



RAFFLES INSTITUTION
YEAR 5 H2 CHEMISTRY 2022
Lecture Notes 10: Alkanes

Content

- Alkanes (exemplified by ethane)
 - (i) free-radical substitution reactions
- Hydrocarbons as fuels

Learning Outcomes

Candidates should be able to:

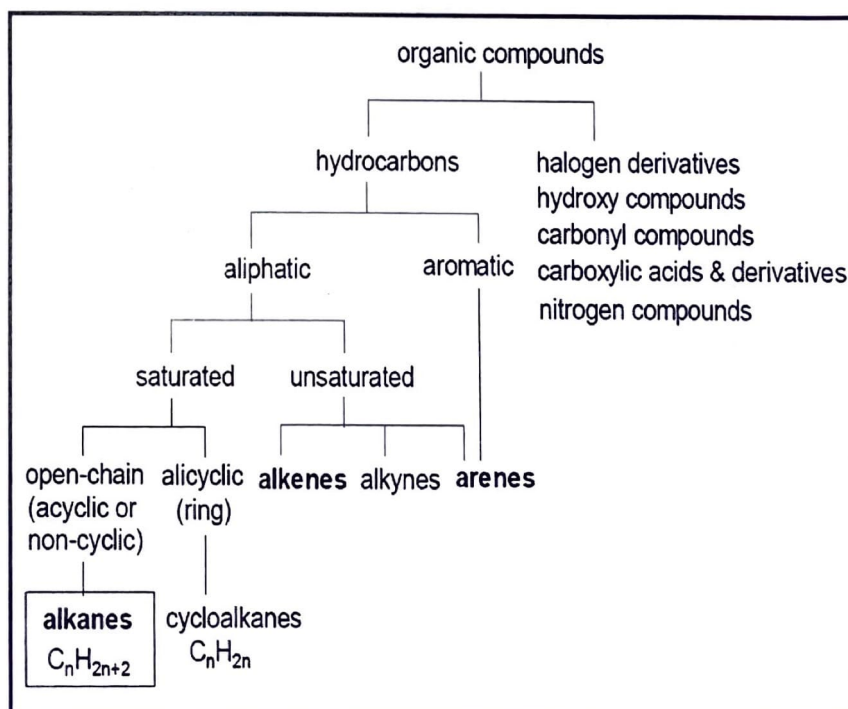
- (a) explain the general unreactivity of alkanes, including towards polar reagents
- (b) describe the chemistry of alkanes as exemplified by the following reactions of ethane:
 - (i) combustion
 - (ii) free-radical substitution by chlorine and by bromine
- (c) describe the mechanism of free-radical substitution with particular reference to the initiation, propagation and termination reactions
- (d) recognise the environmental consequences of:
 - (i) carbon monoxide, oxides of nitrogen and unburnt hydrocarbons arising from the internal combustion engine and of their catalytic removal
 - (ii) gases that contribute to the enhanced greenhouse effect
- (e) recognise that petroleum, a chemical feedstock, is a finite resource and the importance of recycling

Lecture Outline

- 1 Introduction
- 2 Isomerism in alkanes
- 3 Physical properties
- 4 Preparation of alkanes
- 5 Reactions of alkanes
- 6 Free-radical substitution
- 7 Alkanes as fuels
- 8 Summary

References

- Chemistry in Context (by Graham Hill & John Holman)
- Cambridge International AS and A Level Chemistry (by Peter Cann & Peter Hughes)
- Website:
www.chemguide.co.uk



1 Introduction

- The **alkanes** are the simplest of the homologous series found in organic chemistry.
- Alkanes are **hydrocarbons** since they contain only carbon and hydrogen. Other hydrocarbons include alkenes, alkynes and arenes.
- Alkanes are **saturated** hydrocarbons because they contain only carbon-carbon and carbon-hydrogen **single bonds** and do not contain any double or triple bonds. **Unsaturated** hydrocarbons such as alkenes and alkynes contain multiple bonds (either double or triple bonds) between carbon atoms.

- The **open-chain alkanes** form a homologous series of saturated hydrocarbons with the general molecular formula, C_nH_{2n+2} . Successive members differ in composition by one **CH₂ group** (methylene group).
- Each C atom in an alkane molecule is **sp³ hybridised** and has a **tetrahedral** molecular geometry around it. The bond angle around each C atom (in an open-chain alkane) is approximately **109.5°**.

| The first three members of the open-chain alkanes are methane, ethane and propane. | | | |
|--|-------------------|---------------|----------------------|
| condensed structural formula | displayed formula | 3-D structure | ball-and-stick model |
| CH ₄ methane | | | |
| CH ₃ CH ₃ ethane | | | |
| CH ₃ CH ₂ CH ₃ propane | | | |

- Cycloalkanes** are alkanes that contain one or more rings of carbon atoms. They are saturated hydrocarbons in which the carbon atoms are arranged to form rings.
- Cycloalkanes with only one ring have the same general molecular formula (i.e. C_nH_{2n}) as the alkenes with only one C=C bond.

Tip:

For an unknown compound with molecular formula C_nH_{2n} , it could likely be a cycloalkane or an alkene.

| The first four members of cycloalkanes are shown below. | | | |
|---|-------------------------|-----------------------------|----------------------------|
| | | | |
| | | | |
| Cyclopropane C_3H_6 | Cyclobutane C_4H_8 | Cyclopentane C_5H_{10} | Cyclohexane C_6H_{12} |

1.1 Nomenclature for Straight-Chain Alkanes

- Straight-chain alkanes have their IUPAC names as shown in the table below.
- Each member has the suffix 'ane'.

| Alkane | Structural formula | Skeletal formula |
|---------|---|------------------|
| propane | CH ₃ CH ₂ CH ₃ | |
| butane | CH ₃ CH ₂ CH ₂ CH ₃ | |
| octane | CH ₃ (CH ₂) ₆ CH ₃ | |

| IUPAC Names of Straight-Chain Alkanes | | | |
|---------------------------------------|---------|------------------------|-------------|
| Number of carbon atoms | Name | Number of carbon atoms | Name |
| 1 | methane | 11 | undecane |
| 2 | ethane | 12 | dodecane |
| 3 | propane | 13 | tridecane |
| 4 | butane | 14 | tetradecane |
| 5 | pentane | 15 | pentadecane |
| 6 | hexane | 16 | hexadecane |
| 7 | heptane | 17 | heptadecane |
| 8 | octane | 18 | octadecane |
| 9 | nonane | 19 | nonadecane |
| 10 | decane | 20 | icosane* |

* Spelled "eicosane" prior to 1979 version of IUPAC rules

1.2 Nomenclature for Branched-chain Alkanes

- The rules for naming **branched-chain alkanes** are summarised in the table below.

prefix

↓

What and where are the substituents?

+

parent

↓

What is the longest carbon chain?

+

suffix

↓

What is the functional group?

-ane

- Find the **longest continuous chain** of carbon atoms, and use the name of this chain as the **base name**.
- Number each carbon atom in the longest chain, beginning **with the end nearest a substituent**.
- Name the substituents attached to the longest chain (as **alkyl groups**). Give the location of each substituent by the number of the main-chain carbon atom to which it is attached.
 - An **alkyl group** is formed by removing a hydrogen atom from an alkane.
 - General formula of an alkyl group: C_nH_{2n+1}
 - To name an alkyl group, change the **-ane** ending of the alkane to **-yl**.

| Alkyl group | Structure |
|-------------|---------------------|
| methyl | CH_3- |
| ethyl | CH_3CH_2- |
| propyl | $CH_3CH_2CH_2-$ |
| butyl | $CH_3CH_2CH_2CH_2-$ |

an alkane: C_nH_{2n+2} or $R-H$

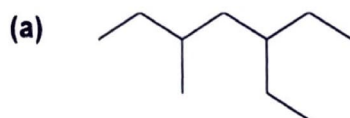
an alkyl group: C_nH_{2n+1} or $R-$

- When two or more substituents are present, list them in **alphabetical order**. When two or more of the same alkyl substituents are present, use the prefixes **di-**, **tri-**, **tetra-**, etc. to avoid having to name the alkyl group repeatedly.
- Note: Use **comma (,)** to separate 2 numbers. Use **hyphen (-)** to separate a number and a word.

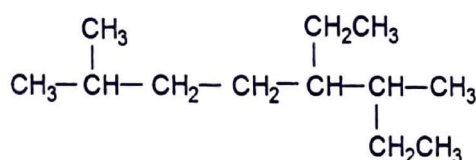
Tip: Numbering your carbons is a useful way to draw structures. Practice it!

■ ■ — **Worked Example 1** — ■ ■

Give the systematic (IUPAC) name for the following alkanes.



3-ethyl-5-methyl heptane



5-ethyl-2,6-dimethyloctane

1.3 Classification of hydrogen and carbon atoms

- Carbon atoms are classified as **primary** (1°), **secondary** (2°), **tertiary** (3°) or **quaternary** (4°) depending on the number of carbon atoms to which they are bonded.

| | | |
|--|---|--|
| <p>two 1° carbons</p> <p>$\text{CH}_3-\text{CH}_2-\text{CH}_3$</p> <p>a 2° carbon</p> <p>propane</p> | <p>a 3° carbon</p> <p>$\text{CH}_3-\text{CH}(\text{CH}_3)-\text{CH}_3$</p> <p>2-methylpropane</p> | <p>a 4° carbon</p> <p>$\text{CH}_3-\text{C}(\text{CH}_3)_2-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{CH}_3$</p> <p>2,2,4-trimethylpentane</p> |
| <ul style="list-style-type: none"> A 1° C atom is bonded to one other C atom. A 2° C atom is bonded to two other C atoms. A 3° C atom is bonded to three other C atoms. A 4° C atom is bonded to four other C atoms. | | |

- Hydrogen atoms are classified as **primary** (1°), **secondary** (2°) or **tertiary** (3°) depending on the type of carbon atom to which they are bonded.

| | | | |
|--|---|---|-------------------------|
| <p></p> <p>1° H atom</p> | <p></p> <p>2° H atom</p> | <p></p> <p>3° H atom</p> | <p>Example:</p> <p></p> |
| A 1° H atom is bonded to a C atom that is bonded to one other C atom. | A 2° H atom is bonded to a C atom that is bonded to two other C atoms. | A 3° H atom is bonded to a C atom that is bonded to three other C atoms. | |

2 Isomerism in Alkanes

2.1 Constitutional (or structural) isomerism

- **Constitutional (or structural) isomerism** arises when there exists compounds with the same molecular formula but different structural formulae.
- From butane onwards, alkanes have constitutional isomers due to the branching of the hydrocarbon chains.

| Example 1 | Example 2: Constitutional isomers with molecular formula C_6H_{14} | | |
|--|---|--|--|
| $CH_3CH_2CH_2CH_3$ butane $CH_3-CH-CH_3$ CH_3 2-methylpropane | $CH_3CH_2CH_2CH_2CH_2CH_3$ hexane $CH_3CH_2CH_2-CH-CH_3$ CH_3 2-methylpentane $CH_3CH_2-CH-CH_2CH_3$ CH_3 3-methylpentane $CH_3CH(CH_3)CH(CH_3)CH_3$ 2,3-dimethylbutane $CH_3CH_2C(CH_3)_2CH_3$ 2,2-dimethylbutane | | |

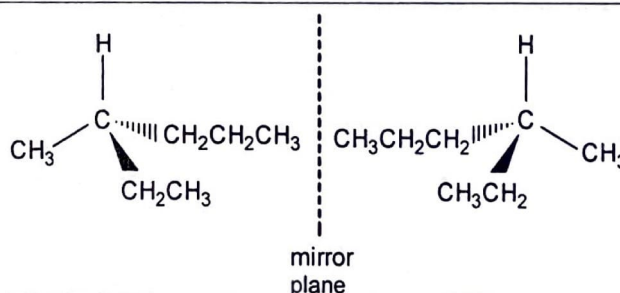
2.2 Stereoisomerism

- **Stereoisomerism** arises when there exists compounds with the same molecular formula and structural formula but differ in the way in which their atoms are arranged in space relative to one another.

(a) Enantiomerism

- Some branched-chain alkanes display **enantiomerism** (or optical isomerism in the old A-level syllabus). This is because they contain a chiral carbon centre with no plane of symmetry and hence can exist as a pair of enantiomers, which are non-superimposable mirror images of each other.

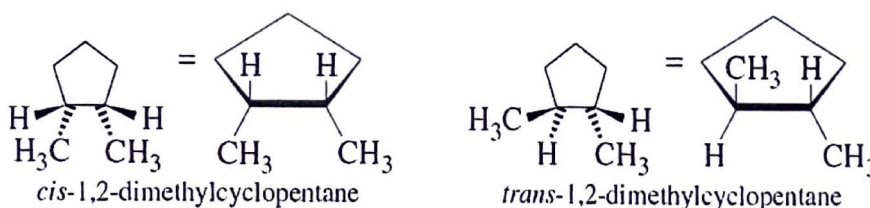
Example:
3-methylhexane displays enantiomerism



(b) Cis-trans isomerism

- Some cycloalkanes display **cis-trans isomerism**. This is because the ring structure restricts the free rotation of the bonds in the ring.

Example: 1,2-dimethylcyclopentane displays cis-trans isomerism



3 Physical Properties

- Alkanes contain C–C and C–H bonds. As the difference in electronegativity between C and H atoms is negligible, the C–H bond is essentially non-polar and alkanes are **essentially non-polar**.
- The intermolecular forces of attraction between alkane molecules are relatively weak **instantaneous dipole-induced dipole interactions**.
- Table showing some physical properties of straight-chain alkanes:

| Name | Formula | Melting point / °C | Boiling point / °C | Density / g cm ⁻³ (20°C) | State at r.t.p. | Remark |
|----------|--|--------------------|--------------------|-------------------------------------|-----------------|---|
| methane | CH ₄ | -182 | -162 | gas | gas | The C ₁ to C ₄ straight-chain alkanes are colourless gases at room temperature. |
| ethane | CH ₃ CH ₃ | -183 | -89 | gas | gas | |
| propane | CH ₃ CH ₂ CH ₃ | -188 | -42 | gas | gas | |
| butane | CH ₃ (CH ₂) ₂ CH ₃ | -138 | -0.5 | gas | gas | |
| pentane | CH ₃ (CH ₂) ₃ CH ₃ | -130 | 36 | 0.626 | liquid | The C ₅ to C ₁₇ alkanes are colourless liquids of increasing viscosity. |
| hexane | CH ₃ (CH ₂) ₄ CH ₃ | -95 | 69 | 0.659 | liquid | |
| heptane | CH ₃ (CH ₂) ₅ CH ₃ | -91 | 98 | 0.684 | liquid | |
| octane | CH ₃ (CH ₂) ₆ CH ₃ | -57 | 126 | 0.703 | liquid | |
| nonane | CH ₃ (CH ₂) ₇ CH ₃ | -53 | 151 | 0.718 | liquid | The remaining alkanes containing 18 carbons or more are solids at room temperature. |
| decane | CH ₃ (CH ₂) ₈ CH ₃ | -30 | 174 | 0.730 | liquid | |
| undecane | CH ₃ (CH ₂) ₉ CH ₃ | -26 | 196 | 0.740 | liquid | |
| dodecane | CH ₃ (CH ₂) ₁₀ CH ₃ | -10 | 216 | 0.749 | liquid | |
| icosane | CH ₃ (CH ₂) ₁₈ CH ₃ | 37 | 343 | 0.789 | solid | |

3.1 Boiling and Melting Points

(a) The boiling and melting points of alkanes **increase with increasing number of carbon atoms**.

- Explanation:** As the number of carbon atoms in alkanes increases, the **number of electrons per alkane molecule** increases and the size of electron cloud of the alkane molecule increases. As a result, the extent of polarisation of the electron cloud increases, leading to increasing strength of instantaneous dipole-induced dipole attractive forces which are overcome at increasingly higher temperatures.

(b) The boiling and melting points of isomeric alkanes **decrease with increasing degree of branching**.

| Alkane | pentane | 2-methylbutane | 2,2-dimethylpropane |
|--------------------|---|---|--|
| | CH ₃ CH ₂ CH ₂ CH ₂ CH ₃ | CH ₃ -CH-CH ₂ CH ₃ CH ₃ | CH ₃ -C-CH ₃ CH ₃ |
| Boiling point / °C | 36 | 28 | 10 |

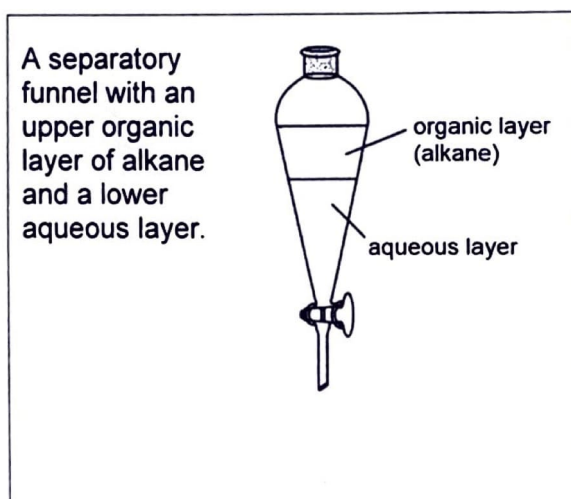
- Explanation:** With branching, the molecule becomes more spherical (or more compact) and its surface area available for intermolecular interactions decreases. This reduces the extent of contact between neighbouring molecules, resulting in weaker instantaneous dipole-induced dipole forces that are overcome at a lower temperature.

3.2 Solubility

- Being essentially non-polar, the alkanes are soluble in non-polar solvents such as benzene and are insoluble in water and other highly polar solvents.
- Some liquid alkanes are used as non-polar solvents (e.g. hexane). These liquid alkanes dissolve compounds of low polarity and do not dissolve compounds of high polarity (refer to section 5.5 of Chemical Bonding Part 1 lecture notes)

3.3 Density

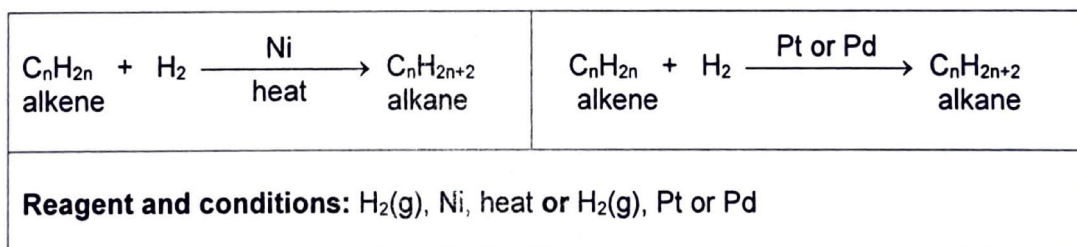
- The density of alkanes increases with increasing molecular size of the alkanes but tends to level off at about 0.8 g cm^{-3} . Thus, all alkanes are less dense than water.



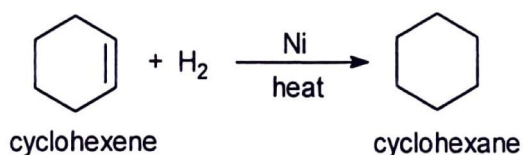
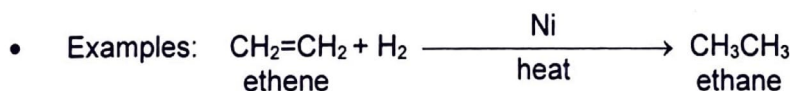
Scan this QR code to see how to use a separatory / separating funnel to separate two immiscible liquids.

4 Preparation of Alkanes

4.1 Reduction of alkenes

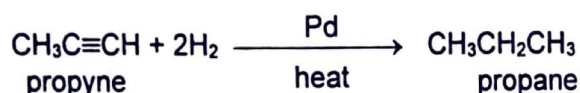


- A mixture of the alkene and hydrogen is passed over finely divided platinum, palladium or nickel catalyst. Nickel is the least active of these catalysts and requires an elevated temperature and pressure, whereas platinum and palladium function adequately at ordinary temperatures and pressures.

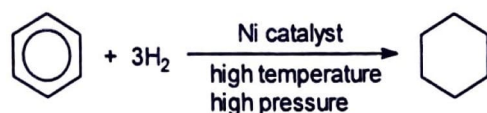


4.2 Reduction of other unsaturated hydrocarbons

- Alkynes can be reduced to alkanes under suitable conditions.



- Benzene can also be reduced to cyclohexane under suitable conditions.



5 Reactions of Alkanes

- The effects of various reagents on hexane, a typical alkane, are shown in the table below.

| Reagent | Effect |
|--------------------------------------|---|
| NaOH(aq) | No effect, whether hot or cold. Two immiscible layers observed. |
| HCl(aq) | No effect, whether hot or cold. Two immiscible layers observed. |
| Conc. H ₂ SO ₄ | No effect, whether hot or cold. Two immiscible layers observed. |
| Acidified KMnO ₄ (aq) | No decolourisation of purple KMnO ₄ even on heating. Two immiscible layers observed. |
| Air | No effect when cold. Burns when heated. |
| Bromine | No effect in the dark. Bromine decolourised in the presence of sunlight. |

- From the above table, it can be seen that hexane is rather unreactive. Its behaviour is typical of that of alkanes which are unaffected by **polar reagents** such as acids, alkalis, dehydrating agents or aqueous oxidising agents.
- Alkanes are **saturated** hydrocarbons and essentially **non-polar**. They consist of molecules which have no centres of electrical charge and are unable to attract charged species like H⁺, OH⁻ or MnO₄⁻. They contain only non-polar C–C bonds and essentially non-polar C–H bonds.

The **general lack of reactivity** of alkanes can be attributed to the following reasons:

- Alkanes **are non-polar**.
 - They **do not contain any region of** high electron density and thus do not attract electrophilic reagents.
 - They also **do not contain any** e⁻ deficient sites to attract nucleophilic reagents.
- Alkanes have **relatively** strong **C–C and C–H bonds** which do not break under normal conditions.

- However, alkanes do undergo reactions with **non-polar reagents** (e.g. Cl₂ and O₂) under the right conditions (e.g. in the presence of ultraviolet light or heat).

5.1 Combustion

- Alkanes burn readily in air or oxygen when ignited. The reaction is very exothermic, thus making alkanes an important source of **fuel** (see Section 7).
- In excess oxygen, alkanes burn with a non-sooty flame. On the other hand, unsaturated hydrocarbons burn with a sooty flame.
- Complete combustion** of alkanes produces $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$.

| | |
|-----------------------------|--|
| Combustion of a hydrocarbon | $\text{C}_x\text{H}_y + \frac{x+\frac{y}{4}}{2} \text{O}_2(\text{g}) \longrightarrow x \text{CO}_2(\text{g}) + \frac{y}{2} \text{H}_2\text{O}(\text{l})$ |
| Combustion of an alkane | $\text{C}_n\text{H}_{2n+2} + \frac{3n+1}{2} \text{O}_2(\text{g}) \longrightarrow n \text{CO}_2(\text{g}) + (n+1) \text{H}_2\text{O}(\text{l})$ |
| E.g. Combustion of methane | $\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$ |

- Incomplete combustion** of alkanes leads to the formation of $\text{CO}(\text{g})$ and C (as soot) in addition to $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$.

| | |
|-----------------------------------|---|
| Formation of CO | $\text{CH}_4(\text{g}) + \frac{3}{2} \text{O}_2(\text{g}) \longrightarrow \text{CO}(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$ |
| Formation of C (as soot) | $\text{CH}_4(\text{g}) + \text{O}_2(\text{g}) \longrightarrow \text{C}(\text{s}) + 2 \text{H}_2\text{O}(\text{l})$ |

5.2 Halogenation (Mechanism: Free Radical Substitution)

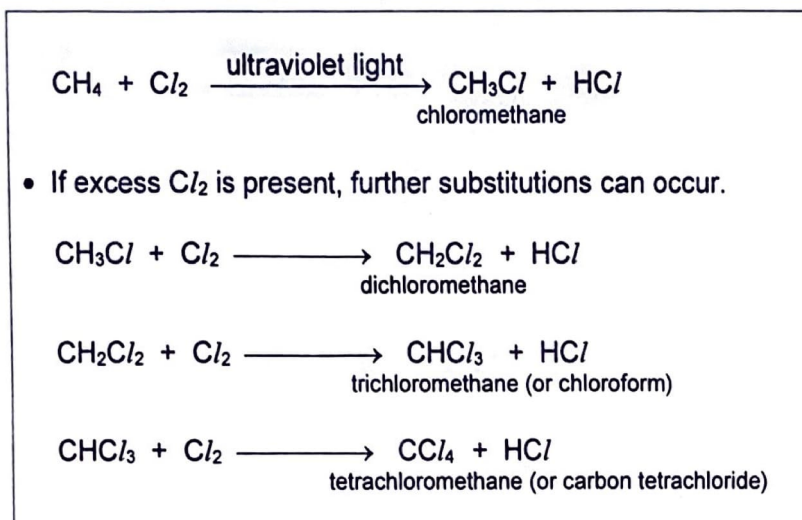
- Halogenation of an alkane involves the substitution of one or more hydrogen atoms of the alkane by halogen atoms.
- Energy input in the form of heat or ultraviolet light is needed to initiate these halogenations. These reactions may be conducted in either liquid or gaseous phase (but not under aqueous condition as the water molecules will react with any radical present).

| | |
|---|---|
| $\text{R-H} + \text{X}_2 \xrightarrow[\text{or heat}]{\text{ultraviolet light}} \text{R-X} + \text{HX}$ | <p>Note: R-H = alkane molecule $\text{X} = \text{Cl}$ or Br</p> <ul style="list-style-type: none"> The focus will be on chlorination and bromination. Fluorination is dangerously exothermic. Iodination does not occur as the overall reaction is endothermic and is thermodynamically unfavourable. |
| <p>Reagent: Cl_2 or Br_2</p> <p>Condition: ultraviolet light or heat</p> <p>Mechanism: Free-radical substitution</p> | |

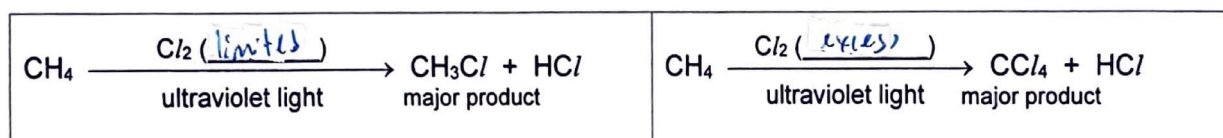
- Examples:

| Reaction | Observations |
|--|--|
| $\text{CH}_4 + \text{Cl}_2 \xrightarrow{\text{ultraviolet light}} \text{CH}_3\text{Cl} + \text{HCl}$ | <ul style="list-style-type: none"> Decolourisation of greenish-yellow Cl_2. Formation of white HCl fumes that turn damp blue litmus paper red. |
| $\text{CH}_4 + \text{Br}_2 \xrightarrow{\text{ultraviolet light}} \text{CH}_3\text{Br} + \text{HBr}$ | <ul style="list-style-type: none"> Decolourisation of reddish-brown Br_2. Formation of white HBr fumes that turn damp blue litmus paper red. |

- The reaction always produces a mixture of products.



- For simplicity:



6.1 Some important terms

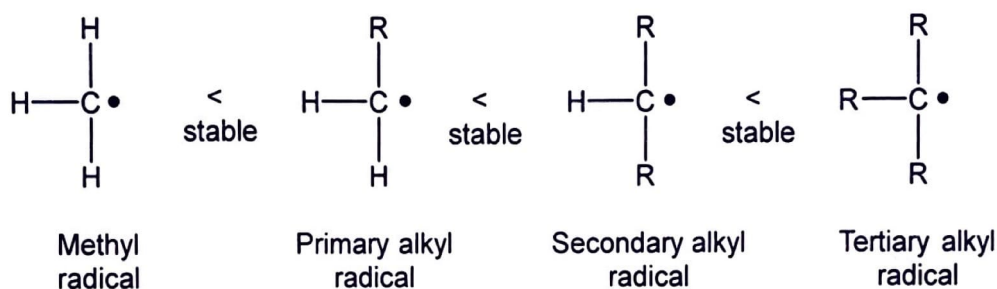
(a) Free radical

- A **free radical** (or radical) is an atom or group of atoms that has an **unpaired electron** (which is represented by •)

| | | | | |
|------------------|--|--|---|---|
| $\text{H}\cdot$ | $\cdot\ddot{\text{Cl}}\cdot$ or $\text{Cl}\cdot$ | $\cdot\ddot{\text{Br}}\cdot$ or $\text{Br}\cdot$ | $\text{CH}_3\cdot$ or $\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}\cdot \\ \\ \text{H} \end{array}$ | $\text{CH}_3\text{CH}_2\cdot$ or $\begin{array}{c} \cdot \\ \\ \text{CH}_3\text{CH}_2 \end{array}$ or $\begin{array}{c} \text{H} \\ \\ \text{H}_3\text{C}-\text{C}\cdot \\ \\ \text{H} \end{array}$ |
| hydrogen radical | chlorine radical | bromine radical | methyl radical | ethyl radical |
| | | | alkyl radical | |

- Free radicals are highly reactive and are intermediates in many of the reactions of alkanes. As they have equal numbers of protons and electrons, they are electrically neutral (unlike cations or anions).
- Stability of alkyl radicals depends on the number of alkyl groups (usually represented by the letter 'R') attached to the carbon atom with the unpaired electron.

The following shows the relative stability of alkyl radicals:



The carbon with the unpaired electron is **electron-deficient**. As alkyl groups are **electron-donating**, the **more alkyl groups attached to the carbon with the unpaired electron, the more stable the alkyl radical**.

(b) Homolytic fission

- Homolytic fission of a covalent bond occurs when the bond breaks in such a way that each of the atom involved in forming the bond acquires one of the two bonding electrons, thus forming free radicals.
- Examples:

| | |
|--|--|
| Homolytic fission of the Cl-Cl bond | $\begin{array}{c} \times \times \times \\ \times \text{Cl} \times \times \times \\ \times \times \end{array} \cdot \cdot \begin{array}{c} \times \times \\ \times \text{Cl} \times \\ \times \times \end{array} \rightarrow \begin{array}{c} \times \times \\ \times \text{Cl} \times \\ \times \times \end{array} \cdot + \cdot \begin{array}{c} \times \times \\ \times \text{Cl} \times \\ \times \times \end{array}$ |
| | $\text{Cl}-\text{Cl} \longrightarrow \text{Cl}\cdot + \cdot\text{Cl}$ |
| Homolytic fission of the C-H bond | $\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H} \end{array} \longrightarrow \begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}\cdot \\ \\ \text{H} \end{array} + \text{H}\cdot$ |
| Note: A curly arrow with half a head (i.e. 'fish-hook' arrow) represents the movement of one electron. | |

6.2 Free-radical Substitution

- Reaction: $\text{CH}_4 + \text{Cl}_2 \xrightarrow{\text{ultraviolet light}} \text{CH}_3\text{Cl} + \text{HCl}$
- The reaction mechanism for this reaction is termed **free-radical substitution**.
- It involves a **chain reaction** consisting of **initiation step**, **propagation steps** and **termination steps**.

| | |
|---|--|
| <p>Step 1: Initiation</p> $\text{Cl}-\text{Cl} \xrightarrow[\text{heat}]{\text{ultraviolet light}} \text{Cl}\cdot + \text{Cl}\cdot$ <p style="text-align: center;">chlorine radicals</p> <ul style="list-style-type: none"> Chlorine is supplied with energy (from uv light or heat) to split into free radicals via homolytic fission of the Cl-Cl bond. | <ul style="list-style-type: none"> This step involves <u>bond breaking</u> and will NOT proceed in the dark or at room temperature. It is easier to break the Cl-Cl bond than the C-H bond or the C-C bond. See <i>Data Booklet</i> for the relevant bond energy values. |
| <p>Step 2: Propagation</p> <p>(a) $\text{H}-\text{C}(\text{H})_3 + \text{Cl}\cdot \rightarrow \text{H}-\text{C}(\text{H})_2\cdot + \text{H}-\text{Cl}$</p> <p style="text-align: center;">methyl radical</p> <p>(b) $\text{H}-\text{C}(\text{H})_2\cdot + \text{Cl}-\text{Cl} \rightarrow \text{H}-\text{C}(\text{H})_2-\text{Cl} + \text{Cl}\cdot$</p> <p style="text-align: center;">chlorine radical</p> <p>Then (a), (b), (a), (b), ...</p> <p>In step 2(a), the reaction that occurs is: $\text{CH}_4 + \text{Cl}\cdot \rightarrow \cdot\text{CH}_3 + \text{HCl}$ Explain why the reaction $\text{CH}_4 + \text{Cl}\cdot \rightarrow \text{CH}_3\text{Cl} + \text{H}\cdot$ does not occur.</p> <p>The formation of the H-Cl bond is <u>more exothermic</u> than the formation of the C-H bond.</p> <p>Note: Hydrogen radical $\text{H}\cdot$ is <u>never formed</u> in free radical substitution.</p> | <ul style="list-style-type: none"> These steps involve both bond breaking and bond formation. The major products are being formed in these steps. Step 2(a) (hydrogen abstraction) – the highly reactive chlorine radical collides with a methane molecule and abstracts one hydrogen atom from it, forming hydrogen chloride and a methyl radical. Step 2(b) (halogen abstraction) – the methyl radical can react with a chlorine molecule, leading to the formation of chloromethane and a chlorine free radical. The chlorine free radical produced can proceed to attack another methane molecule and hence the steps (a), (b), (a), (b), are repeated. Note: sum of all propagation steps gives overall chemical equation. As a result, thousands of molecules of chloromethane are formed by steps 2(a) and 2(b) for every photon of light absorbed in step 1. |
| <p>Step 3: Termination</p> $\text{Cl}\cdot + \text{Cl}\cdot \rightarrow \text{Cl}_2$ $\text{H}-\text{C}(\text{H})_2\cdot + \text{Cl}\cdot \rightarrow \text{H}-\text{C}(\text{H})_2-\text{Cl}$ $\text{H}-\text{C}(\text{H})_2\cdot + \text{H}-\text{C}(\text{H})_2\cdot \rightarrow \text{H}-\text{C}(\text{H})_2-\text{C}(\text{H})_2-\text{H}$ | <ul style="list-style-type: none"> This step involves bond formation. The reaction ends when two free radicals collide and combine to form a stable product. Trace quantities of compounds containing at least twice the no. of C atoms when compared to the starting alkane can be detected in the mixture of products, e.g. ethane being formed from methane. |

- Note:** A **chain reaction** is a reaction that involves a series of steps, each of which generates a reactive species that brings about the next step. Such a reaction essentially consists of
 - a chain-initiating step, in which energy is absorbed and a reactive species generated,
 - one or more chain-propagating steps, each of which consumes a reactive species and generates another,
 - chain-terminating steps, in which reactive species are consumed but not generated.

■ ■ — Worked Example 2 — ■ ■

Propane can undergo reaction to give 2-chloropropane.

(a) Suggest the reagent and condition for this reaction.

uv light, chlorine (chlorine)

(b) Write a balanced equation for this reaction.



(c) Describe the mechanism for this reaction.

| | |
|--|---|
| <p>Mechanism: <u>Free-radical substitution</u> Name</p> <p>Step 1: Initiation Name each impt step of FRS</p> $\text{Cl}-\text{Cl} \xrightarrow[\text{or heat}]{\text{ultraviolet light}} \text{Cl}\cdot + \text{Cl}\cdot$ <p>- Write equation - Show half arrows for initiation step - State condition</p> <p>Step 2: Propagation Name each impt step of FRS</p> <ul style="list-style-type: none"> Label propagation steps (a) and (b). Then (a), (b), (a), (b), <p>Recall: This reaction is to give 2-chloropropane</p> <p>(a) $\text{CH}_3\text{CH}_2\text{CH}_3 + \text{Cl}\cdot \rightarrow \text{CH}_3\dot{\text{C}}\text{HCH}_3 + \text{HCl}$</p> <p>(b) $\text{CH}_3\dot{\text{C}}\text{HCH}_3 + \text{Cl}_2 \rightarrow \text{CH}_3\text{CH}(\text{Cl})\text{CH}_3 + \text{Cl}\cdot$</p> <p>Then (a), (b), (a), (b), ...</p> <p>Step 3: Termination Name each impt step of FRS</p> <p>$\text{Cl}\cdot + \text{Cl}\cdot \rightarrow \text{Cl}_2$</p> <p>$\text{CH}_3\dot{\text{C}}\text{HCH}_3 + \text{Cl}\cdot \rightarrow \text{CH}_3\text{CH}(\text{Cl})\text{CH}_3$</p> <p>$\text{CH}_3\dot{\text{C}}\text{HCH}_3 + \text{CH}_3\dot{\text{C}}\text{HCH}_3 \rightarrow \text{CH}_3\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{CH}_3$</p> <p>The termination steps must include one of which that forms the required product.</p> <p>Write 3 equations for termination</p> | <p>Name of mechanism: <u>Free-radical substitution</u></p> <p>Initiation:</p> $\text{Cl}-\text{Cl} \xrightarrow[\text{heat}]{\text{ultraviolet light}} \text{Cl}\cdot + \text{Cl}\cdot$ <p>Propagation:</p> <p>(a) $\text{CH}_3\text{CH}_2\text{CH}_3 + \text{Cl}\cdot \rightarrow \text{CH}_3\dot{\text{C}}\text{HCH}_3 + \text{HCl}$</p> <p>(b) $\text{CH}_3\dot{\text{C}}\text{HCH}_3 + \text{Cl}_2 \rightarrow \text{CH}_3\text{CH}(\text{Cl})\text{CH}_3 + \text{Cl}\cdot$</p> <p>Then (a), (b), (a), (b), ...</p> <p>Termination:</p> <p>$\text{Cl}\cdot + \text{Cl}\cdot \rightarrow \text{Cl}_2$</p> <p>$\text{CH}_3\dot{\text{C}}\text{HCH}_3 + \text{Cl}\cdot \rightarrow \text{CH}_3\text{CH}(\text{Cl})\text{CH}_3$</p> <p>$\text{CH}_3\dot{\text{C}}\text{HCH}_3 + \text{CH}_3\dot{\text{C}}\text{HCH}_3 \rightarrow \text{CH}_3\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{CH}_3$</p> |
|--|---|

• Essential points

- ✓ Name of mechanism (free-radical substitution)
- ✓ Headings for 3 steps. (initiation, propagation, termination)
- ✓ Conditions for initiation. (uv light or heat)
- ✓ Half arrows from bond to halogen atoms in initiation step.
- ✓ Label propagation steps (a) and (b).
- ✓ Then (a), (b), (a), (b),
- ✓ The termination steps must include a reaction which forms the required product.
- ✓ Placing of • on correct atoms in all steps.

■ ■ — Worked Example 3 — ■ ■

Methane can react with bromine in the presence of ultraviolet light to produce CH_2Br_2 .

Write an equation to represent this reaction and describe the mechanism for this reaction.

Reaction:

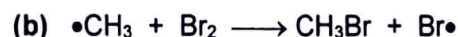


The above reaction occurs via **free-radical substitution** mechanism, which consists of the following steps:

Step 1: Initiation



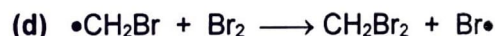
Step 2: Propagation



Then (a), (b), (a), (b),

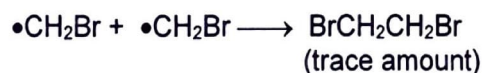
Propagation steps (a) and (b) give rise to many molecules of CH_3Br .

CH_3Br can undergo further bromination via propagation steps (c) and (d) to form CH_2Br_2 .



Then (c), (d), (c), (d),

Step 3: Termination

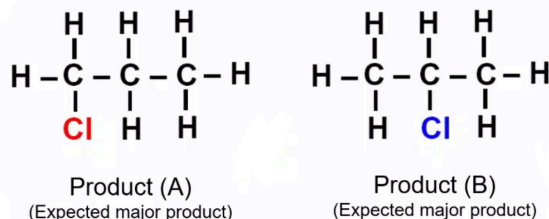
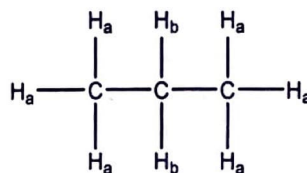


■ ■ — Worked Example 4 — ■ ■

Chlorination of propane in the presence of ultraviolet light gives a mixture of two mono-chlorinated products.

- (a) Draw the displayed formulae of these two products and suggest (with a reason) the expected ratio in which they might be formed.

Let's start by labelling the different types of H atoms on propane:



To form (A), any one of the 6 H_a in propane can be replaced by the Cl atom.

To form (B), any one of the 2 H_b in propane can be replaced by the Cl atom.

Hence, based on probability factor and assuming that all the H atoms have the same reactivity, molar ratio of (A) to (B) is 3:1.

- (b) When propane is chlorinated, the ratio of the two products formed in a 1:1 ratio instead. Suggest an explanation for the difference between this ratio and the expected ratio from (a).

The expected ratio is obtained by assuming that all H atoms have the same reactivity.

(A) is formed from $\cdot\text{CH}_2\text{CH}_2\text{CH}_3$ intermediate while (B) is formed from $\text{CH}_3\dot{\text{C}}\text{HCH}_3$.

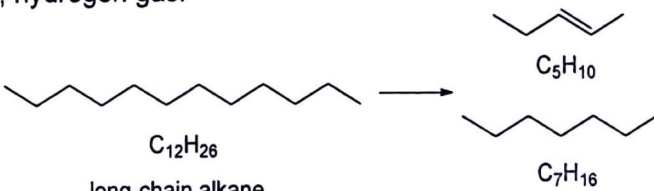
$\text{CH}_3\dot{\text{C}}\text{HCH}_3$ is a 2° radical that is more stable than $\cdot\text{CH}_2\text{CH}_2\text{CH}_3$, a 1° radical, due to the presence of one more electron-donating alkyl group attached to the electron deficient C atom. Therefore, it gives rise to a greater proportion of (B) than expected.

7.1 Natural Occurrences of Alkanes (for self reading)

- The principal sources of alkanes are **natural gas** and **crude oil (or petroleum)**.
- Natural gas** contains mainly methane with smaller amounts of the other gaseous alkanes such as ethane, propane and butane.
- Crude oil (or petroleum)** is a complex mixture of hydrocarbons consisting of alkanes, cycloalkanes and aromatic compounds. It contains a wide range of alkanes, from the low molecular weight gases to the high molecular weight solids.
- The hydrocarbons in crude oil are separated into fractions by **fractional distillation** in an oil refinery. The different fractions obtained from crude oil are shown in the table below.

| Approximate boiling range / °C | C's per molecule | Name of fraction | Fraction | Approximate boiling temperature/°C | Length of carbon chain | Uses |
|--------------------------------|------------------|-------------------------------|---------------------|--|-----------------------------------|--|
| < 25 | 1 - 4 | LPG (Liquefied Petroleum Gas) | Refinery gas | 20 | C ₁ - C ₄ | Fuel: domestic heating, gas cookers |
| 40-100 | 6 - 12 | GASOLINE | Light petroleum | 20 - 60 | C ₅ - C ₆ | Solvent |
| 100-150 | 7 - 14 | NAPHTHA | Light naphtha | 60 - 100 | C ₆ - C ₇ | Solvent |
| 150-200 | 11 - 15 | KEROSINE | Gasoline (petrol) | 30 - 200 | C ₅ - C ₁₂ | Fuel for internal combustion engine (cars etc.) |
| 220-350 | 15 - 19 | GAS OIL | Kerosene (paraffin) | 175 - 300 | C ₁₂ - C ₁₈ | Fuel for jet engines |
| > 350 | 20 - 30 | LUBRICATING OIL | Gas oil | 275 - 400 | C ₁₈ - C ₂₅ | Does not vaporise easily. Used in diesel engines where it is injected into compressed air to make it ignite. Used in industrial furnaces, being introduced as a fine mist to help the oil to burn. |
| > 400 | 30 - 40 | FUEL OIL | Lubrication oil | Non-volatile | C ₂₀ - C ₃₄ | Lubricants |
| > 400 | 40 - 50 | WAX, GREASE | Paraffin wax | Solidifies from lubricating oil fraction | C ₂₅ - C ₄₀ | Polished waxes, petroleum jelly |
| > 400 | > 50 | BITUMEN | Bitumen (asphalt) | Residue | >C ₃₀ | Road surfacing, roofing. |

- In the petroleum industry, some fractions of obtained from the distillation of crude oil can be further converted to other useful products via cracking, reforming or alkylation.

| Process | Products |
|------------|--|
| Cracking | <ul style="list-style-type: none"> Smaller straight-chain/branched-chain alkanes, cyclic hydrocarbons, alkenes, hydrogen gas. <p>An example of cracking:</p>  <p style="text-align: center;">C₁₂H₂₆ C₅H₁₀ C₇H₁₆</p> <p style="text-align: center;">long-chain alkane shorter-chain alkanes and alkenes</p> |
| Reforming | <ul style="list-style-type: none"> Aromatic hydrocarbons |
| Alkylation | <ul style="list-style-type: none"> Highly branched alkanes |

- Many of the fractions obtained from the distillation of crude oil are used as fuels. These include LPG, petrol, kerosene, diesel, fuel oil and wax.
- Combustion of alkanes as fuels can give rise to pollution problems (see Section 7.3).

7.2 Pollution Problems

(a) Pollutants from internal combustion engines

- Car exhaust fumes contain carbon monoxide, oxides of nitrogen and unburnt hydrocarbons as a result of **incomplete combustion**.
- One reason why products of incomplete combustion are formed although there may be an excess of oxygen is that the reaction time in the combustion engine is too short.
- A typical composition of gases in petrol engine exhaust fumes is shown in the table on the right.

| Substance | % composition |
|--------------------|-------------------|
| water vapour | 9 |
| carbon dioxide | 8 |
| carbon monoxide | 4 – 6 |
| oxygen | 4 |
| hydrogen | 2 |
| hydrocarbons | 0.2 |
| oxides of nitrogen | 0.3 |
| nitrogen | (chief component) |

(b) Environmental Consequences of CO, NO_x and unburnt hydrocarbons

| Pollutant | Effect | How they are formed | Methods for reducing pollution |
|--|---|---|---|
| Carbon monoxide, CO | Combines with haemoglobin in blood and renders it ineffective to transport oxygen. May affect mental alertness. 10% in air in confined spaces fatal in 2 minutes. | Incomplete combustion of fuel. | 1. Careful adjustment of fuel/air proportions and design of engines. 2. Inclusion of catalytic converters in exhaust assembly to finish the combustion reaction. |
| Unburnt hydrocarbons and carbon particulates | A mixture of unburnt hydrocarbons and oxides of nitrogen can take part in a complex sequence of chemical reactions that lead to the formation of photochemical smog (in the presence of sunlight). Photochemical smog is a yellowish-white haze containing chemical species, which irritate the respiratory tract and results in chest pains and breathing difficulties. It has a harmful effect on plants. | Incomplete combustion of fuel. | As for carbon monoxide. |
| Oxides of nitrogen, NO _x (i.e. NO and NO ₂) | Acidic gases contributing to the formation of ' acid rain ', which renders farmlands unsuitable for cultivation, causes corrosion of architecture and adversely affects marine lives (due to the increased acidity of water). Contributor to photochemical smog. | Combination of nitrogen and oxygen in air at high temperature in the internal combustion engines. | Inclusion of catalytic converter to reduce the oxides to nitrogen. |

(c) Use of Catalytic Converters

- Cars are fitted with reaction **catalytic converters** in the exhaust system to remove three main pollutants (CO, NO_x and unburnt hydrocarbons) from exhaust gases. These pollutants are **converted into CO₂, N₂ and water vapour**.
- Refer to lecture notes on **Reaction Kinetics** for the actions of the different catalysts in the catalytic converter.

(d) Other pollutants from hydrocarbon fuels

| Pollutant | Remarks |
|---------------------------------|--|
| Carbon dioxide, CO ₂ | <ul style="list-style-type: none"> Carbon dioxide is a greenhouse gas. Greenhouse gases in the atmosphere trap a lot of heat that would otherwise escape to space, thus helping to keep the Earth's surface warm. This natural greenhouse effect keeps the Earth's surface much warmer than it would be if there was no atmosphere. Since the Industrial Revolution, mankind has been releasing extra quantities of greenhouse gases into the atmosphere, which trap more heat, enhancing the natural greenhouse effect. This "enhanced" greenhouse effect is the direct result of human activities. Processes such as the burning of fossil fuels, industrial operations and forests clearing release carbon dioxide, methane and nitrous oxide into the atmosphere. Man-made emissions of carbon dioxide, more than any other greenhouse gas, have contributed most to the enhancement of Earth's natural greenhouse effect. The enhanced greenhouse effect has led to an increase in the earth's temperature, causing global warming. The result is the melting of the polar ice caps, which is likely to cause severe flooding in the future, as well as serious damage to numerous ecosystems. science.org.au/nova/016/016glo.htm <p>enhanced greenhouse effect. An increase in the natural process of the greenhouse effect, brought about by human activities, whereby greenhouse gases such as carbon dioxide, methane, chlorofluorocarbons and nitrous oxide are being released into the atmosphere at a far greater rate than would occur through natural processes and thus their concentrations are increasing. Also called anthropogenic greenhouse effect or climate change.</p> <p>global warming. An increase in the average temperature of the Earth's surface. Global warming is one of the consequences of the enhanced greenhouse effect and will cause worldwide changes to climate patterns.</p> <p>greenhouse effect. The trapping and build-up of heat in the lower atmosphere near a planet's surface. Some of the heat flowing back towards space from the Earth's surface is absorbed by water vapour, carbon dioxide, methane and other gases in the atmosphere. If the atmospheric concentration of these gases rises, then theory predicts that the average temperature of the lower atmosphere will gradually increase. The greenhouse effect in part explains the temperature differences of Mars, Venus and Earth.</p> |
| Sulfur dioxide, SO ₂ | <ul style="list-style-type: none"> Most crude oil deposits contain sulfur as an impurity. Oil refineries are increasingly treating the petrol fractions to lower the sulfur content, but some sulfur is still present in most hydrocarbon fuels. When the fuel is burned, the sulfur also burns, producing sulfur dioxide. Sulfur dioxide can be further oxidised to sulfur trioxide under suitable conditions. $\text{S(s)} + \text{O}_2\text{(g)} \longrightarrow \text{SO}_2\text{(g)}$ $\text{SO}_2\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)} \longrightarrow \text{SO}_3\text{(g)}$ Both SO₂ and SO₃ can dissolve in water to form acidic solutions. Hence, when they dissolve in rainwater, acid rain is produced. This causes various problems, including corrosion of buildings and statues, killing of plants and trees, and killing of fish through contamination of lakes. Flue-gas desulfurisation (FGD) is used in power stations to reduce the amount of SO₂ reaching the atmosphere. In this process, the flue gases are passed through a slurry of CaCO₃. CaCO₃ (limestone) is cheap and the CaSO₄ produced can be sold as gypsum, a component of plaster. |
| Lead compounds | <ul style="list-style-type: none"> Lead compounds resulting from leaded petrol are poisonous. Accumulation of lead in the body can lead to brain damage, especially in young children. |

7.3 Petroleum as a finite resource

(a) Importance of petroleum

- Petroleum (or crude oil) is a natural source of hydrocarbons. It is perhaps the most important substance consumed in modern society.
 - The fuels that are derived from petroleum form a large part of the world's total supply of energy. Gasoline, kerosene, and diesel oil provide fuel for automobiles, tractors, trucks, aircraft, and ships. Fuel oil and natural gas are used to heat homes and commercial buildings, as well as to generate electricity.
 - Petroleum also serves as a source of basic raw materials (i.e. chemical feedstocks) for the chemical industry to produce useful products such as dyes, drugs, plastics, synthetic fibers, paints, detergents and insecticides.
- Petroleum, like coal, is a fossil fuel. Fossil fuels are formed when marine plants and animals die and the remains become buried under several thousand feet in the sea beds in the absence of air. Under the extreme chemically reducing conditions, oxygen and nitrogen are removed from the carbohydrates and proteins that make up the organisms, and long carbon chains form. This formation of fossil fuels requires millions of years.
- As a fossil fuel, petroleum is a **finite resource**. It is present in the Earth in a fixed amount and this amount is **non-renewable** and cannot last forever!
- Given our dependence on petroleum, not only for fuel, but also as a chemical feedstock to produce the many necessities of modern society, it becomes clear that we must not only find alternative sources of energy but also **conserve the remaining limited oil reserves by recycling**.

(b) Recycling

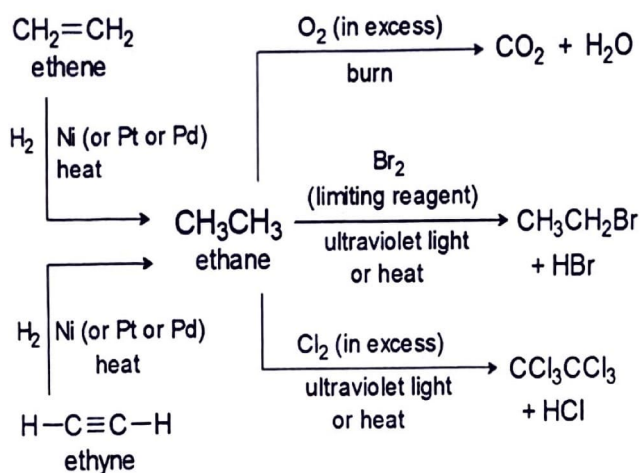
- **Recycling** is the process of converting waste materials into reusable objects. Recycling can ease major environmental problems. Recycling is an important way of conserving the Earth's natural resources for future generations. It also helps to cut back the rising amount of waste for disposal.
- Importance of recycling
 - Recycling reduces the need for fresh raw materials and so **conserves natural resources**.
 - Recycling reduces the amount of waste materials that go to the landfills and so saves space in landfills and lowers collection and disposal costs.
 - Recycling reduces energy consumption; less energy is required to recycle metals (e.g. Al) than to produce it from ores.
 - Recycling **protects the environment**.
 - It reduces pollution associated with waste such as metal cans, papers and plastics.
 - It reduces global warming. This is because with less waste to be disposed by burning, less fossil fuel is burned at power stations and so less heat-trapping CO₂ is released into the atmosphere.
 - Recycling creates green jobs.

Alkanes are generally unreactive. Why?

- Alkanes are non-polar. They do not contain any region of high electron density or electron-deficient sites.
 - Alkanes contain relatively strong C–H and C–C bonds.
- Be able to elaborate and explain.

Main pollutants that are formed when fossil fuels (e.g. crude oil, natural gas and coal) are burnt:

- carbon dioxide (not strictly a pollutant since it occurs in nature, but its overproduction can cause problems such as enhanced greenhouse effect)
- carbon monoxide
- unburnt hydrocarbons
- nitrogen oxides
- sulfur dioxide

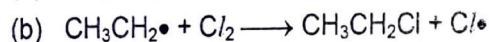
Preparation of CH₃CH₃ Reactions of CH₃CH₃

Be able to explain/discuss:

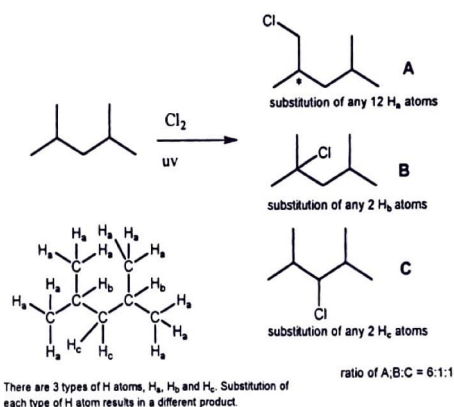
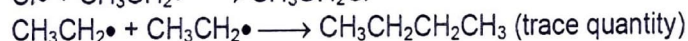
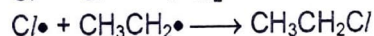
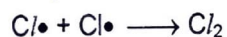
- catalytic removal of CO, NO_x and unburnt hydrocarbons arising from the internal combustion engine
- greenhouse effect and greenhouse gases (e.g. CO₂ and CH₄)
- enhanced greenhouse effect and global warming

Combustion of a hydrocarbon**Combustion of an alkane****Mechanism: Free-radical substitution****Overall reaction:**

This reaction involves **free-radical substitution** mechanism which consists of the following steps:

Step 1: Initiation**Step 2: Propagation**

Then (a), (b), (a), (b), ...

Step 3: Termination

Be able to define/explain the following:

- homolytic bond fission
- free radical substitution reaction

Be able to explain/discuss:

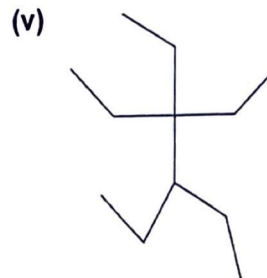
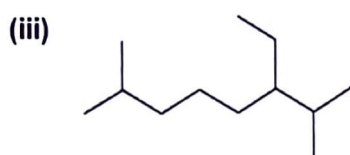
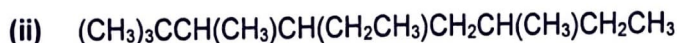
- petroleum as a finite resource
- importance of recycling



Raffles Institution
Year 5 H2 Chemistry 2022
Tutorial 10: Hydrocarbons – Alkanes

Self-Check Questions

1 (a) Name the following alkanes:

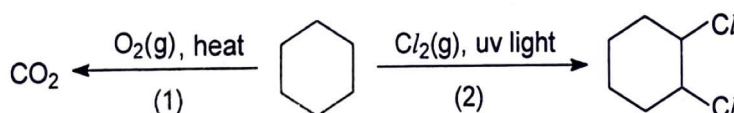


(b) Write the structural formula for the following alkanes:



2 Arrange the following hydrocarbons in order of increasing boiling point and explain your answer:
2-methylhexane, heptane, 3,3-dimethylpentane, hexane and 2-methylpentane

3 Cyclohexane undergoes reactions (1) and (2) shown below. For each reaction, write a balanced equation and name the type of reaction that occurs.



4 Write a balanced equation for the complete combustion of an alkane, $\text{C}_n\text{H}_{2n+2}$. Hence, sketch a graph to show how the number of moles of oxygen gas (y-axis) needed for complete combustion varies with the number of carbon atoms in an alkane (x-axis).

5 30 cm³ of a gaseous hydrocarbon is completely burnt in 340 cm³ excess of oxygen and the volume of residual gases is measured at room temperature and pressure (r.t.p.). The gases are then shaken with aqueous sodium hydroxide. Once again, the volume of gas is measured. The results, measured at r.t.p., are as follow:

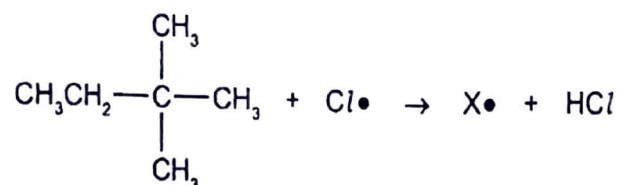
| | |
|---|-----------------------|
| Volume of residual gas (before shaking with NaOH) | = 250 cm ³ |
| Volume of residual gas (after shaking with NaOH) | = 100 cm ³ |

(a) Using the given data, determine the molecular formula of the hydrocarbon.

(b) Hence, draw and name all the possible isomers of this hydrocarbon.

6 [2012/1/20]

When heated with chlorine, the hydrocarbon 2,2-dimethylbutane undergoes free radical substitution. In a propagation step, the free radical $X\bullet$ is formed by the loss of one hydrogen atom.



How many different forms of $X\bullet$ are theoretically possible?

- A 1 B 2 C 3 D 4

7 [2014/1/20]

Two structural isomers of molecular formula C_6H_{14} are shown.



P and Q react with chlorine to form monochloro compounds $\text{C}_6\text{H}_{13}\text{Cl}$.

How many possible structural isomers, each with formula $\text{C}_6\text{H}_{13}\text{Cl}$, could be produced by P and by Q?

| | isomers formed by P | isomers formed by Q |
|---|------------------------|------------------------|
| A | 5 | 3 |
| B | 5 | 4 |
| C | 6 | 3 |
| D | 6 | 4 |

Practice Questions

- 8 (a) There are 18 constitutional isomers with molecular formula C_8H_{18} and octane is one of them. Some of these isomers may be distinguished by the number of mono-brominated products they form upon reaction with bromine in the presence of ultraviolet light.

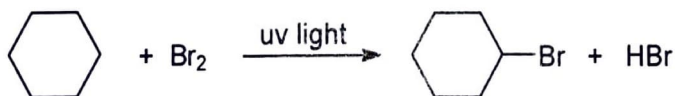
Draw an isomer with molecular formula C_8H_{18} which reacts with bromine to give

- (i) only one mono-brominated product
 - (ii) three mono-brominated products (ignore stereoisomers).
- (b) Octane and bromine dissolved in an inert solvent can react to form 3-bromooctane under ultraviolet light.
- (i) Write a balanced equation for the above reaction.
 - (ii) Describe what is observed from this reaction.
 - (iii) Name and describe the mechanism of the above reaction.
 - (iv) Explain why the reaction requires only a flash of ultraviolet light rather than prolonged radiation.
 - (v) Explain why bromine radicals are considered homogeneous catalysts in the propagation steps.
 - (vi) How may experimental conditions be adjusted to produce 3-bromooctane and other monobromooctanes as major products?
 - (vii) Octane, however, does not react with iodine to form 3-iodooctane or any other substituted product.

With the aid of suitable bond energy values from the *Data Booklet*, calculate the enthalpy change of reaction for the first propagation step of the reaction between octane and iodine to form 3-iodooctane.

Hence, suggest why it is not possible to make 3-iodooctane by this method.

- 9 Describe the mechanism for the following reaction.



- 10 F is an alkane which contains 83.72% by mass of carbon. When reacted with bromine under ultraviolet light, F produced only two isomeric mono-brominated compounds G and H. Compound H was chiral.
- (a) Suggest the structures of F, G and H, explaining your reasoning.
 - (b) Suggest, with reasoning, the approximate ratio in which G and H are formed.

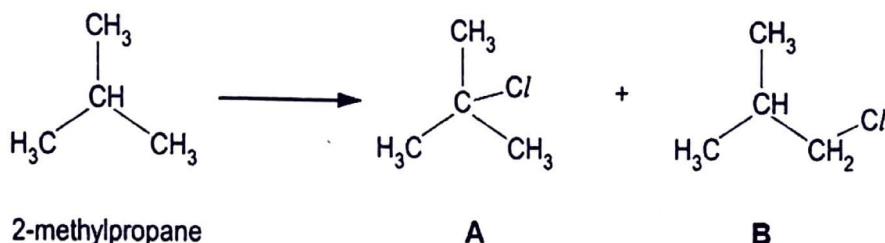
- 11 (a) Alkanes are generally considered to be unreactive compounds, showing an inertness to common reagents such as NaOH, H₂SO₄, and K₂Cr₂O₇.

Suggest two reasons why these reagents **do not** attack an alkane such as hexane.

- (b) Alkanes react with chlorine in the presence of ultraviolet light. It is found by experiment that, during this type of reaction, primary, secondary and tertiary hydrogen atoms are replaced by chlorine atoms at different rates, as shown in the following table.

| reaction | relative rate |
|---|---------------|
| $\text{RCH}_3 \rightarrow \text{RCH}_2\text{Cl}$ | 1 |
| $\text{R}_2\text{CH}_2 \rightarrow \text{R}_2\text{CHCl}$ | 7 |
| $\text{R}_3\text{CH} \rightarrow \text{R}_3\text{CCl}$ | 21 |

Using the above information, and considering the number of hydrogen atoms of each type (primary, secondary or tertiary) within the molecule, predict the relative ratio of the two possible products **A** and **B** from the chlorination of 2-methylpropane. Explain your answer. [2]



- (c) Draw the **skeletal** formulae of **four** different structural isomers of C₅H₁₁Cl that could be obtained from the chlorination of 2-methylbutane. Indicate any chiral centres in your structures by an asterisk (*), and hence state the total number of isomers that could be obtained from the monochlorination of 2-methylbutane. [3]

12 [RI Promo 2017/III/2]

- (a) If all the hydrogen atoms were equally reactive, the mono-chlorination of propane should give a 3:1 ratio of 1-chloropropane to 2-chloropropane. However, an experiment carried out at 25 °C gave 45% 1-chloropropane and 55% 2-chloropropane, via the formation of primary and secondary free radical intermediates.
- (i) Based on the information given above, comment on the relative stability of the primary and secondary free radical intermediates.
- (ii) Given that alkyl groups are electron donating groups, explain your answer to (a)(i).
- (iii) Hence, justify why the bond dissociation energy of the (CH₃)₂CH–H bond is less endothermic than that of the CH₃CH₂CH₂–H bond.

| C–H bond | bond dissociation energy / kJ mol ⁻¹ |
|--|---|
| CH ₃ CH ₂ CH ₂ –H | 422.2 |
| (CH ₃) ₂ CH–H | 410.5 |

- (b) Using skeletal formula, describe the mechanism between propane and bromine to form 1,2-dibromopropane.