

Chains and Rings: Organic Chemistry

Introduction: “Welcome! You are now at the launching point of a new adventure. An adventure called Organic Chemistry. To succeed in this adventure, you must accept the intellectual challenge to look at things from a viewpoint that is perhaps different from any you have ever used before. By committing yourself to hard work and self-discipline, you are ready to make this adventure well worth the journey.” Quote from an American University syllabus.

Organic Chemistry:

Organic literally means “derived from living organisms”. Originally organic chemistry was the study of the chemistry of life. Now, however, a slightly more general definition is used, such as one of the following:

1. The study of carbon-containing compounds and their properties. (Usually excluding carbon oxides, carbonates and a few other inorganic compounds).
2. The study of compounds that contain carbon and hydrogen (carbon hydrides and their derivatives) and/or carbon and a halogen (carbon halides and their derivatives).

There is an infinite number of organic compounds!!

Why Carbon?

1. Carbon has an unusually strong ability to covalently bond with itself, forming C-C bonds, C=C double bonds and C≡C triple bonds. This bonding of an element to itself is called catenation. Carbon has the strongest ability to catenate is virtually unlimited and chains of dozens or hundreds of carbon atoms bonded to each other occur in nature. This is because the C-C bond is very strong.
2. Carbon has a valency of 4, meaning that not only can carbon bonded together in a large chain, but other chemical atoms or groups of atoms may be bonded to the sides of these chains. The chains may also be branched, or closed to form rings.

Carbon hydrides: The Hydrocarbons

Hydrocarbons are compounds of carbon and hydrogen only. There is an infinite number of hydrocarbons!! They are divided into several chemical groups:

1. **Alkanes** contain only C-C single bonds (and C-H bonds!). **Cycloalkanes** are alkenes in which the chain of carbon atoms joins to itself to form a ring-shaped compound. Other alkanes are either straight-chain alkanes or branched-chain alkanes.
2. **Alkenes** contain one or more C=C double bond.
3. **Alkynes** contain one or more C≡C triple bond.
4. **Arenes (aromatics)** are ring-shaped hydrocarbons containing delocalised electrons, which gives them many unusual and useful chemical properties.

Hydrocarbons: Alkanes

Alkanes are hydrocarbons with the general formula: C_nH_{2n+2} . Alkanes are saturated hydrocarbons: that is they contain the maximum amount of hydrogen possible (I.e. they contain no C=C or C≡C bonds). The alkanes form an homologous series: a series of related compounds with the same general formula.

Alkanes occur naturally in crude oil. Some alkanes occurring in crude oil are:

Name of alkane	Molecular formula	Boiling Point (°C)
methane	CH ₄	-162
ethane	C ₂ H ₆	-89
propane	C ₃ H ₈	-42
butane	C ₄ H ₁₀	-05
pentane	C ₅ H ₁₂	36
hexane	C ₆ H ₁₄	69
heptane	C ₇ H ₁₆	98
octane	C ₈ H ₁₈	126
nonane	C ₉ H ₂₀	151
decane	C ₁₀ H ₂₂	174
undecane	C ₁₁ H ₂₄	196
dodecane	C ₁₂ H ₂₆	216
octadecane	C ₁₈ H ₃₆	

N.B. Names of alkanes end in -ane.

Q1. These alkanes are all straight-chain alkanes. Hexane is a straight-chain alkane consisting of a chain of 6 C atoms. Draw the structural formula of hexane.

Q2. Cyclohexane is a ring-shaped (cyclic) alkane containing 6 C atoms. Draw the structural formula of cyclohexane.

Q3. What is the formula for the group of atoms that is added each time you move one step down the alkane series?

Fractional Distillation of Crude Oil



Crude oil is separated into fractions by distillation in cylindrical towers typically 8 m in diameter and 40 m high

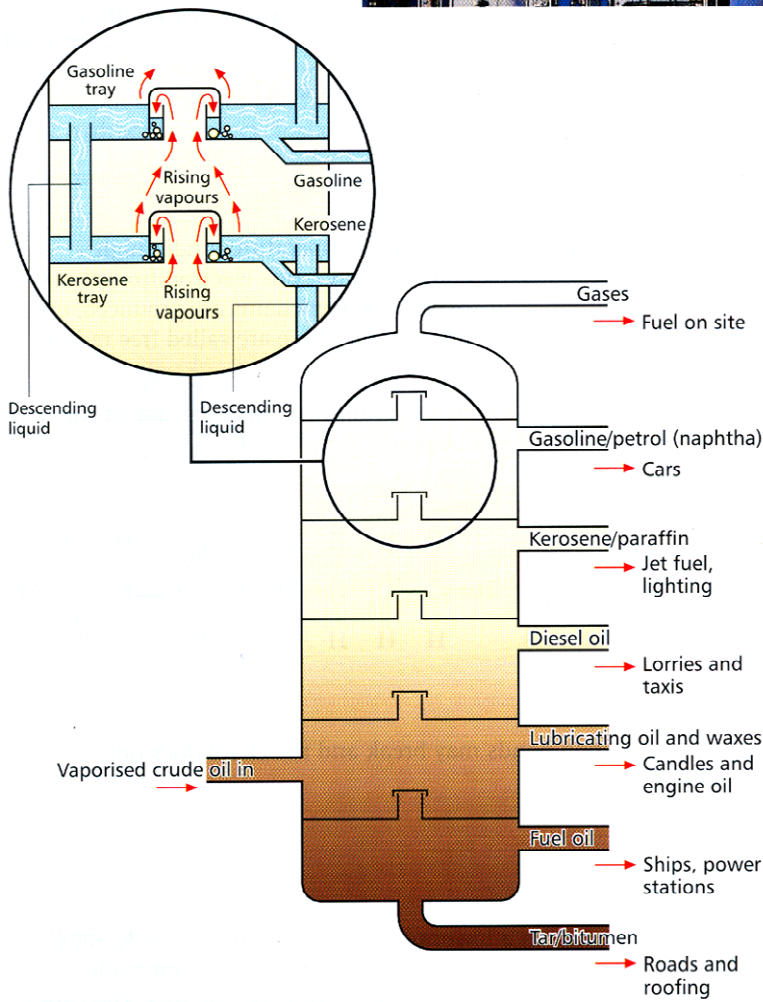


Fig 9.1 The fractional distillation of crude oil

Products from Oil

Fractional Distillation of Crude Oil - Names and Uses of Different Fractions

The hydrocarbon fractions are mainly alkanes.

Name	Number of Carbon Atoms	Boiling Point (°C)	Uses
Refinery Gas	1-4	<30	
Petrol / naphtha / gasoline	5-10	100-200	
Kerosene (paraffin)	11-16	200-300	
Diesel Oil / Gas Oil	14-20	250-350	
Lubricating Oil	20-25	300-400	
Fuel Oil	20-30	350-450	
Greases and Waxes	25-50	400-500	
Bitumen / Asphalt	>50	>500	

- Q4. Why do longer chain alkanes have higher boiling points?
- Q5. What is the molecular formula of hexadecane?
- Q6. What are the empirical formulae of: (i) butane, (ii) hexane, (iii) heptadecane?

Combustion of alkanes: fuels

Notice that many of the uses of alkanes are as **fuels** - petrol, diesel, paraffin wax candles. This is because alkanes burn in the presence of oxygen/air to give out large quantities of heat and producing carbon dioxide and water. Alkanes make good fuels because they produce a lot of heat when burnt - they have a high **energy density**. For example, methane (CH_4) is burned as natural gas, butane (C_4H_{10}) as bottled gas, and octane (C_8H_{18}) is a constituent of petrol. Alkanes give out about 50KJ of energy per gram when burned.

- Q7. Write a balanced equation for the combustion of butane:

Cracking of Hydrocarbons

Different crude oils have different compositions. There is a great demand for the smaller chain fractions - those used as petrol and kerosene. Often more longer chain alkanes are produced from the fractional distillation of crude oil than are actually required. One solution is to break these long-chain alkanes into shorter-chain alkanes - a process carried out on an industrial scale and known as cracking.

Thermal Cracking

The alkanes are heated to high temperatures, under high pressure. Some of the C-C bonds break homolytically (homolytic fission or homolysis (equal breaking; fission = 'breaking')) meaning that one electron from the pair in the bond goes to each carbon atom. Thus two shorter chains are produced, each with a carbon possessing one unpaired electron at one end of the chain.

N.B. The chain may break any number of times and in any place.

These chains are free radicals - a free radical is a molecule or atom with an unpaired electron. Free radicals are extremely reactive - electrons prefer to be in pairs! Thus, these free radicals do not last for long, but are short-lived intermediates. One of the free radicals binds to a hydrogen to form an alkane. The other must form a C=C double bond, and so becomes an alkene, since there is not enough H atoms to go round.

Example: thermal cracking of hexane:

Catalytic Cracking

This takes place at a lower temperature (800 K or 527°C) than thermal cracking because it uses a zeolite catalyst made of silicon dioxide and aluminium oxide. Zeolites have a honeycomb structure (and so have a large surface area) and are acidic. Catalytic cracking is used mainly to produce motor fuels and aromatic compounds.

Cracking summary:

- Cracking produces more useful shorter-chain hydrocarbons.
- Cracking produces alkanes and also alkenes. Alkenes are chemically more reactive than alkanes and are used to manufacture many chemicals, including plastics.

Other processes used to produce better fuels:

Reforming

Reforming is an industrial process whereby straight-chain alkanes of 6-10 C (petrol) are converted into cycloalkane ring compounds and then into aromatic ring compounds, by heating to 500°C and passing over a platinum catalyst (finely dispersed over the surface of aluminium oxide). Each industrial reforming unit contains £5 million worth of platinum! Reforming reduces 'knocking' in petrol. For example, the reforming of hexane:

Isomerisation

Isomers are molecules with the same molecular formula, but differing in the spatial arrangement of their atoms.

Isomers are distinct compounds with different physical properties, and often different chemical properties. Isomerism is the occurrence of isomers.

Structural isomers have different structural formulae, i.e. the atoms are bonded together in a different order in each isomer.

Structural formula: the minimum detail, using conventional groups, for an unambiguous structure, e.g. butane: $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$.

A displayed formula is the full structural formula, showing all the bonds, e.g. butane:

Branched-chain alkanes make better motor fuels than do straight-chain alkanes. Straight-chain alkanes burn by detonating rapidly and cause 'knocking' in the engine. Branched-chain alkanes burn more smoothly and more efficiently. Straight-chain alkanes are converted into branched-chain alkanes in the industrial process of isomerisation: the straight-chain alkanes are heated under pressure with a platinum catalyst. For example, isomerisation of octane:

Octane numbers

Fuels are given an octane number rating - the higher the octane number the more 'knocking' the petrol causes - that is it ignites too easily and spontaneously (when compressed by the piston in each cylinder of the engine). Heptane easily detonates and is given an octane number of 0 (it would make bad petrol!). 2,2,4-Trimethylpentane (old name: isooctane) burns smoothly and is given an octane number of 100. Four star petrol has an octane number of 97.

Hydrocarbons: Alkanes

- Q8. Undecane is cracked to produce nonane and compound A, Name compound A and write its empirical formula, its molecular formula, its structural formula and its displayed (full structural) formula.
- Q9. Octadecane, $C_{18}H_{38}$ is cracked into hexane and an alkene. What is the molecular formula of the alkene?
- Q10. Write a balanced equation for the complete combustion of pentane.
- Q11. Draw three structural isomers of C_5H_{12} .
- Q12. These three isomers are separated by fractional distillation. State the order in which they would distil.
- Q13. Calculate the percentage by mass of carbon in undecane, $C_{11}H_{24}$.

Branched Hydrocarbons

Nomenclature: a system of naming organic compounds. IUPAC (International Union of Pure and Applied Chemistry) have developed a system of conventions for naming organic compounds. This system is used in the OCR syllabus. Systematic names are the names for organic compounds as determined by the IUPAC rules.

- Q14. What other compounds have the same molecular formula as hexane, but different structures? Draw them and name them.

Rules of Organic Nomenclature:

1. The longest unbranched chain or ring in a molecule forms the root of the systematic name:

<u>Number of C atoms</u>	<u>Root</u>
1	meth
2	eth
3	prop
4	but
5	pent
6	hex
7	hept
8	oct
9	non
10	dec

2. The syllable after the root tells us whether the compound contains any double (or triple) bonds:

- ane means that there are no double or triple bonds;
- ene means that there are one or more double bonds;
- yne means that there are one or more triple bonds.

3. Side chains are shown by a prefix (goes before the root) indicating the number of C atoms in the side chain:

<u>Prefix</u>	<u>Side-chain</u>	<u>Number of C atoms in the side-chain</u>
methyl	CH ₃ -	1
ethyl	C ₂ H ₅ -	2
propyl	C ₃ H ₇ -	3
butyl	C ₄ H ₉ -	4

4. Functional groups: a functional group is a reactive group of atoms and is named using a suffix or prefix. You will see examples of these throughout this module. E.g. the suffix -ol means that the compound contains an OH- hydroxyl group and is an alcohol, for example, ethanol, C₂H₅OH.

5. Locants: a locant is a number that tells us where (I.e. on which C atom) along the main chain or ring a side-chain or functional group is located. Where there is a choice of locants, use the smallest locant possible. Sometimes more than one locant is needed, in which case they are put into alphanumeric order, e.g. 2-bromo-1-iodopropane.

Q15. Draw the displayed formulae for (i) 1-chloropropane and (ii) 2-chloropropane. Is there a third distinct molecule called 3-chloropropane?

Q16. Draw displayed formulae for the following organic compounds:

(a) Iodoethane

(b) 1,2-dibromoethane

(c) 2-bromo-1-iodopropane

(d) 1,1-dichlorobutane

(e) but-1-ene

(f) 2-methylbutane

(g) but-1,3-diene

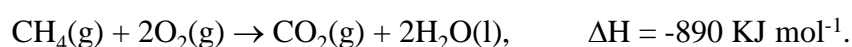
(h) 1-ethyl-but-3-ene

Reactions of alkanes:

Alkanes are generally unreactive. They contain no C=C double bonds and no reactive functional groups. Both the C-C and the C-H bonds are strong. The H atoms also shield the C atoms from other chemical reagents (this spatial obstruction of one part of a molecule by another is called: steric hindrance).

1. Combustion

Shorter chain alkanes burn completely in oxygen to give carbon dioxide and water. E.g. the combustion of methane:

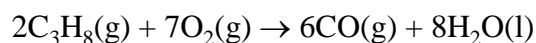


Note that a lot of heat is also generated - these reactions have large negative enthalpies of combustion. This is why these alkanes make such good fuels.

E.g. methane (natural or 'North sea' gas),
propane ('camping' gas)
butane ('Calor' gas)
petrol (a mixture of hydrocarbons of average chain length about C₈)
paraffin (a mixture of hydrocarbons of chain lengths C₁₀-C₁₈).

2. Incomplete Combustion

If the supply of oxygen is limited, then combustion will be incomplete and carbon monoxide will be produced, e.g.:



Q17. Write a balanced equation for the incomplete combustion of ethane:

In an even more limiting supply of oxygen, carbon is produced as black soot. Longer chain hydrocarbons produce more soot when they burn, since they require more oxygen for complete combustion.

3. Cracking

4. Halogenation

Alkanes react with halogens in the presence of sunlight (UV light) but alkanes do not react with halogens in the dark at room temperature. E.g. if bromine is mixed with hexane in a test-tube and kept in the dark, then the solution retains the red-brown colour of bromine. However, if UV light is shone onto the mixture, then it will turn colourless as the bromine reacts. (N.B. hexane will NOT react with bromine water!).

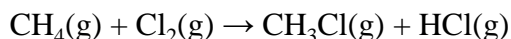
Q.18. Complete the equation below:

hexane bromine bromohexane hydrogen bromide

Chain Reactions:

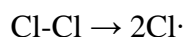
The substitution reaction above, in which one of the H atoms in the alkane has been replaced by a halogen atom is called a free-radical substitution. It is a chain reaction which takes place in three stages: initiation, propagation and termination. The reaction between any alkane and a halogen proceeds by the same reaction mechanism.

E.g. methane + chlorine:



1. Initiation

The first step in the reaction is the breaking of the Cl-Cl bond by homolytic fission to produce two chlorine free radicals: this occurs when the Cl₂ molecule absorbs one photon (quantum) of UV light. The UV photon has more energy than that required to break the Cl-Cl bond, so the bond breaks when this photon is absorbed by the molecule. (The reaction will also occur at high temperatures in the absence of light).

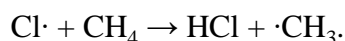


The dot on each chlorine free radical represents the unpaired electron: the bond breaks by homolytic fission, meaning that one electron from the bond went to each chlorine atom.

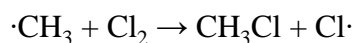
Note: UV light has insufficient energy to break the stronger C-H bonds.

2. Propagation

The free radicals are highly reactive (because the unpaired electron prefers to be with another electron!) and so steals a H atom from methane to form hydrogen chloride and a methyl free radical:



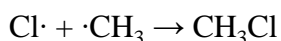
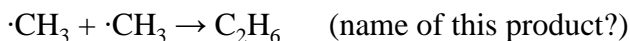
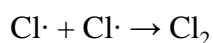
The methyl radical is also highly reactive (because its electron prefers to be with another electron) and so it steals a Cl atom from a Cl₂ molecule, forming methyl chloride and a chlorine free radical.



So far we have produced hydrogen chloride, chloromethane, and another chlorine free radical. What do you think happens to this chlorine free radical? Can you see what this becomes a chain reaction (that may take place thousands of times before the free radicals are eventually destroyed in the termination stage).

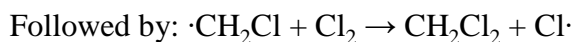
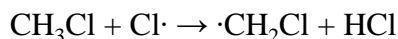
3. Termination:

The free radicals are eventually removed by reacting with each other:



The main products of this chain reaction are chloromethane and hydrogen chloride, but some ethane (C₂H₆) is also produced in the termination stage.

Additionally some dichloromethane may be produced during the propagation stage by the following reactions:



Q.19. Which H atom gets replaced when longer chain alkanes react with chlorine?

Q.20 Why do you think that chain reactions are of limited use to a chemist trying to make a halogen alkane?

Crude Oil and the Environment

Crude oil is not only used as a source of fuels and lubricants, but provides many chemicals that are the starting points in the synthesis of many commercial products, including plastics, drugs and dyes. We say that oil is a chemical feedstock and is so crucial to our way of life that we can not afford to burn it all up as fuel, for both environmental and long-term economic reasons.

Crude oil-based fuels:

We have seen our fuels are synthesised from crude oil by fractional distillation and cracking (and isomerisation and reforming). All these fuels contain mostly alkanes that release **large quantities of heat** when burned in air (oxygen). We say that these fuels have a high energy density: that is when they are burned they give out lots of energy per unit mass. E.g. butane gives out about 50 KJ per gram when burned. Clearly it would defeat the purpose if a vehicle had to carry more than its own weight in fuel!

Q. 21. The enthalpy change of combustion of methane (the amount of heat given out) is -2877 KJ mol⁻¹. Write a balanced equation for the complete combustion of butane to carbon dioxide and water.

Q.22. Why is it important for us to develop alternative sources of energy?

Pollution:

All hydrocarbon fuels produce various pollutants when they burn, including:

- Carbon monoxide, CO, a toxic gas.
- Unburnt hydrocarbons, that may form yellow haze in the air (smog).
- Carbon dioxide, a greenhouse gas.
- Nitrogen oxides (as nitrogen from the air reacts with oxygen under high temperatures) which contribute to acid rain.
- Sulphur dioxide (from the combustion of sulphur-containing impurities in the fuel) which also contributes to acid rain.

Q.23. How do nitrogen oxides and sulphur dioxide contribute to acid rain?

Alternative fuels?

Biofuels:

Biofuels are fuels obtained from fast-growing plants (and so are renewable!). Wood is one example of a biofuel that can be used directly, as it is. Other crop products such as sugar and rape-seed oil can be converted into useful fuels by chemical processes.

The Physical Properties of Some Organic Compounds

Chain length	Alkane	bp (°C)	Alcohol	bp(°C)	Carboxylic acid	bp(°C)
1C	Methane	-162	Methanol	65	Methanoic acid	101
2C	Ethane	-89	Ethanol	78	Ethanoic	118
3C	Propane	-42	Propanol	97	Propanoic	141
4C	Butane	-5	Butanol	118	Butanoic	163
5C	Pentane	36	Pentanol	138	Pentanoic	186
6C	Hexane	69	Hexanol	156	Hexanoic	206
7C	Heptane	98	Heptanol	176	Heptanoic	
8C	Octane	126	Octanol	194	Octanoic	240 (l/s)
9C	Nonane	151	Nonanol	214	Nonanoic	(s)
10C	Decane	174	Decanol	235	Decanoic	269 (s)
11C	Undecane	196	Undecanol		Undecanoic	(s)
12C	Dodecane	219	Dodecanol		Dodecanoic	(s)
18C	Octadecane					
20C	Eicosane					

Alkanes are insoluble in water. Benzene has a mp of 5.5°C and a bp of 80.1°C and so is a liquid at room temperature and is also insoluble in water.

Phenol is a crystalline solid at room temperature, mp 40.9°C and is 15 times more soluble in water than hexanol. However, the presence of liquid water lowers the melting point of phenol and so it is often found semi-liquid and 8% water completely melts it (but does not dissolve it!).

The solubility of straight-chain alcohols decreases with increasing chain-length. Methanol, ethanol and propanol are very soluble in water, pentanol and hexanol only sparingly soluble

Benzoic acid is insoluble in water and has a mp of 122°C.

The solubility of (mono)carboxylic acids also decreases with increasing chain-length, with methanoic, ethanoic, propanoic and butanoic acids being very soluble in water, hexanoic acid sparingly soluble and dodecanoic acid upwards completely insoluble. Dicarboxylic acids are all solids at room temperature and are of variable solubility in water.