ALKENES

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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 structure:

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: pent-1,3-diene.

Structure and Bonding

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

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

Bond Type	**Bond Energy(kJ mol^{-1})**	**Hybridisation**	**Bond Length (nm)**
C – C	347	σ bond	0.154
C = C	612	σ + π bond	0.134

The π-bond has an energy equivalent to 612 - 347 = 265 kJ mol^{-1}. Thus, as can be seen the π-bond in double bonds is easier to break, while the σ-bond remains intact. This happens in most reactions of C = C, the π-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, as opposed to __________reactions in alkanes.

The H– C– H bond angles in ethene are about 118^0, less than 120^0, 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 σ-bond. As a result of hindered, i.e. restricted rotation about the double bond, geometrical isomerism, i.e. cis -trans isomerism is exhibited by alkenes.

Example: but-2-ene

Example: 1, 2-dichloroethene

Example: 1, 1-dichloroethene

Thus, if there are identical groups on a carbon atom, then geometrical isomerism is not exhibited.

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, (type of IMFA ....?).

Thus, the melting points and boiling points increase with increasing molecular mass.

The cis-alkenes are generally more labile, (i.e. ....), 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 $CO_{2(g)}$ and $H_2O_{(l)}$.

Alkenes with more than one double bond produce a noticeably sooty flame, .: 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, C_3H_6:

Addition Reaction of Alkenes

Addition reactions can take place between carbon-carbon double bonds in alkenes.

The C = C as in ethene can be represented as…

The double bond between the two C-atoms consists of a σ-bond and a weaker π -bond formed by the overlap of p-orbitals on the two C-atoms; which is highly reactive with a variety of reagents.

The π-bond is formed by the overlap of the two parallel p-orbitals on the sp^2 carbons- producing electron density above and below the plane of the carbons and hydrogens.

Since the σ-bond has electron density concentrated in a line between the two carbon nuclei, it is very strong.

However, the π-bond has much less electron density concentrated between the carbon nuclei due to the 'sideways overlap' of the p-orbitals,
π-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).

1. Addition of a Halogen, X_2

Consider the addition of Br_2 to C_2H_4:

$$C_2H_4 + Br_2 \longrightarrow Br\text{-}CH_2 - CH_2\text{-}Br$$

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

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

$$CH_2 = CH_2 + Br{-}OH \longrightarrow BrCH_2CH_2OH$$

Write an equation for the addition of bromine to:
a. propene

b. but-2--ene

2. Addition of Hydrogen Halide, HX, to Alkenes

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

$$H_2C = CH_2 + H{-}X \longrightarrow X - CH_2 - CH_3$$

Consider the addition reaction between propene,C_3H_6 and HBr, in theory two products are possible…

$$H_3C - CH = CH + HX \longrightarrow$$

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:

3. Addition of Concentrated Sulphuric Acid

The addition of concentrated sulphuric acid across a double bond is similar to that of a hydrogen halide, addition of H^{+1}-$O^{-1}SO_3H$

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

$$CH_2 = CH_{2(g)} + H_2SO_{4(l)} \longrightarrow \underset{H}{H_2C} - \underset{OSO_2OH}{CH_{2\ (l)}} \xrightarrow{H_2O/warm} CH_3 - CH_2OH$$

Ethyl hydrogen sulphate, upon warming and addition of water, undergoes hydrolysis to form ethanol. The net result is the addition of H– 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 ^{O}C and 60 atm:

$$CH_2 = CH_2 \quad + \quad H_2O_{(g)} \xrightarrow[H_3PO_4 \text{ catalyst}]{300\ ^{O}C,\ 60 \text{ atm}} C_2H_5OH_{(g)}$$

4. Oxidation of Alkenes: acidic Potassium Manganate (VII)

Alkenes can be oxidised by cold, dilute, acidic $KMnO_4$, the purple colour of the MnO_4^{-1} ion disappears rapidly, producing a diol, (FYI: a diol is a compound containing two hydroxyl groups).

Reaction of ethene with acidified $KMnO_4$:

Write an equation for the reaction of propene with acidified $KMnO_4$:

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.

5. 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:

$$R_2C = CR_2' + H_{2(g)} \xrightarrow[100\ ^{O}C]{\text{Ni powder}} R_2\,CH - CHR_2'$$

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.

POLYMERIZATION

Polymerisation is the creation of long, high molecular mass (up to 1×10^6), chains of polymers, composed of repeating subunits, called **monomers**.
A typical example is the formation of poly(ethene), often called polythene for short, from ethene, (ethylene), under high temperatures and pressures:

$$n\ H_2C = CH_{2(g)} \xrightarrow[\text{High pressure}]{R\bullet,\ \text{heat}} RCH_2CH_2(CH_2CH_2)_n\ CH_2CH_2R_{(s)}$$

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, 1×10^5), 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

1. Hydrocarbon, A, contains 85.71 % carbon.
a) Show that the empirical formula of A is CH_2.
b) Given that the relative molecular mass of A is 56, derive its molecular formula.
c) Draw the structural formula of one of the possible isomers of A.
d) Show the reaction of this isomer with HBr, and clearly indicate the mechanism of this reaction, stating the major product and the minor product obtained in this reaction.
e) State two possible tests with results that may be successfully performed on A, indicating the homologous series that A may belong to.
2. Give the names and formulae of the products formed when the following reagents add to propene:(a) chlorine in tetrachloromethane
(b) chlorine water