15.1 Alkanes

a Compounds containing only carbon and hydrogen are called hydrocarbons. This class of compound can be sub-divided into alkanes, alkenes and arenes.

b understand the general unreactivity of alkanes, including towards polar reagents ☐

c describe the chemistry of alkanes as exemplified by the following reactions of ethane:

(i) combustion ☐

(ii) substitution by chlorine and by bromine ☐

d describe the mechanism of free-radical substitution at methyl groups with particular reference to the initiation, propagation and termination reactions ☐

e explain the use of crude oil as a source of both aliphatic and aromatic hydrocarbons ☐

f suggest how cracking can be used to obtain more useful alkanes and alkenes of lower Mr from larger hydrocarbon molecules ☐

ALKANES

15.1 Alkanes	a)	understand the general unreactivity of alkanes, including towards polar reagents
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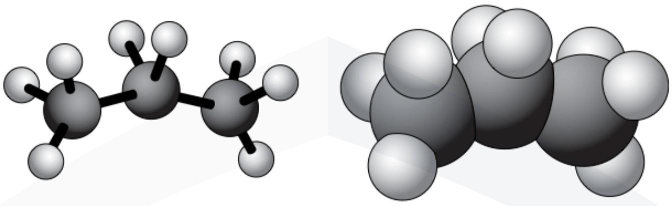
	e)	suggest how cracking can be used to obtain more useful alkanes and alkenes of lower M_r from larger hydrocarbon molecules

ALKANES

Alkanes are the hydrocarbons that make up most of crude oil and natural gas.

In alkane molecules, every carbon atom forms four single covalent bonds.The electrons in these four bonds repel each other to tetrahedral positions around each carbon atom.



structure of propane showing the tetrahedral shape around each carbon atom.

1

PROPERTIES

The alkanes are non-polar molecules with only van der Waals' forces between molecules. This means that they are volatile (evaporate easily), with the first four members being gases at room temperature. Due to their non-polar nature, they are also insoluble in water.

As the molecules get longer and larger, the intermolecular forces increase, so the melting and boiling points rise as the number of carbon atoms per molecule increases.

Because of the weak intermolecular forces they are highly volatile. As the series is ascended due to the increase in the number of electrons the strength of the van der Waals' forces increases.

Consequently the melting and boiling point, density and viscosity increases, while volatility and vapour pressure decreases.

2

PROPERTIES

For any one set of isomers the boiling point decreases as branching increases.

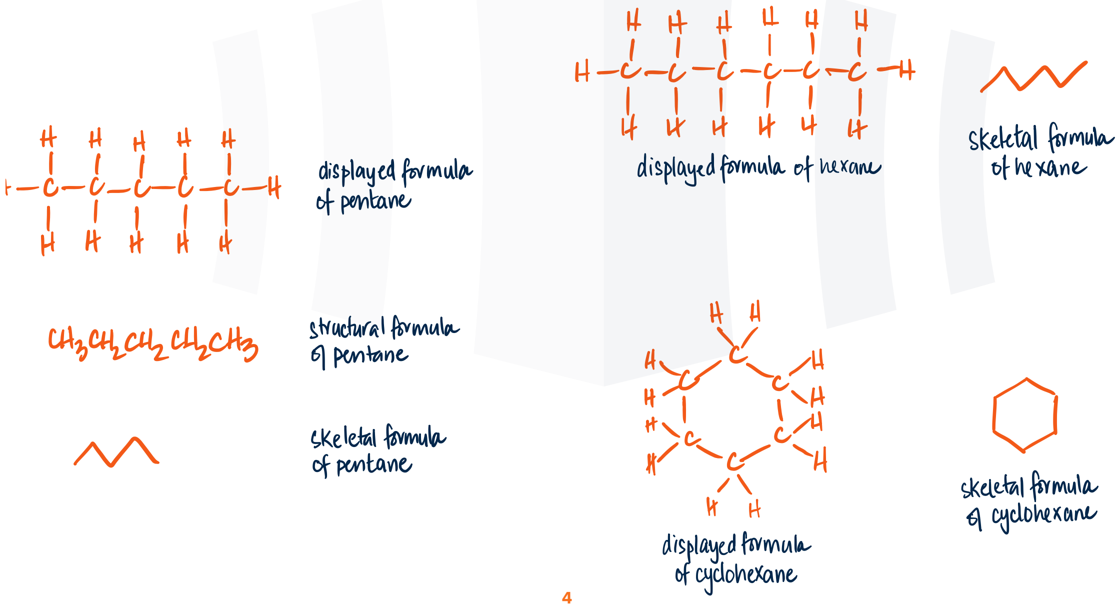
This is because as branching increases the molecules become more nearly spherical and expose less surface area.

Hence less intermolecular forces are exerted. The melting point also depends on the packing of the molecules.

Closer packing leads to higher melting point.

3

STRUCTURES



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REACTIVITY

The bond enthalpies of C–C and C–H bonds are relatively high, so the bonds in alkanes are difficult to break.

In addition, these bonds in alkanes are non- polar. This means that alkanes are very unreactive with ionic reagents in water, such as acids, alkalis, oxidising agents and reducing agents.

There are, however, three important reactions of alkanes involving combustion, halogenation and cracking.

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COMBUSTION

In air or oxygen, alkanes are completely oxidised to carbon dioxide and water, and the reaction is highly exothermic. e.g.

$$C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$$

In a limited supply of air or oxygen, alkanes burn incompletely forming highly toxic carbon monoxide, as well as carbon dioxide and water.

If the supply of air or oxygen is even more restricted, the major products will be soot (carbon) and water.

$$C_3H_8 + 3.5O_2 \longrightarrow 3CO + 4H_2O$$
$$C_3H_8 + 2O_2 \longrightarrow 3C + 4H_2O$$

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COMBUSTION

The exothermic nature of the combustion of alkanes has led to their widespread use as fuels.

Combustion is an exothermic reaction. The greater the number of carbon atoms, the more energy produced and the greater the amount of oxygen needed for complete combustion.

$$C_xH_{y\,(g)} + (x + y/4)\,O_{2\,(g)} \longrightarrow xCO_{2\,(g)} + y/2\,H_2O_{(l)}$$

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O(l) \qquad \Delta H^{\ominus} = -890\ kJmol^{-1}$$

$$C_{20}H_{42(l)} + 30.5O_{2(g)} \longrightarrow 20CO_{2(g)} + 21H_2O_{(l)} \qquad \Delta H = -13368\ kJmol^{-1}$$

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POLLUTION

Motor vehicles are generally the main source of air pollutants. Engines that burn petrol or diesel fuels can pollute the air for three main reasons:

- they do not burn the fuel completely
- the fuel contains impurities
- they run at such a high temperature that nitrogen and oxygen in the air can react.

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POLLUTION

POLLUTANT	PROBLEMS
Carbon monoxide	A toxic gas that combines strongly with haemoglobin, which means that the blood can carry less oxygen. In low doses, this can put a strain on the heart. In higher doses, it kills
Oxides of nitrogen: NO & NO_2	Reacts with moist air to make nitric acid in acid rain. Affects the lungs and can cause breathing problems
Unburned hydrocarbons	Some of the hydrocarbons, such as benzene, are carcinogenic. Others react with ozone to form harmful pollutants

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CATALYTIC CONVERTERS

Catalytic converters have done a great deal to improve air quality.

The catalyst speeds up reactions that remove pollutants from motor vehicle exhausts.

The reactions convert oxides of nitrogen to nitrogen and oxygen.

They also convert carbon monoxide to carbon dioxide and unburned hydrocarbons to carbon dioxide and steam.

$$2CO + 2NO \rightarrow 2CO_2 + N_2$$

$$NO \rightarrow N_2 + O_2$$

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GREENHOUSE EFFECT

Without the atmosphere, the whole Earth would be colder than Antarctica. The greenhouse effect keeps the surface of the Earth about 30 °C warmer than it would be if there were no atmosphere. With no greenhouse effect, there would be no life on Earth.

When the Sun's radiation reaches the Earth's atmosphere, about 30% is reflected into space, 20% is absorbed by gases in the air and about 50% reaches the surface of the Earth.

The surface of the Earth is very much cooler than the Sun. This means that it radiates most of its energy back into space. Some of this infrared radiation is absorbed by molecules in the air and warms up the atmosphere. This is the greenhouse effect.

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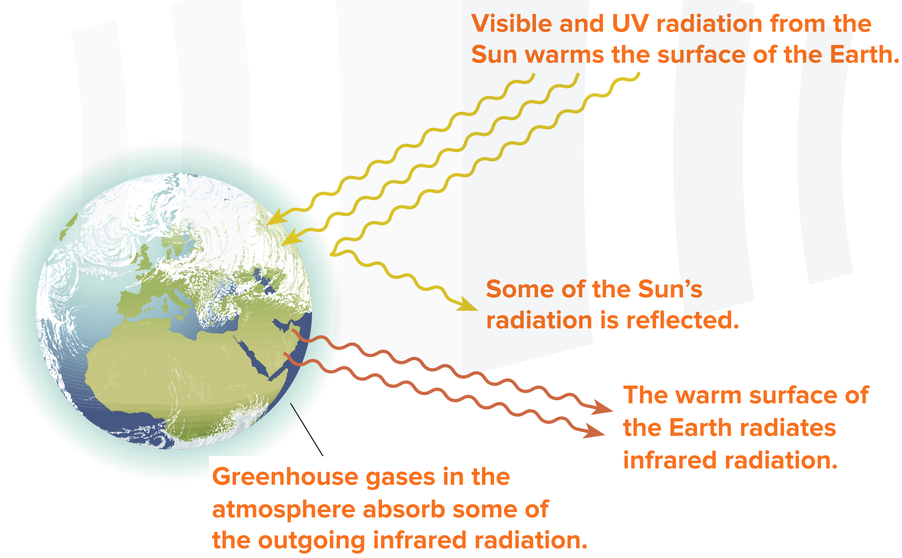
GREENHOUSE EFFECT



ENHANCED GREENHOUSE EFFECT

The Earth's average temperature stays the same if the energy input from the Sun is balanced by the re-radiation of energy back into space. Anything that changes this steady state gradually leads to global warming or global cooling.

The gases in the air that do absorb infrared radiation are called greenhouse gases. The natural greenhouse gases that help keep the Earth warm are water vapour, carbon dioxide and methane. Water vapour makes the biggest contribution.

Since the Industrial Revolution, human activity has led to a marked increase in the concentrations of greenhouse gases in the atmosphere. This enhances the greenhouse effect. As a result, the Earth warms up more than it would naturally, and as the Earth warms up, its climate changes.

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GREENHOUSE GASES

This increase in temperature could cause rising sea levels, resulting in the flooding of low-lying areas of land. The climate will also change around the world, with more extreme weather predicted.

Unfortunately, catalytic converters can do nothing to reduce the amount of carbon dioxide (a greenhouse gas) given off in the exhaust gases of cars.

Carbon dioxide is not a toxic gas but it is still considered a pollutant because of its contribution to enhanced global warming.

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FRACTIONAL DISTILLATION OF CRUDE OIL

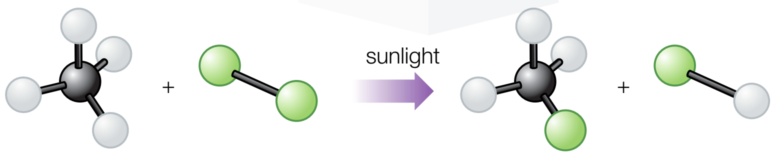
B.P / °C	# of C atoms	Name of fraction	Uses
< 25	1 - 4	LPG	Camping Gas
40-100	6 - 12	GASOLINE	Petrol
100-150	7 - 14	NAPHTHA	Petrochemicals
150-200	11 - 15	KEROSINE	Aviation Fuel
220-350	15 - 19	GAS OIL (DIESEL)	Central Heating Fuel
>350	20 - 30	LUBRICATING OIL	Lubrication Oil
> 400	30 - 40	FUEL OIL	Power Station Fuel
> 400	40 - 50	WAX, GREASE	Candles
> 400	> 50	BITUMEN	Road surfaces

REACTION WITH HALOGENS

Alkanes react with chlorine and bromine on exposure to ultraviolet light.

During the reactions, hydrogen atoms in the alkane molecules are replaced (substituted) by halogen atoms. These are described as substitution reactions.

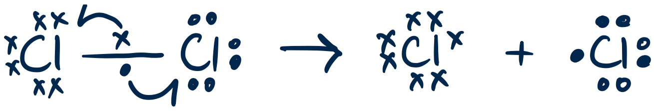
Any or all of the hydrogen atoms in an alkane may be replaced and the reaction can continue until all of the hydrogen atoms have been substituted by halogen atoms.



$CH_4(g)$ + $Cl_2(g)$ $\xrightarrow{\text{sunlight}}$ $CH_3Cl(g)$ + $HCl(g)$

FREE RADICAL FORMATION

In the presence of u.v light chlorine undergoes homolysis to give Cl free radicals.



FREE RADICALS are reactive species (atoms or groups) which possess an unpaired electron. However, they are neutral.

Their reactivity is due to them wanting to pair up the single electron.

Formed by homolytic fission (homolysis) of covalent bonds.

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FREE RADICAL FORMATION

During initiation, the **WEAKEST BOND IS BROKEN** as it requires less energy.

There are three possible bonds in a mixture of alkanes and chlorine.

C — H	C — C	Cl — Cl
410	**350**	**242**

The Cl-Cl bond is broken in preference to the others as it is the weakest and requires requires less energy to separate the atoms.

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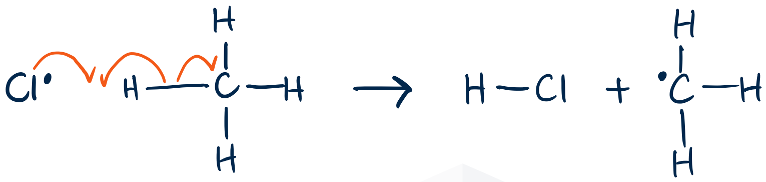
PROPAGATION

The free radicals then attack the methane molecules abstracting a hydrogen atom to form hydrogen chloride and a methyl $CH_3\bullet$ free radical.



$$Cl^{\bullet} + CH_4 \longrightarrow HCl + CH_3^{\bullet}$$

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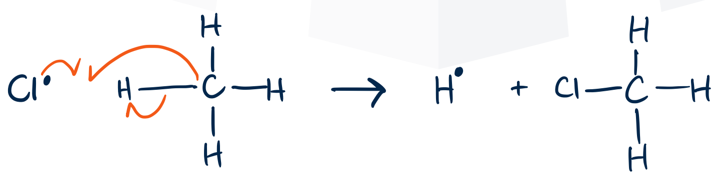
PROPAGATION

Reaction with methane could occur in one of two ways. In the previous reaction, a C—H bond has been broken, and a H—Cl bond has been formed, an exothermic reaction.

C—H = 413 KJ mol^{-1}
H—Cl = 431 KJ mol^{-1}

ΔH = 413 − 431 = −18 KJ mol^{-1}

IF the Cl were to combine with the C atom, a C—H bond would be broken, and a C—Cl bond form and would result in an endothermic reaction.



C—Cl = 338 KJ mol^{-1}

ΔH = 413 − 338 = +75 KJ mol^{-1}

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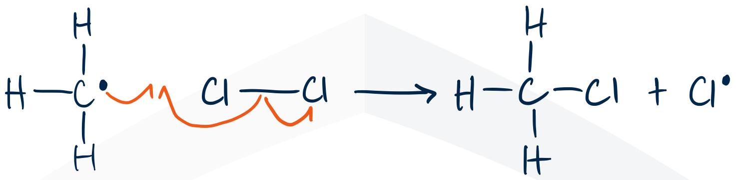
PROPAGATION

The methyl radical formed in the first step of propagation is equally as reactive as a chlorine radical.

It is likely to react with the first molecule it collides with. If it collides with a chlorine molecule, the following highly exothermic reaction occurs:



Cl – Cl = 242
C – Cl = 338

$\Delta H = 242 - 338 = -96 \text{ kJmol}^{-1}$

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PROPAGATION SO FAR

In the initiation reaction, we had produced two reactive chlorine atoms and the following two reactions occur.

$$Cl^{\bullet} + CH_4 \rightarrow CH_3^{\bullet} + HCl$$

$$CH_3^{\bullet} + Cl_2 \rightarrow CH_3Cl + Cl^{\bullet}$$

After these two reactions have taken place we have:

- used up one molecule of methane, and one molecule of chlorine
- produced one molecule of chloromethane, and one molecule of hydrogen chloride
- used up a chlorine atom, but regenerated another one.

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TERMINATION

$Cl^\bullet + CH_4 \rightarrow CH_3^\bullet + HCl \quad CH_3^\bullet + Cl_2 \rightarrow CH_3Cl + Cl^\bullet$

The above two reactions together constitute a never-ending chain reaction. They could, in theory, continue until all the methane and chlorine had been converted into chloromethane and hydrogen chloride.

This situation does not occur in practice, however. UV light initiates the production of many thousands of molecules of chloromethane.

Eventually the chain reaction comprising the above two reactions stops, because there is a (small) chance that two radicals could collide with each other, to form a stable molecule.

$$Cl^\bullet + Cl^\bullet \rightarrow Cl_2$$

$$CH_3^\bullet + Cl^\bullet \rightarrow CH_3Cl$$

$$CH_3^\bullet + CH_3^\bullet \rightarrow CH_3CH_3$$

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OVERALL

Any of these reactions would use up the free radicals Cl· and CH·3, and so stop the chain reaction.

It would require another chlorine molecule to slit in order to restart the chain.

Overall, the chlorination of methane is an example of a radical substitution reaction.

The different stages of the chain reaction are named as **initiation**, **propagation** and **termination**.

$Cl_2 \rightarrow 2Cl^\bullet$ — initiation

$Cl^\bullet + CH_4 \rightarrow CH_3^\bullet + HCl$
$CH_3^\bullet + Cl_2 \rightarrow CH_3Cl + Cl^\bullet$ — propagation

$Cl^\bullet + Cl^\bullet \rightarrow Cl_2$
$CH_3^\bullet + Cl^\bullet \rightarrow CH_3Cl$
$CH_3^\bullet + CH_3^\bullet \rightarrow CH_3CH_3$ — termination

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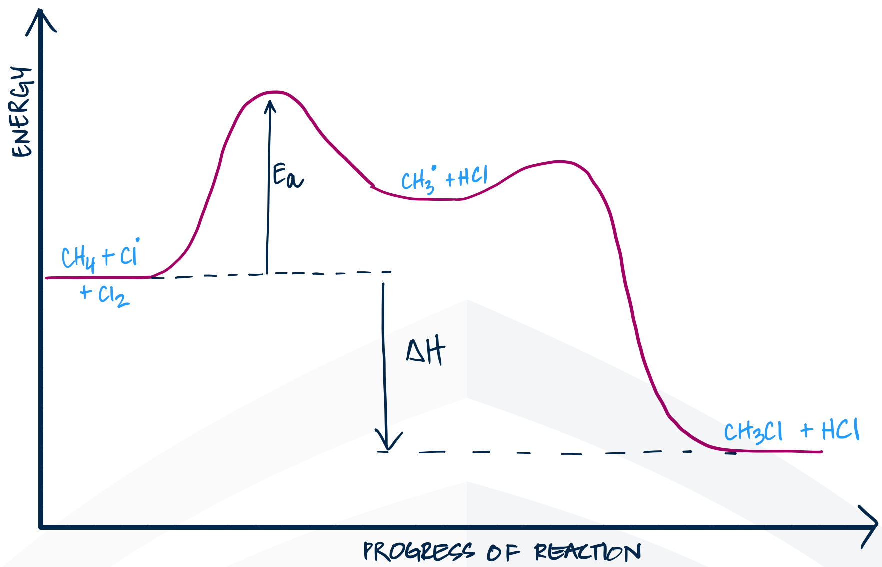
CHLORINATION OF METHANE: ENERGY CHANGES



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FURTHER SUBSTITUTION

As the reaction takes place, the concentration of methane is being reduced, and the concentration of chloromethane is increasing.

Chlorine atoms are therefore increasingly likely to collide with molecules of chloromethane, causing the following reactions to take place:

$$Cl^{\bullet} + CH_3Cl \longrightarrow HCl + {}^{\bullet}CH_2Cl$$
$${}^{\bullet}CH_2Cl + Cl_2 \longrightarrow CH_2Cl_2 + Cl^{\bullet}$$

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FURTHER SUBSTITUTION

Further substitution gives dichloromethane, trichloromethane and eventually tetrachloromethane. A mixture is formed.

dichloromethane

$$Cl^{\bullet} + CH_3Cl \longrightarrow CH_2Cl^{\bullet} + HCl$$
$$Cl_2 + CH_2Cl^{\bullet} \longrightarrow CH_2Cl_2 + Cl^{\bullet}$$

trichloromethane

$$Cl^{\bullet} + CH_2Cl_2 \longrightarrow CHCl_2^{\bullet} + HCl$$
$$Cl_2 + CHCl_2^{\bullet} \longrightarrow CHCl_3 + Cl^{\bullet}$$

tetrachloromethane

$$Cl^{\bullet} + CHCl_3 \longrightarrow CCl_3^{\bullet} + HCl$$
$$Cl_2 + CCl_3^{\bullet} \longrightarrow CCl_4 + Cl^{\bullet}$$

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BY PRODUCTS

A set of by-products are chlorinated ethanes.

These arise from the ethane produced in termination) undergoing a similar set of substitution reactions, or chloromethyl radicals combining at termination stages.

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BROMINATION OF ETHANE

Bromine reacts with ethane to produce bromoethane, C_2H_5Br. The reaction is a free radical substitution reaction.

Initiation: Bromine splits by homolytic fission using UV light.

$$Br_2(g) \longrightarrow 2Br^\bullet$$

Propagation: The Br• radical removes a hydrogen atom from ethane.

$$Br^\bullet + C_2H_6 \longrightarrow C_2H_5^\bullet + HBr$$
$$C_2H_5^\bullet + Br_2 \longrightarrow C_2H_5Br + Br^\bullet$$

Termination: Two radicals join to form a molecule.

$$Br^\bullet + C_2H_5^\bullet \longrightarrow C_2H_5Br$$

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HALOGENATION OF HIGHER ALKANES

There are two monochloropropane isomers: 1-chloropropane, $CH_3CH_2CH_2Cl$, and 2-chloropropane, $CH_3CHClCH_3$.

When propane reacts with chlorine, a mixture of the two monochloro- compounds is produced.

This is because the chlorine atom can abstract either one of the end-carbon hydrogens or one of the middle-carbon hydrogens, the former resulting in $CH_3CH_2CH_2Cl$ and the latter $CH_3CHClCH_3$.

$$Cl^\bullet + CH_3-CH_2-CH_3 \longrightarrow CH_3-CH_2-\dot{C}H_2 + H-Cl$$

$$Cl^\bullet + CH_3-CH_2-CH_3 \longrightarrow CH_3-\dot{C}H-CH_3 + H-Cl$$

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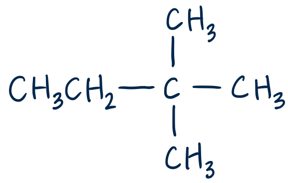
SKILL CHECK

Draw the structures of all possible free radicals in the mono-chloro substitution of:



HALOGENATION OF HIGHER ALKANES

The above reaction can produce organic by-products, in addition to C_2H_5Cl. Draw the structural formulae of four possible organic by-products. Two of your by-products should contain 4 carbon atoms per molecule and write the equation of the formation of each of your four products.

SKILL CHECK

Predict the major organic products formed during the monobromination of:

(a) $CH_3CH_2CH_2CH_3$

(b) $(CH_3)_2CH—CH_3$

CRACKING

Cracking is the decomposition of hydrocarbons by heat and pressure with or without a catalyst to produce lighter hydrocarbons, specially in oil refining. It is the breakdown of a large alkane into smaller, more useful alkenes and an alkane.

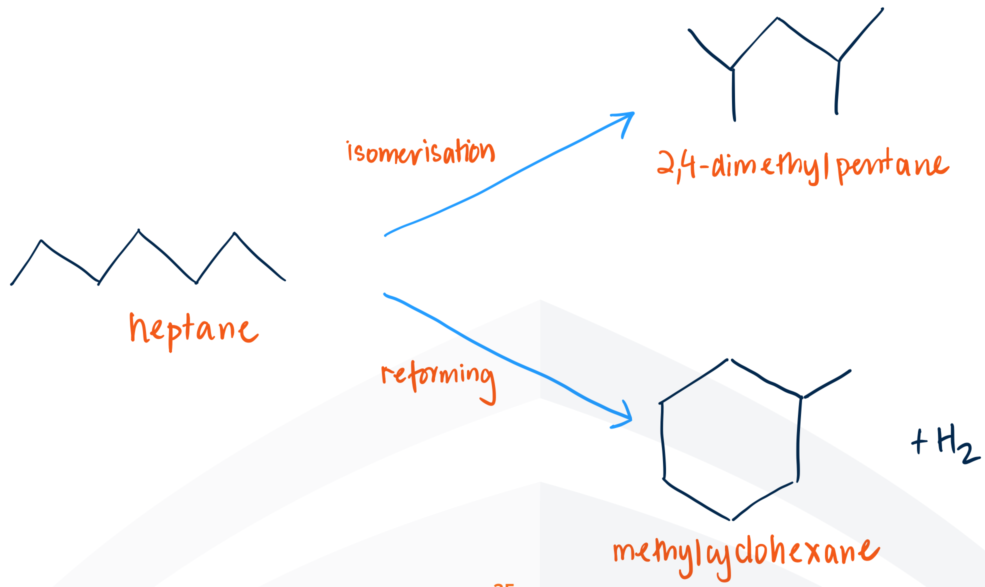
The larger hydrocarbon molecules are fed into a steel chamber which contains no oxygen, so combustion does not take place. The larger hydrocarbon molecules are heated to a high temperature and are passed over a catalyst.

When large alkane molecules are cracked they form smaller alkane molecules and alkene molecules. Possible examples of a cracking reaction are:

$$C_{10}H_{22} \longrightarrow C_6H_{14} + C_4H_8$$

$$C_{10}H_{22} \longrightarrow C_3H_8 + C_2H_4 + C_5H_{10}$$

OTHER REACTIONS



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