Chapter 16b (AS-Level)

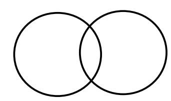
Hydrocarbons: Alkenes

Physical properties of alkenes

- Simple alkenes are hydrocarbons that contain one C=C double bond.
- The simplest is ethene, $CH_2=CH_2$.
- The general formula of the homologous series of the alkenes is C_nH_{2N}.

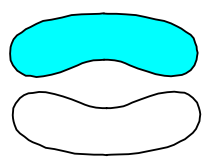
Bonding in alkenes: σ and π bonds

Electrons in molecules may occupy σ and π orbitals. In double bonds, the first bond involves an overlap of atomic orbitals directly in between the nuclei of the two atoms:



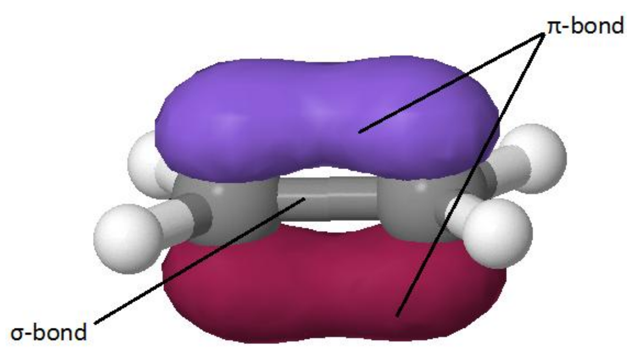
This is known as a σ-bond. All single covalent bonds are σ-bonds.

The second bond, however, cannot bond in the same place. Instead two p-orbitals overlap above and below the internuclear axis:



This is known as a π-bond. All double covalent bonds consist of one σ-bond and one π-bond, in which the π-bond exists on each side of the σ-bond.

For example, ethene has one sigma bond and one pi bond”



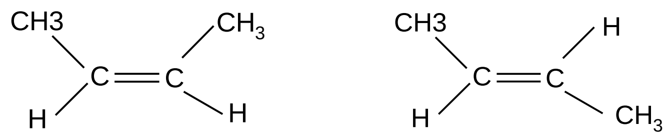
Compounds which contain π-bonds, such as ethene, are called unsaturated hydrocarbons. The term unsaturated indicates that the compound will combine by addition reactions with hydrogen and other chemicals, losing its double bond.

Saturated compounds contain only one C-C single bond. Polyunsaturated compounds have more than one C=C double bond.

Cis-trans isomerism

Many alkenes exhibit cis-trans isomerism. It is caused by the restricted rotation about a carbon-carbon double bond.

It arises when the carbon atoms on both sides of the bond are attached two different groups. E.g. but-2-ene has two geometrical isomers:

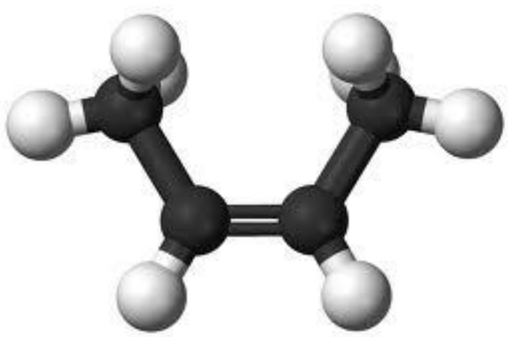


These two isomers cannot be interconverted without breaking the π-bond.

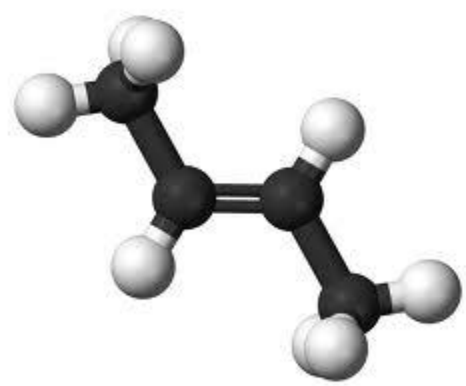
In cases where both C atoms are attached to one hydrogen atom, it is possible to distinguish the isomers by a simple prefix.

If both hydrogen atoms are on the same side of the molecule, the prefix cis- is used.

If the hydrogen atoms are on different sides of the molecule, the prefix trans- is used.



Cis-but-2-ene



Trans-but-2-ene

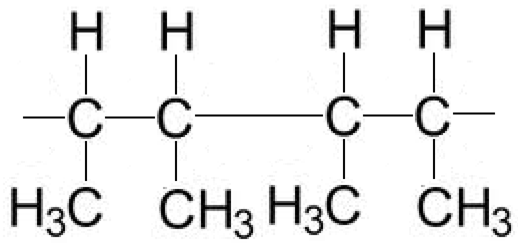
It is only possible to name geometrical isomers using cis- and trans- prefixes if both carbon atoms are attached to a hydrogen atom.

Note that molecules which show geometrical isomerism always have two specific structural features:

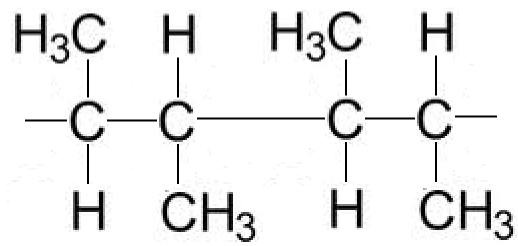
- There is a carbon-carbon double bond;
- Both the carbon atoms are attached to two different groups.

Polymers of ethene can also be exhibit cis-trans isomerism. For example, there are two polymers of butene:

- Cis-poly(but-2-ene):



- Trans-poly(but-2-ene):



Characteristic reactions of alkenes

Most reactions involving alkenes involve the breakage of the π-bond. It is weaker than the σ-bond and can react with a variety of reagents.

Addition reactions to the double bond

The characteristic reaction of an alkene involves a simple molecule such as hydrogen, water or a halogen, which joins to the double bond to form a single product.

Addition of hydration

This converts the unsaturated alkene to a saturated alkene. Hydrogen gas and a gaseous alkene are passed over a finely divided nickel catalyst supported on an inert material. For example, the addition of hydrogen to ethene:

$$CH_2{=}CH_2\ (g) + H_2\ (g) \rightarrow CH_3{-}CH_3\ (g)$$

Addition of halogens

When an alkene such as propene is bubbled through a solution of bromine at room temperature, the bromine solution is rapidly decolourized. This reaction doesn't need UV light to occur. The bromine joins to propene to form 1,2-dibromopropane:

$$CH_3CH{=}CH_2 + Br_2 \rightarrow CH_3CHBrCH_2Br$$

Chlorine and iodine produce similar reactions as bromine. This reaction is also a test for unsaturated hydrocarbons like ethene.

Addition of hydrogen halides

Hydrogen halides also react with alkenes in addition reactions. Ethene produces chloroethane when it is bubbled through concentrated hydrochloric acid:

$$CH_2{=}CH_2\ (g) + HCl\ (aq) \rightarrow CH_3CH_2Cl\ (l)$$

The reactivity of the hydrogen halides increases from HF to HI, following the order of decreasing bond energy. Alkenes such as propene can give rise to 2 different products.

Addition of steam

These reactions convert alkenes into alcohols. Steam and an alkene are mixed together in the presence of phosphoric acid to make an alcohol. A temperature of 600K and a pressure of 6MPa are used. For example, the addition of steam to ethene produces ethanol:

$$CH_2{=}CH_2\ (g) + H_2O\ (g) \rightarrow CH_3CH_2OH$$

Fission

Fission is the breaking of bonds. It can be of two types:

- Homolytic fission, in which a covalent bond is broken and the 2 atoms around the bond would each take one electron. This normally happens in non-polar molecules such as Cl_2. This process produces 2 free radicals:

  $$Cl\text{-}Cl\ (g) \rightarrow Cl^{\cdot}\ (g) + Cl^{\cdot}\ (g)$$

  The free radicals are noted by a dote representing an electron next to the free radical. The free radicals are very reactive, have high energy and are very unstable.

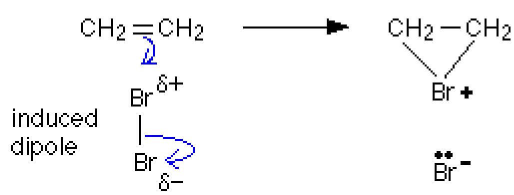
- Heterolytic fission, in which one atom in the covalent bond takes both electrons, becoming a negative ion and leaving a positive ion. This is process happens in polar molecules, including the ones that have induced poles. For example, in the electrophilic addition of bromine to alkenes, in which the bromine molecule becomes polarized due to the π-bond of the alkene.

$$Br\text{-}Br \rightarrow Br^{+} + Br{:}^{-}$$

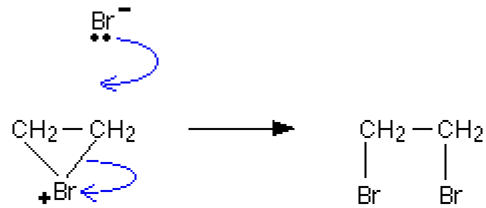
The mechanism of the reaction; how the reaction proceeds

Bromine and ethene are non-polar reagents. The bromine molecule becomes polarized when near to a region of negative charge, like the π-bond of ethene. In the first stage of the reaction, the π-bond breaks and the bromine molecule undergoes heterolytic fission, in which one of the bromine atoms takes all the electrons, becoming a negatively charge ion and the other atom becoming positively charged.

The positive ion becomes attached to both carbon atoms, with the positive charge being found on the bromine atom. A bromonium ion is formed, which is a carbocation.



The bromonium ion is then attacked from the back by a bromide ion formed in a nearby reaction.



In this reaction, the polarized bromine behaved as an electrophile, therefore the reaction is called the electrophilic addition of bromine.

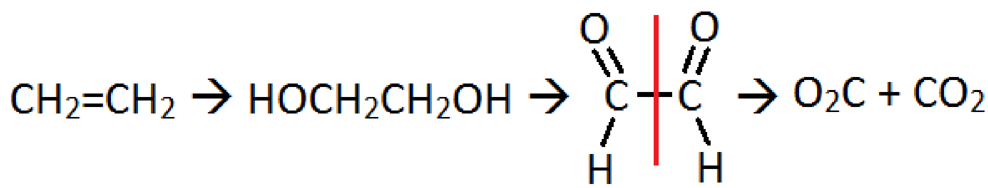
Reactions of alkenes with manganate (VII) ions

Alkenes undergo a different type of reaction with manganate (VII) ions, depending on the conditions:

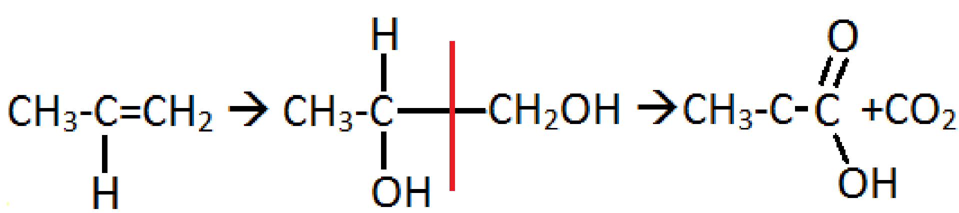
- With cold, acidified or alkaline dilute potassium manganate (VII) ions, the alkenes react readily at room temperature. The purple colour disappears and a diol is formed.

$$CH_2{=}CH_2 + H_2O + [O] \rightarrow HOCH_2CH_2OH$$

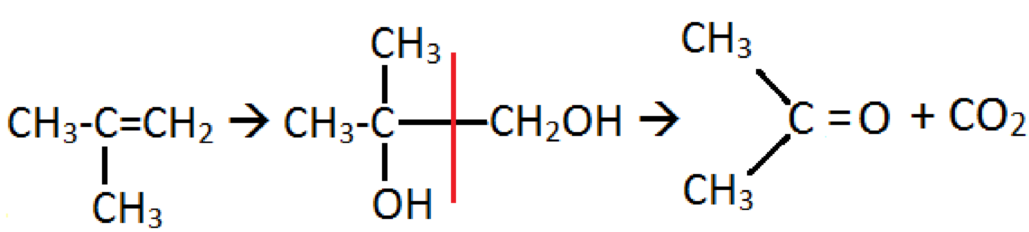
- With hot, acidified solution of potassium manganate (VII), any diol produced is split into fragments which are further oxidised into ketones or carboxylic acids.
  - Ethene oxidises into ethan-1,2-diol and then further oxidised into carbon dioxide



  - Propene will give Ethanoic acid and carbon dioxide

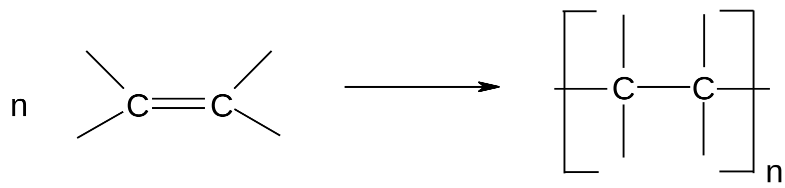


  - 2-methyl prop-1-ene will give Propanone and carbon dioxide



Polymerisation of alkenes

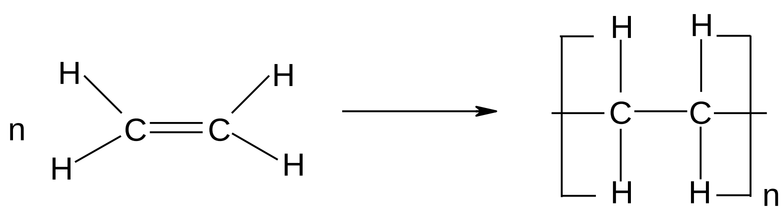
Alkenes can be made to join together in the presence of high pressure and a suitable catalyst. This is known as **addition polymerisation**.



The product of this addition process is a very long hydrocarbon chain. This is known as a polymer. Since it is a product of an addition reaction (unlike some other polymers) it is known as an **addition polymer**. Since it is made from an alkene it is known as a poly(alkene).

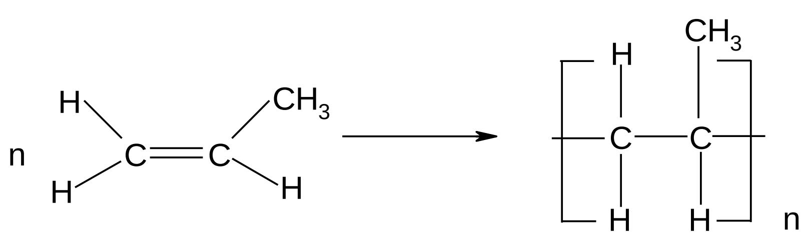
Poly(alkenes) are saturated, like alkanes. They are therefore unreactive.

Addition polymers can be made from any alkene:



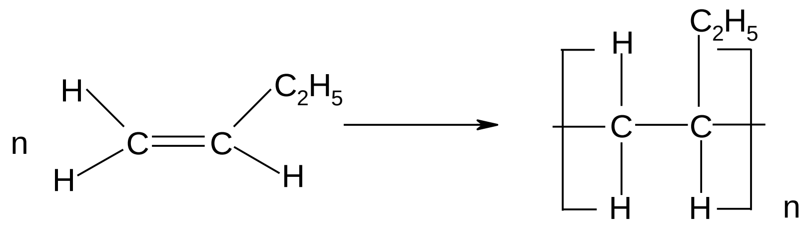
Eg ethene poly(ethene)

Poly(ethene) is most widely used in plastic shopping bags.

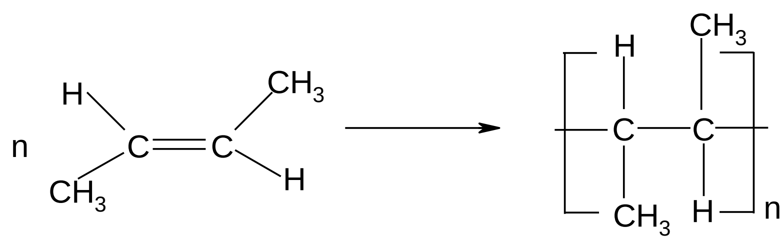


E.g. propene poly(propene)

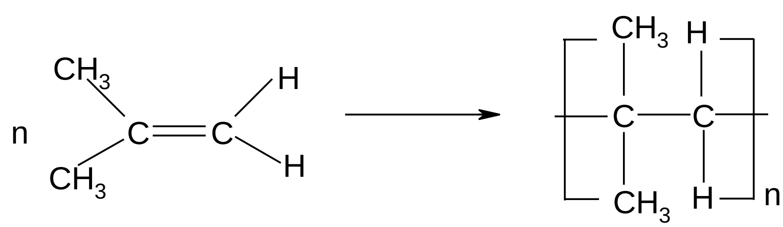
Poly(propene) is used in biros, straws and plastic food containers. It can be recycled commercially.



E.g. but-1-ene poly(but-1-ene)



Eg but-2-ene poly(but-2-ene)



E.g. 2-methylpropene poly(2-methylpropene)

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