

**An
Introduction
to
Organic
Chemistry**

Organic Chemistry

Organic chemistry is the study of compounds containing carbon with the exception of simple compounds e.g. carbonates (CO_3^{2-}), carbon dioxide (CO_2) and carbon monoxide (CO).

Nomenclature

There are over 6 million known organic compounds. **Nomenclature** is therefore very important.

Here are some basic guidelines that should help in the naming of the simple compounds you will come across during this course. You will get practice at this in your tutorials.

- 1) Find the longest carbon chain in the molecule. This will give you the base of the name:

No of C atoms	Name
1	meth-ane
2	eth-ane
3	prop-ane
4	but-ane
5	pent-ane
6	hex-ane
7	hept-ane
8	oct-ane
9	non-ane
10	dec-ane

2) Determine the principle functional group and its position.

<i>principal functional group</i>	<i>formula</i>	<i>ending becomes</i>
<i>alkane</i>	C-C	-ane
<i>alkene</i>	C=C	-ene
<i>alkyne</i>	C≡C	-yne
<i>alcohol</i>	-OH	-anol
<i>aldehyde</i>	-CH=O	-anal
<i>ketone</i>	>C=O	-anone
<i>carboxylic acid</i>	-COOH	-anoic acid

Position is indicated, where necessary, by numbering the carbons in the main chain. Position need not be indicated for alkanes, as they have no functional group, and aldehydes and acids, as they are terminal functional groups. Positioning numbers are flanked by dash signs. Multiple positions for a given functional group are separated by commas and indicated by the prefixes di, tri, tetra, penta, hexa, hepta, octa, nona and deca.

3) Ancillary functional groups are given in alphabetical order, with their position at the beginning of the name.

<i>ancillary functional group</i>	<i>formula</i>	<i>prefix</i>
<i>methyl</i>	-CH ₃	methyl
<i>ethyl</i>	-C ₂ H ₅	ethyl

propyl	$-\text{C}_3\text{H}_7$	propyl
butyl	$-\text{C}_4\text{H}_9$	butyl
pentyl	$-\text{C}_5\text{H}_{11}$	pentyl
hexyl	$-\text{C}_6\text{H}_{13}$	hexyl
heptyl	$-\text{C}_7\text{H}_{15}$	heptyl
octyl	$-\text{C}_8\text{H}_{17}$	octyl
nonyl	$-\text{C}_9\text{H}_{19}$	nonyl
decyl	$-\text{C}_{10}\text{H}_{21}$	decyl
fluorine	-F	fluoro
chlorine	-Cl	chloro
bromine	-Br	bromo
iodine	-I	iodo
amine	$-\text{NH}_2$	amino
hydroxyl	-OH	hydroxy
cyanide	-CN	cyano
benzyl	$-\text{CH}_2\text{C}_6\text{H}_5$	benzyl
phenyl	$-\text{C}_6\text{H}_5$	phenyl

Empirical and Molecular Formulae

Quantitative elemental analysis tells us what elements make up a compound and in what proportions.

The percentage of each element present in a compound is determined by total combustion. C, H, S and N burn to give CO_2 , H_2O , SO_2 and NO_2 . The quantities of these gases may readily be measured and this leads to information that can be used to calculate the % composition and hence **empirical** and **molecular formulae**.

How is this done? First some definitions:

One mole of a substance is 6.02×10^{23} particles of that substance. This huge value is termed **Avogadro's number**. One mole of any substance has a mass equal to the **relative molecular mass** (RMM) of that substance in grams.

Relative molecular mass is the sum of the **relative atomic masses** (RAMs) of the constituent elements in the compound.

e.g. for ethanol C_2H_5OH

$$\begin{aligned} \text{RMM} &= (2 \times 12.010 \text{ g mol}^{-1}) + (6 \times 1.006 \text{ g mol}^{-1}) + (15.999 \text{ g mol}^{-1}) \\ &= 46.057 \text{ g mol}^{-1} \end{aligned}$$

0.152 g of an organic compound X containing only C, H and O produces:

0.223 g of CO_2

0.091 g of H_2O

upon total combustion. Calculate the empirical formula of the compound X.

Consider the CO_2

$$CO_2 \text{ RMM} = 12.010 \text{ g mol}^{-1} + 2 \times 15.999 \text{ g mol}^{-1} = 44.008 \text{ g mol}^{-1}$$

$$0.223 \text{ g of } CO_2 = 0.223 \text{ g} / 44.008 \text{ g mol}^{-1} = 5.07 \times 10^{-3} \text{ mol}$$

5.07×10^{-3} mol of CO_2 were produced from 5.07×10^{-3} mol of C

$$\text{The mass of C} = 5.07 \times 10^{-3} \text{ mol} \times 12.010 \text{ g mol}^{-1} = 0.061 \text{ g}$$

$$\% \text{ C in X} = 100\% \times 0.061 \text{ g} / 0.152 \text{ g} = 40.1\%$$

Consider the H₂O

$$\text{H}_2\text{O RMM} = 2 \times 1.006 \text{ g mol}^{-1} + 15.999 \text{ g mol}^{-1} = 18.011 \text{ g mol}^{-1}$$

$$0.091 \text{ g of H}_2\text{O} = 0.091 \text{ g} / 18.011 \text{ g mol}^{-1} = 5.05 \times 10^{-3} \text{ mol}$$

$$5.05 \times 10^{-3} \text{ mol of H}_2\text{O were produced from } 1.01 \times 10^{-2} \text{ mol of H}$$

$$\text{The mass of C} = 1.01 \times 10^{-2} \text{ mol} \times 1.006 \text{ g mol}^{-1} = 0.010 \text{ g}$$

$$\% \text{ C in X} = 100\% \times 0.010 \text{ g} / 0.152 \text{ g} = 6.7\%$$

Consider the O

$$\% \text{ O in X} = 100\% - 40.1\% - 6.7\% = 53.2\%$$

Mass % are used to calculate mole % which yield the empirical formula or simplest ratio of the elements present.

	C	H	O
<i>relative mass %</i>	40.1	6.6	53.2
<i>divide by RAM</i>	12.010	1.006	15.999
<i>relative mole %</i>	3.3	6.6	3.3
<i>divide by smallest</i>	1	2	1

This gives the ratio 1:2:1 and the empirical formula CH₂O. The molecular formula could be any multiple of the empirical formula e.g. C₂H₄O₂, or C₃H₆O₃ since these would all have the same percentage mass ratios.

$$5.05 \times 10^{-3} \text{ mol of C means } 5.05 \times 10^{-3} \text{ mol of X in } 0.152 \text{ g}$$

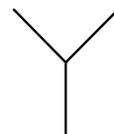
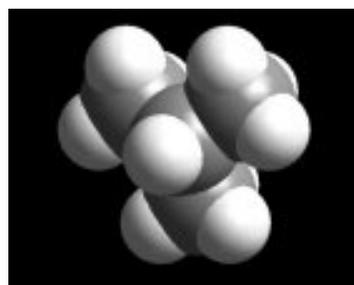
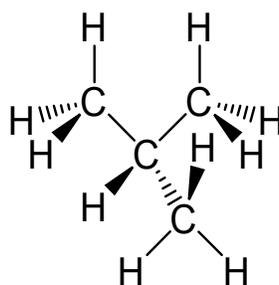
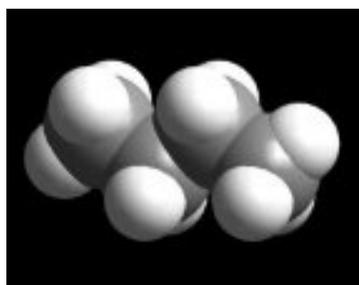
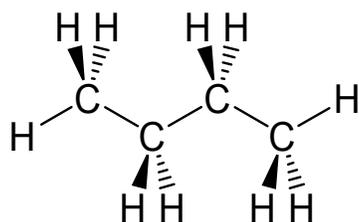
$$\text{RMM of X} = 0.152 \text{ g} / 5.05 \times 10^{-3} \text{ g mol}^{-1} = 30.10 \text{ g mol}^{-1}$$

The molecular formula is also CH₂O and X is actually methanal or formaldehyde.

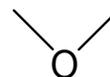
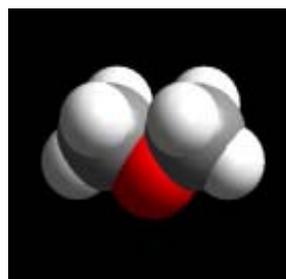
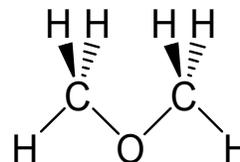
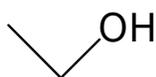
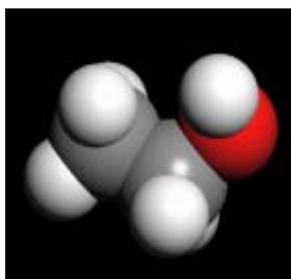
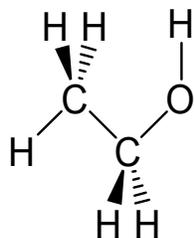
Structural and Isomerism Structural Formulae

Different arrangements of atoms for a given molecular formula are often possible. Such compounds are called isomers.

Example one: C_4H_{10}



Example two: C₂H₆O



Both exemplify **structural isomerism**. C₄H₁₀ is a molecular formula as it shows constituent atoms. CH₃HC₂CH₂CH₃ is a structural formula as it shows constituent atoms AND connectivities.

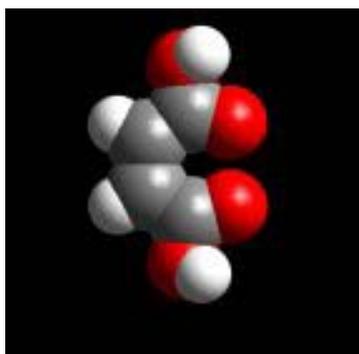
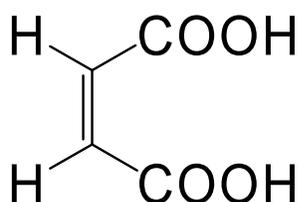
Stereoisomerism

It is also possible to arrange the atoms in molecules with the same structural formulae such that they have different spatial orientation. This is known as **stereoisomerism**. There are two distinct types of **stereoisomer**: **geometric** and **optical**.

Geometric isomerism

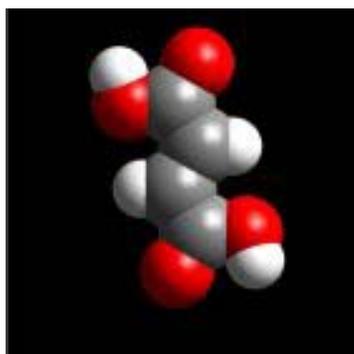
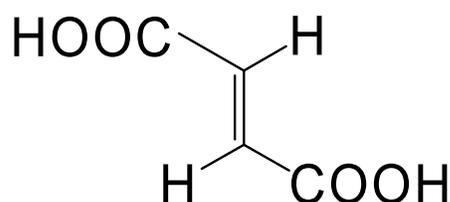
It is possible for single C-C bonds to rotate freely, however, double C=C bonds cannot.

Thus if the two carbon atoms of a C=C bond carry different groups, it becomes possible to orientate these groups in two ways to create **geometric isomers**.



cis-isomer

Z (🇩🇪 Zusammen - together)



trans-isomer

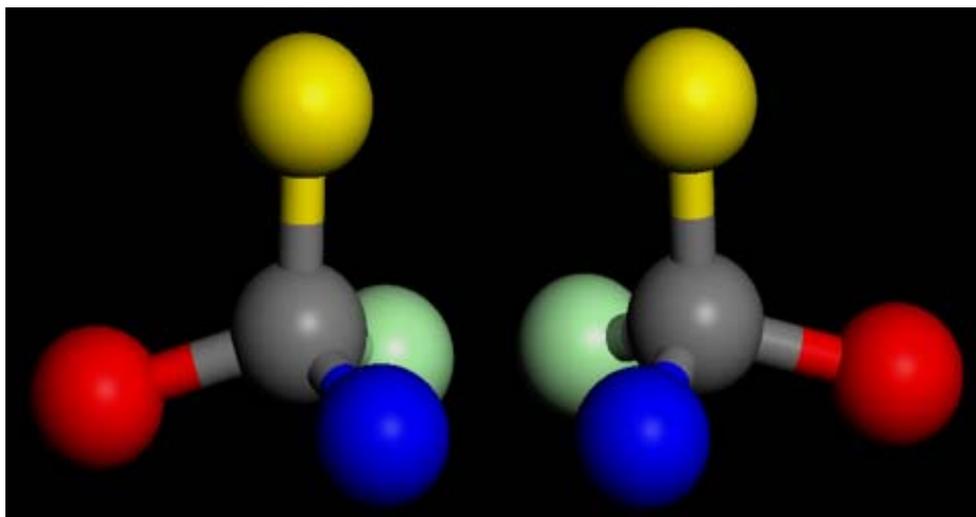
E (🇩🇪 Entgegen - opposite)

Geometric isomers have *different* physical and chemical properties

Optical isomerism

A carbon atom attached to four *different* groups (**substituents**) is termed a **chiral** centre.

Two *different* **non-superimposable** mirror images are possible.



These mirror images are called **enantiomers**.

Enantiomers have identical physical properties, except for the direction in which they rotate the plane of plane polarised light.

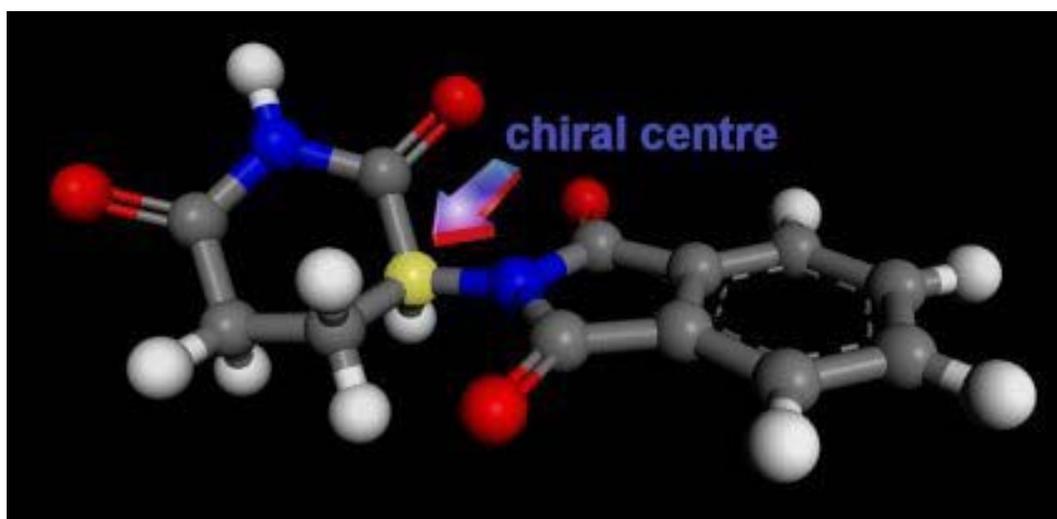
Rotation to right termed *dextro* or *d*

Rotation to left termed *laevo* or *l*

They have identical chemical properties except towards optically active reagents.

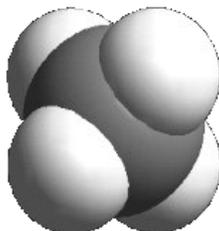
If a compound contains a chiral centre but does not rotate the plane of plane polarised light then it must be an equal mixture of *d*- and *l*-enantiomers. Such a mixture is termed a **racemic** mixture or a **racemate**.

Stereochemistry is crucially important to the pharmaceutical industry. The drug thalidomide, prescribed to pregnant women as a powerful sedative from 1956 exists as two enantiomers. One was the powerful sedative. The other caused human transmutation...



Hybridisation

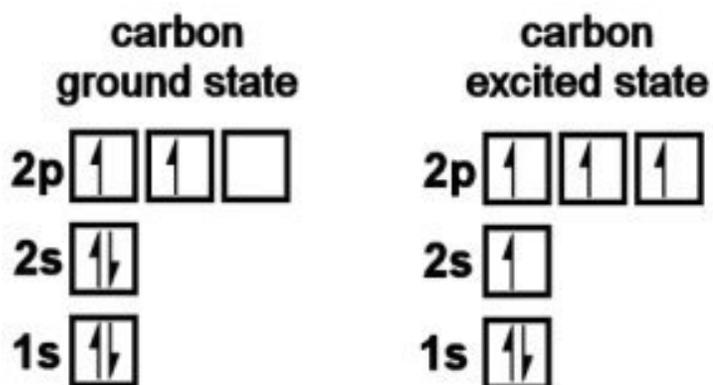
The simplest organic molecule is methane CH₄.



The **ground electronic state** of carbon suggests it should form 2 bonds as there are two unpaired electrons.

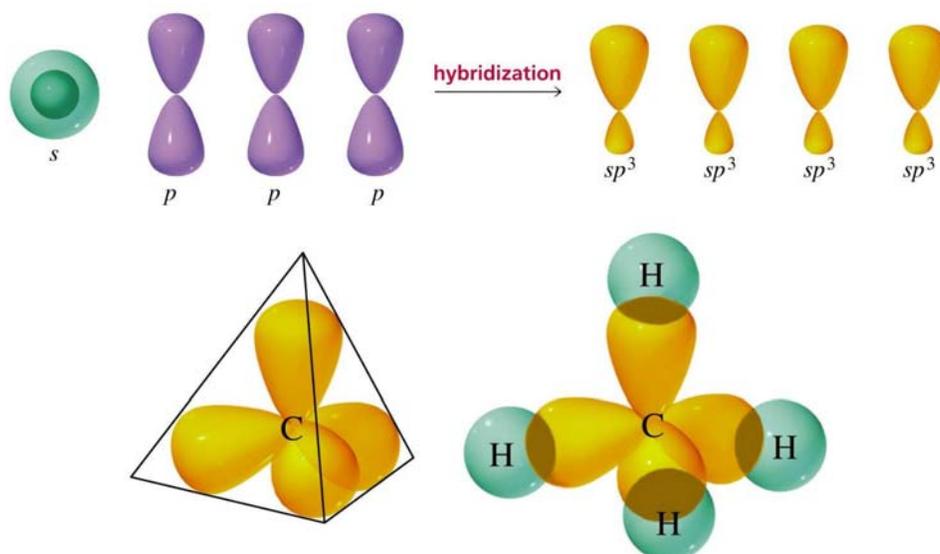
Q How and why does carbon form 4 bonds?

A

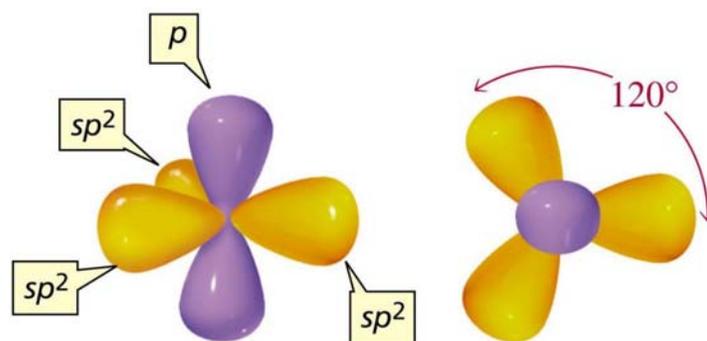


Promotion of one of the two 2s electrons increases energy but the formation of four bonds causes a four-fold decrease.

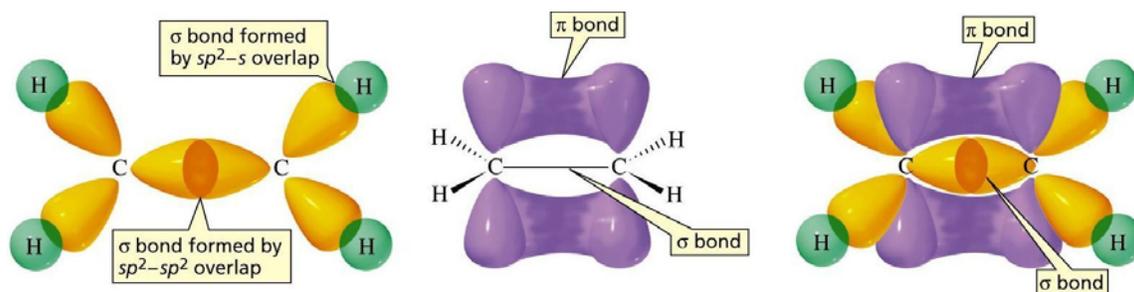
Q How can the four bonds formed be identical?

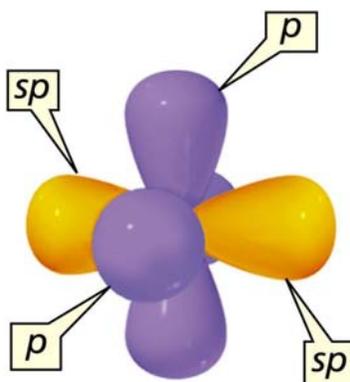


This mixing of an s orbital and three p orbitals to produce four hybrid orbitals is called **sp³ hybridisation**. ALL tetrahedral carbon and nitrogen atoms in organic chemistry are sp³ hybridised.

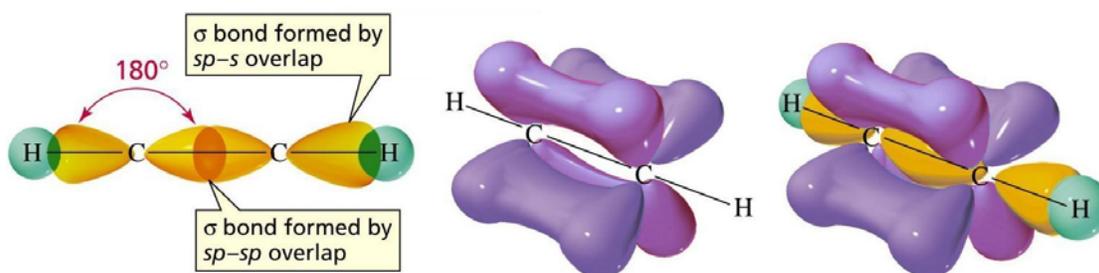


ALL trigonal carbons such as those found in double bonds are **sp² hybridised**. The unused p orbital on each carbon overlaps to form the π part of the double bond, e.g. ethene.





ALL linear carbons such as those found in triple bonds are **sp hybridised**. The unused p orbitals on each carbon overlap to form the π parts of the triple bond, e.g. ethyne (acetylene).



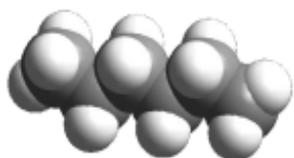
Hydrocarbons

Hydrocarbons are a family of compounds containing only hydrogen and carbon. There are two main classes:

aliphatic and aromatic

Within the aliphatic class there are both saturated and unsaturated hydrocarbons.

The Alkanes



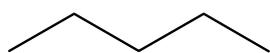
A homologous series of saturated compounds with general molecular formula C_nH_{2n+2} (where n is an integer).

methane CH_4 , ethane C_2H_6 , propane C_3H_8 , butane C_4H_{10} , pentane C_5H_{12} , hexane C_6H_{14} , heptane C_7H_{16} , octane C_8H_{18} , nonane C_9H_{20} , decane $C_{10}H_{22}$, etc.

Homologous series: a series of compounds in which each successive compound differs from the previous one by a CH_2 unit.

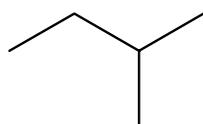
At $n = 4$ it becomes possible to arrange the carbon skeleton differently *i.e.* it becomes possible for structural isomers to exist. The result is termed branching of the C-C backbone.

How does this affect a physical property such as the boiling point?



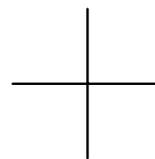
n-pentane

36 °C



2-methylbutane

28 °C



2,2-dimethylpropane

9 °C

As branching increases, the strength of the **van der Waals** interactions between molecules decreases, resulting in the lowering of boiling points.

Occurrence

Natural gas - principally methane CH_4

Petroleum oil - mixture up to *ca.* $n = 40$

Separation of crude oil is achieved by **fractional distillation**. This forms the basis of the petroleum and petrochemical industries.

Chemistry

Relatively, alkane chemistry is very limited.

Their main use is as fuels for **combustion** or **oxidation**.

Methane domestic gas supply

Propane LPG (liquid propane gas)

Butane camping stove gas

Octane petrol

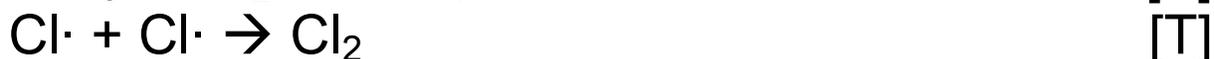
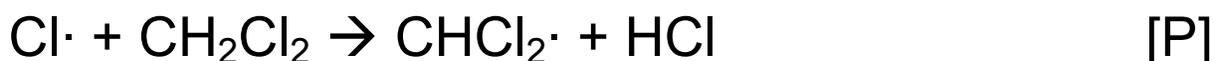
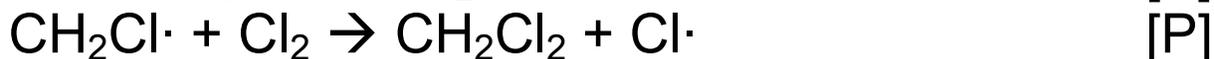
Complete combustion yields carbon dioxide and water. Incomplete combustion is dangerous as it produces carbon monoxide. Always provide a good supply of air to any process in which a hydrocarbon is being burned



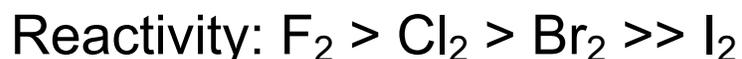
Chemically this is more accurately described as oxidation. Both reactions produce energy in the form of heat and are said to be **exothermic**.

Halogenation

In the presence of a halogen and ultraviolet light a series of reactions take place:



The first step is **homolytic fission** of the halogen to produce halide radicals. This is termed the **initiation step**, [I]. Radicals are extremely reactive species with single unpaired electrons denoted \cdot . Radicals react with non-radical and radical species in **propagation** and **termination steps**, [P] and [T] respectively. The result is an extensive, indiscriminate mixture of halogenated hydrocarbons that is very expensive to separate.



Provides an albeit prohibitively expensive route to useful compounds since polarity (and thus chemical reactivity) has been introduced.

Cracking

This is enormously important industrially. The bonds in longer chain alkanes are cleaved using heat in a process called **pyrolysis**. The process produces smaller more useful hydrocarbon molecules.

The Alkenes

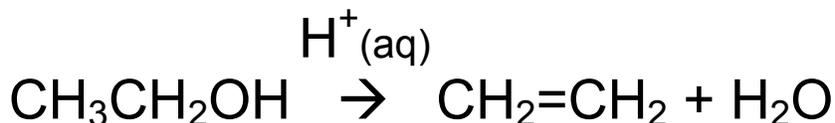


A homologous series of unsaturated compounds with general molecular formula C_nH_{2n} (n is an integer greater than 1) that contain a double bond.

ethene C_2H_4 , propene C_3H_6 , butene C_4H_8 , pentene C_5H_{10} , hexene C_6H_{12} , heptene C_7H_{14} , octene C_8H_{16} , nonene C_9H_{18} , decene $C_{10}H_{20}$, etc.

Preparation

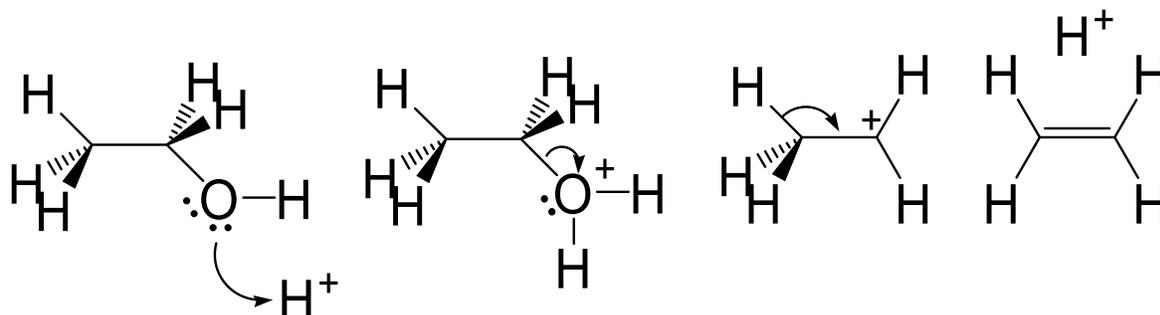
Alkenes are defined by the presence of a $C=C$ double bond. In the laboratory, they can be prepared *via* the dehydration of alcohols by strong acid.



One of the most important principles in organic chemistry is the understanding of how reactions happen at a molecular level. This is termed the **reaction mechanism**.

Mechanisms are represented by "pushing electrons" between and/or around molecules. The arrows **MUST** be accurately drawn to show both the origin and destination of the electrons.

So what is the mechanism for the dehydration of ethanol?



A mechanism can NEVER be proven, only supported by experimental evidence.

The mechanism shown above may be applied to the dehydration of *any* alcohol with acid to yield *any* alkene.

Chemistry

Alkenes are much more reactive than alkanes. Most of their chemistry involves **addition** to the C=C double bond.

Hydrogenation (Addition)

Addition of H₂ to C=C in the presence of a suitable catalyst e.g. Pd activated charcoal or Raney Ni (treat nickel aluminium alloy with hot NaOH)

