

# ALKENES

Alkenes are unsaturated hydrocarbons. They have one or more C–C double bonds. Ethene,  $C_2H_4$ , is the simplest member of the alkene homologous series. Ethene has a number of effects on plant growth, it inhibits stem growth, it encourages buds to open, and promotes the ripening of fruit, When the plant starts to ripen it produces ethene, and the ethene produced promotes further ripening.

Alkenes have the general formula  $C_nH_{2n}$ . The first member is ethene, followed by propene. Longer chains than propene can form three different types of isomers:

1. those with different positioning of the double bond
2. cis-trans-isomers, example: but-2-ene
3. Chain branching isomers

When naming branched chain alkenes, the position of the double bond and of the side chains must be located, example: 2-methylbut-2-ene.

Compounds with more than one double bond are named using di-, tri-, etc. to indicate the number of double bonds as locants to show where they are, example: penta-1,3-diene.

The two carbon atoms in alkenes are  $sp^2$  hybridised, containing a  $\sigma$ -bond and a  $\pi$ -bond; and have a trigonal planar geometry around each carbon. The cloud of electrons which forms the  $\pi$ -bond lies above and below the plane of the three hybrid bonds formed by each of the unsaturated carbon atoms:

In these position, the  $\pi$ -electrons are more susceptible than the  $\sigma$ -electrons to attack by an - reagent. This is why alkenes are much more reactive than alkanes.

See Data Book, Table 9 and 10: Bond Energies:

Bond Type	Bond Energy(kJ mol <sup>-1</sup> )	Hybridisation	Bond Length
C – C	347	$\sigma$ bond	
C = C	612	$\sigma + \pi$ bond	

The  $\pi$ -bond has an energy equivalent to  $612 - 347 = 265$  kJ mol<sup>-1</sup>. Thus, as can be seen the  $\pi$ -bond in double bonds is easier to break, while the  $\sigma$ -bond remains intact. This happens in most reactions of  $C = C$ , the  $\pi$ -part of the double bond is broken, each of the carbon atoms is left capable of forming a new bond. Hence, allowing \_\_\_\_\_ reactions to take place.

The H–C–H bond angles in ethene are about  $118^\circ$ , less than  $120^\circ$ , because the four electrons in the  $C = C$  bond repel more than the pairs of electrons in the C–H single bonds. The structure of ethene is represented as:

No rotation is possible about the double bond, as this would break the  $\sigma$ -bond, thus leading to cis-trans isomerism in alkenes.

Example: but-2-ene

## Physical properties of alkenes

The double bond has little effect on the intermolecular forces which act between the molecules, so the physical properties of the alkenes are similar to those of the alkanes. Thus, the melting points and boiling points increase with increasing molecular mass. The cis-alkenes are generally more labile, having lower melting points than the trans-isomers, why?

Trans-isomers are less polar than the cis-isomers; polarity results from the asymmetrical distribution of electrons in a molecule, in trans the dipole moments are orientated in opposite directions and cancel each other.

## **REACTIONS OF ALKENES**

### Combustion

All alkenes burn to form  $\text{CO}_{2(g)}$  and  $\text{H}_2\text{O}_{(l)}$ . Alkenes with more than one double bond produce a noticeably sooty flame,  $\therefore$  of the higher percentage of carbon; unburnt carbon is left behind as soot. Alkenes are not normally used as fuels, because their reactivity makes them useful as starting materials to manufacture other important chemicals.

Write the balanced equation for the complete combustion of propene:

## **ADDITION REACTIONS**

Addition reactions can take place between carbon-carbon double bonds in alkenes or in carbon-oxygen double bonds in alkanals and alkanones.

### Addition to alkenes – **electrophilic addition**

The  $\text{C} = \text{C}$  as in ethene can be represented as...

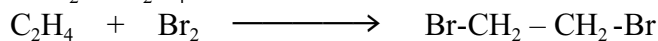
The double bond between the two C-atoms consists of a  $\sigma$ -bond and a weaker  $\pi$ -bond formed by the overlap of p-orbitals on the two C-atoms; which is highly reactive with a variety of reagents. The  $\pi$ -bond is formed by the overlap of the two parallel p-orbitals on the  $\text{sp}^2$  carbons- producing electron density above and below the plane of the carbons and hydrogens. Since the  $\sigma$ -bond has electron density concentrated in a line between the two carbon nuclei, it is very strong. However, the  $\pi$ -bond has much less electron density concentrated between the carbon nuclei due to the 'sideways overlap' of the p-orbitals,  $\pi$ -bond is a weaker bond ...

There is a concentration of negative charge between the two C-atoms making it susceptible to attack by electrophiles (positive species).

## Mechanism of Addition of Bromine to Alkenes

Alkenes react rapidly with chlorine gas or with solutions of bromine or iodine, in organic solvents, to produce dihaloalkanes. Unlike the reaction of alkanes with halogens, ultraviolet light is not required.

Consider the addition of Br<sub>2</sub> to C<sub>2</sub>H<sub>4</sub>:

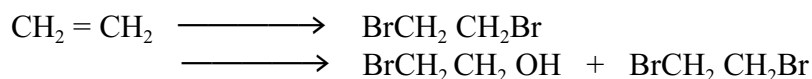


This is an addition reaction, the decolourisation of a bromine solution is used as a **test for the presence of carbon-carbon multiple bonds**.

The fact that the reaction takes place in the dark, this indicates that the reaction does not occur via a free radical mechanism as such as when an alkane reacts with halogens.

Evidence for the mechanism are:

- ethene reacts with bromine in an inert solvent to produce 1,2-dibromoethane, however, if bromine dissolved in water is reacted with ethene, some 2-bromoethan-1-ol is formed also.



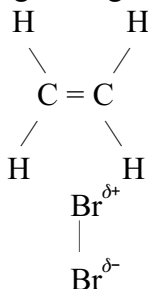
- if the bromine is dissolved in sodium chloride solution, Na<sup>+</sup>Cl<sup>-</sup><sub>(aq)</sub>, then some 1-bromo-2-chloroethane is also produced

**The following mechanism is proposed:**

Rate of the reaction  $\propto$  [alkene] [X<sub>2</sub>] ∴ the rate determining stage depends on...

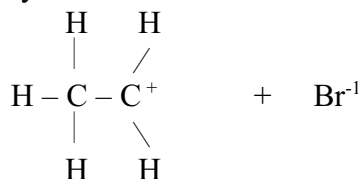
At any instant, a bromine molecule is likely to have an instantaneous dipole: Br<sup>δ+</sup> – Br<sup>δ-</sup>. This is because the electrons are in constant motion and at any moment are unlikely to be distributed exactly symmetrically.

The δ<sup>+</sup> end of this dipole, (acting as an electrophile), is attracted to the electron-rich π-bond in the alkene. The π-bond attracts the Br<sup>δ+</sup> and repels the electrons shared by the two bromine atoms, thus strengthening the dipole:



Eventually, two of the electrons from the π-bond form a bond with the bromonium ion, Br<sup>δ+</sup>, and the electrons shared by the bromine atoms are repelled away from the Br<sup>δ-</sup> to form a Br<sup>-</sup> ion. (Use **curly arrows** to represent the movement of a pair of electrons from the tail of the arrow to its tip.)

This leaves a positively charged species which is called a carbocation; the positive charge on the carbocation is localised on the carbon atom that is not bonded to the bromine, because the C-atom is forming only three bonds:



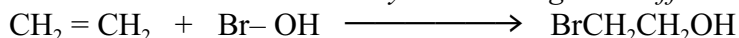
The carbocation is immediately attacked by any negative ion. The only negative ion present in a non-aqueous solution will be the  $\text{Br}^{-1}$ , however in aqueous solution the  $\text{OH}^{-1}$  will be present, as well as the  $\text{Cl}^{-1}$  in a solution of sodium chloride; thus accounting for the formation of 1,2-dibromoethane, 2-bromoethan-1-ol and 1-bromo-2-chloroethane.

**In conclusion the addition of bromine takes place in two steps:**

1. formation of the carbocation, followed by
2. rapid reaction with a negative ion.

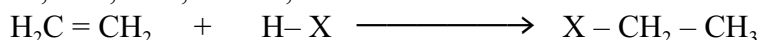
The whole sequence of reaction is an **electrophilic addition reaction**.

*Bromine water is also decolourised by alkenes to give a different product, bromoalcohol:*



**Mechanism of Addition of Hydrogen Halide to Alkenes**, (“the rich get richer”)

Hydrogen halides, HCl, HBr, and HI, add on across the double bond to form haloalkanes:



The reaction between HBr and  $\text{C}_2\text{H}_4$  has a similar mechanism to that for the addition of bromine. A molecule of hydrogen bromide,  $\text{H}^{\delta+} - \text{Br}^{\delta-}$  is permanently polarised, the  $\pi$ -electrons of the alkene bond to the electrophilic H atom:

This is the slow step in the reaction. Once formed, the carbocation,  $\text{CH}_2^+ - \text{CH}_3$ , reacts rapidly with the bromide ion,  $\text{Br}^{-1}$ :

**Evidence for the mechanism:**

1. The rate of addition increases with increasing acid strength:  $\text{HCl} < \text{HBr} < \text{HI}$ , this is to order of readiness to release a proton. The reaction of the carbocation with the  $\text{X}^{-1}$  is rapid, and its speed is much the same for all  $\text{X}^{-1}$  ions.
2. Addition follows Markovnikov’s Rule: when hydrogen halides react with alkenes, the hydrogen adds on to the carbon atom that already has most hydrogens, or “the rich get richer”. Markovnikov’s Rule can be explained by the carbocation theory.

Consider the addition reaction between propene,  $\text{C}_3\text{H}_6$  and HBr, in theory two products are possible...

This can occur because the groups attached to the two C-atoms, joined by the double bond, are different. The alkene is not symmetrical.

In practice, addition produces 2-bromopropane only according to Markovnikov’s Rule:

During addition reactions the more negative part of the molecule adding on to the alkene adds to the carbon atom attached to the lesser number of hydrogen atoms.

Markownikoff’s Rule can be explained in terms of the stability of carbonium ions, (alkyl substituents stabilize carbocations,  $3^{\circ} > 2^{\circ} > 1^{\circ}$ ). Depending upon which carbon atom the  $\text{H}^{+1}$  of the HBr attaches to, there are two possible carbonium ions which can be formed:

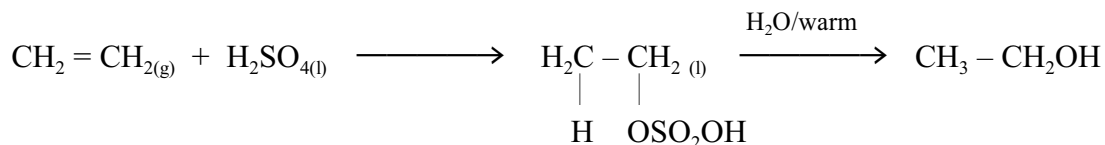
The *secondary carbonium ion is more stable than the primary carbonium ion*. **Why?**

It is therefore formed in preference to the primary carbonium ion and leads to the formation of 2-bromopropane.

## Reaction with Concentrated Sulphuric Acid

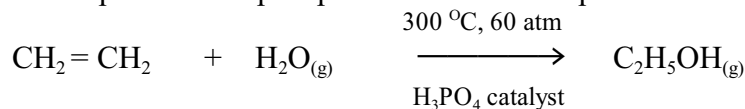
The addition of concentrated sulphuric acid across a double bond is similar to that of a hydrogen halide, electrophilic addition of  $\text{H}^+ \cdot \text{O}^- \text{SO}_3\text{H}$ . The  $\text{H}^+$  ion acting as the electrophile, the carbocation being then immediately attacked by the negatively charged hydrogen sulphate ion. With an unsymmetrical alkene, Markovnikov's Rule is followed; the hydrogen bonds to the carbon atom which already has more hydrogens.

When ethene is bubbled into concentrated sulphuric acid at room temperature, addition across the double bond occurs exothermically, producing ethyl hydrogen sulphate:



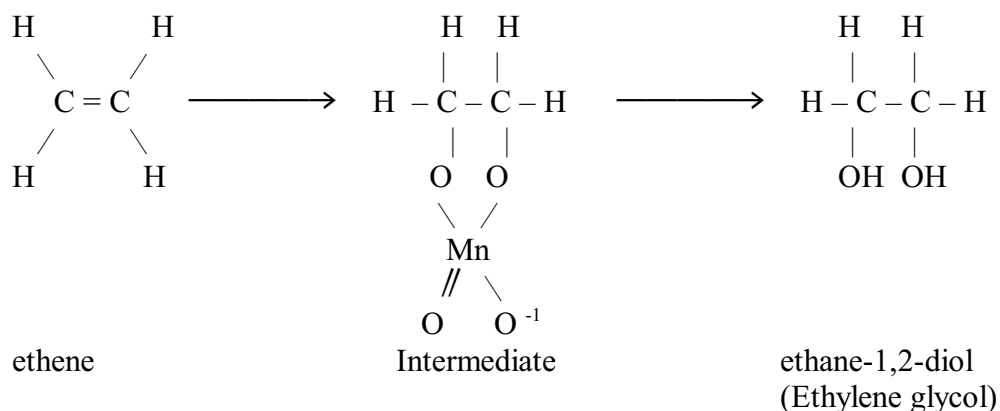
Ethyl hydrogen sulphate, upon warming and addition of water, undergoes hydrolysis to form ethanol. The net result is the addition of  $\text{H} - \text{OH}$  across the double bond.

The industrial method of accomplishing this is the catalytic hydration of ethene. Ethene and steam are passed over phosphoric acid on silica pellets at  $300^\circ\text{C}$  and 60 atm:



## Oxidation of Alkenes: alkaline Potassium Manganate (VII)

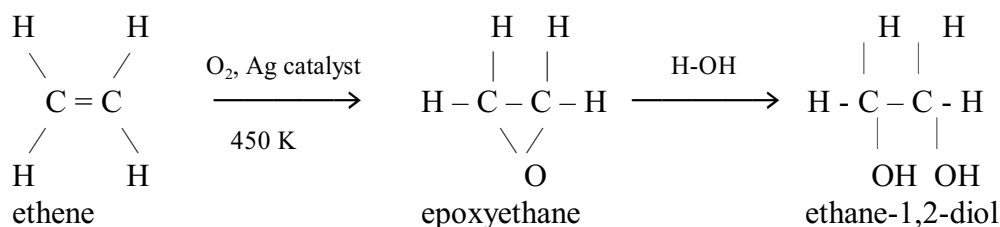
Potassium manganate(VII) in alkaline solution is a weak oxidising agent, ( $\text{Mn}^{+7} + 3\text{e}^- \rightarrow \text{Mn}^{+4}$  is a reduction in the electrochemical sense, the organic compound is oxidised). Alkenes can be oxidised by cold, dilute, aqueous  $\text{KMnO}_4$ , the purple colour of the  $\text{MnO}_4^-$  ion disappears rapidly and a precipitate of brown manganese (IV) oxide appears, also yielding a diol, (FYI: a diol is a compound containing two hydroxyl groups).



This reaction is used as an alternative **test for carbon – carbon multiple bonds**, (other test is -----?).

Ethane -1,2-diol (formerly called ethylene glycol) is used as 'antifreeze' in vehicle radiators to lower the freezing temperature of water.

Industrially ethane-1,2-diol is prepared by the reaction of ethene with oxygen using silver catalyst, producing epoxyethane:



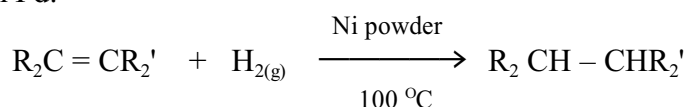
Epoxyethane is unstable, and therefore very reactive, due to ring strain. The C – C – O bond and C – O – C bond angle must both be 60° whereas the normal bond angle should be 109.5°. Epoxyethane reacts with water to form ethane-1,2-diol, being used to prepare antifreeze, polyesters (such as Terylene), polymers and in plasticizers used to improve the flexibility of plastics.

### Addition of Hydrogen: Reduction

Catalytic hydrogenation is the reductive process of adding molecular hydrogen to a double bond with the aid of a metal catalyst. Typical catalysts are transition metals such as platinum, palladium, and nickel (usually Raney nickel, a special powdered form), but occasionally rhodium, iridium, or ruthenium are used. These metals are able to act as catalysts because they have variable oxidation state.

The reaction takes place on the surface of the catalyst, (**heterogeneous catalysis** — the reactants must be adsorbed on the catalyst, and, after the reaction, the products must be desorbed. Some transition metals, e.g. tungsten, adsorb too strongly and are ∴ not effective, whilst other transition metals, e.g. Ag, adsorb too weakly to catalyse the reaction. Pt, Ni, and other transition metals have the right ability to adsorb the reactants and release the products).

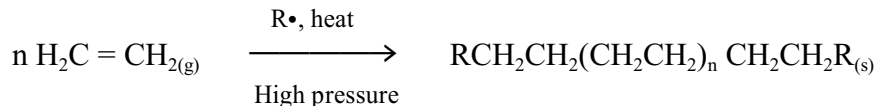
Hydrogen is added across the double bonds, using Ni as the catalyst, since it is less expensive than Pd:



Catalytic hydrogenation is used industrially in the manufacture of margarines. Plant oils, such as sunflower seed oil and peanut oil, are “polyunsaturates”: they are esters of carboxylic acids which contain more than one carbon – carbon double bond. They are ‘hardened’ by reducing the number of double bonds, i.e. hydrogenation converts unsaturated edible oils into edible fats. In soft margarine some of the double bonds remain: the degree of softness can be controlled by regulating the amount of hydrogenation. Saturated oils have higher melting points than unsaturated ones because their molecules are more regularly shaped and pack together better, making them harder to separate.

## Polymerisation

Polymerisation is the creation of long, high molecular mass (up to  $1 \times 10^6$ ), chains of polymers, composed of repeating subunits, called monomers. Polymerization usually occurs through a radical mechanism, (although anionic and even cationic polymerisation are observed, depending on the conditions). A typical example is the formation of poly(ethene), often called polythene for short, from ethene, (ethylene), under high temperatures and pressures:



This type of reaction is called **addition polymerisation** as no molecule is eliminated, (see notes on Polymerisation for other examples of Polyalkenes).

Use of powerful catalysts, (Ziegler-Natta catalysts, these are a mixtures of triethyl aluminium and titanium(IV) chloride, proceeding via an ionic mechanism), nowadays, enable the addition reaction to take place at atmospheric pressure. The polythene formed at high pressure is a low density, (a product with side chains, and thus of lower molecular mass,  $1 \times 10^5$ ), extremely pliable material, used for making plastic bags. While the polymer formed at low pressure is of a higher density and is tougher, (a product with no chain branching and a higher molecular mass), used for kitchenware, food boxes, bowls, buckets, etc.

### ASSIGNMENT

- Hydrocarbon, A, contains 85.71 % carbon.
  - Show that the empirical formula of A is  $\text{CH}_2$ .
  - Given that the relative molecular mass of A is 56, derive its molecular formula.
  - Draw the structural formula of one of the possible isomers of A.
  - Show the reaction of this isomer with  $\text{HBr}$ , and clearly indicate the mechanism of this reaction, stating the major product and the minor product obtained in this reaction.
  - State two possible tests with results that may be successfully performed on A, indicating the homologous series that A may belong to.
- Give the names and formulae of the products formed when the following reagents add to propene:
  - chlorine in tetrachloromethane
  - chlorine water

Write the mechanism for each reaction.

- When propene is bubbled through chlorine water containing nitrate ions, three products are formed. Give the names and formulae of the three products, and explain how they come to be formed. What product do you think would be formed in the reaction between propene and nitrogen chloride oxide,  $\text{NOCl}$ , which reacts as  $\text{NO}^+\text{Cl}^-$ ?
- Complete the following equations, indicating the conditions needed for the reaction:
  - $\text{CH}_2 = \text{CH}_2 + \underline{\hspace{2cm}} \xrightarrow{\hspace{2cm}} \text{CH}_3\text{CH}_2\text{OH}$
  - $(\text{CH}_3)_2\text{C} = \text{CH}_2 + \text{Br}_2 + \text{H}_2\text{O} \xrightarrow{\hspace{2cm}}$
  - $\text{CH}_3\text{CH} = \text{CH}_2 + \text{HBr} \xrightarrow{\hspace{2cm}}$
  - $\text{CH}_3\text{CH} = \text{CH}_2 + \text{H}_2\text{O} (\text{H}_3\text{PO}_4, \text{catalyst}) \xrightarrow{\hspace{2cm}}$
  - $\text{CH}_3\text{CH}_2\text{CH} = \text{CH}_2 + \underline{\hspace{2cm}} \xrightarrow{\hspace{2cm}} \text{CH}_3\text{CH}_2\text{CHOHCH}_2\text{OH}$