.

In this test the product contains a Br and an OH.

This is because the bromine water contains hydroxide ions from water.

The reaction mechanism for the test on ethene shows why this product is formed.



Addition Polymers

An addition polymer is formed when monomers containing double bonds are polymerised. In the process of polymerisation the double bond breaks and the molecules join to form molecules of thousands or millions of units.

Polymer	structure of Monomer	structure of polymer
Ethene	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{C} = \text{C} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	$\left[\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C} - \text{C}- \\ \quad \\ \text{H} \quad \text{H} \end{array} \right]_n$
Propene	$\begin{array}{c} \text{H} \quad \text{CH}_3 \\ \quad \\ \text{C} = \text{C} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	$\left[\begin{array}{c} \text{H} \quad \text{CH}_3 \\ \quad \\ -\text{C} - \text{C}- \\ \quad \\ \text{H} \quad \text{H} \end{array} \right]_n$
Chloroethene	$\begin{array}{c} \text{H} \quad \text{Cl} \\ \quad \\ \text{C} = \text{C} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	$\left[\begin{array}{c} \text{H} \quad \text{Cl} \\ \quad \\ -\text{C} - \text{C}- \\ \quad \\ \text{H} \quad \text{H} \end{array} \right]_n$
Tetrafluoroethene	$\begin{array}{c} \text{F} \quad \text{F} \\ \quad \\ \text{C} = \text{C} \\ \quad \\ \text{F} \quad \text{F} \end{array}$	$\left[\begin{array}{c} \text{F} \quad \text{F} \\ \quad \\ -\text{C} - \text{C}- \\ \quad \\ \text{F} \quad \text{F} \end{array} \right]_n$

Independent research: Consider the uses of energy and resources over the life cycle of a polymer in the context of how renewable resources, recycling and energy recovery can lead to a more sustainable use of materials.