

H2 ORGANIC CHEMISTRY: ALKANES

Lecture Outline

- 1 Introduction
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- 3 Physical Properties
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- 5 Reactions
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- 6 Petroleum and its Environmental Consequences
 - 6.1 Environmental Pollutants
 - 6.2 Use of Catalytic Converter
 - 6.3 Enhanced Greenhouse Effect

Assessment Objectives

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

References

- 1 Chemistry in Action by Michael Freemantle
- 2 'A' Level Chemistry by E.N. Ramsden
- 3 Chemistry Longman 'A' Level Guides by J.G.R. Briggs
- 4 Organic Chemistry by H.L. Heys
- **5** Organic Chemistry by B.J. Stokes

Lecture	1	2
Pages	1–8	8–15
Complete by	18 Aug	23 Aug
Tutorial Qns	1–3	4–7

Hydrocarbons (Compounds containing only carbon and hydrogen atoms)



ALKANES

1 Introduction

- Homologous series of **saturated aliphatic hydrocarbon** of general formula C_nH_{2n+2} .
- Names of alkanes end with 'ane'.

n	molecular formula	name	structural formula
1	CH4	meth ane	CH ₄
2	C ₂ H ₆	eth ane	CH ₃ CH ₃
3	C ₃ H ₈	prop ane	CH ₃ CH ₂ CH ₃
4	C_4H_{10}	but ane	CH ₃ (CH ₂) ₂ CH ₃
5	C ₅ H ₁₂	pent ane	CH ₃ (CH ₂) ₃ CH ₃
6	C ₆ H ₁₄	hex ane	CH ₃ (CH ₂) ₄ CH ₃

- Constitutional isomerism exists in alkanes containing of more than three carbon atoms due to branching of chains.
 - E.g. C_4H_{10} has 2 constitutional isomers.







branched chain

E.g. C_5H_{12} has 3 constitutional isomers.



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(ii) If some alkyl groups occur more than once as substituents, indicate prefix di–, tri–, tetra–, etc.



E.g.



4–ethyl–2–methylhexane (wrong name: 2–methyl–4–ethylhexane)

(Wrong name: 3–ethyl–5–methylhexane or 5–methyl–3–ethylhexane. This is obtained when we numbered from the right. The correct order is the one that gives the lower number at the first point of substituent.)

Self–practice 1 (Check your answers on SLS Alkanes Lesson 1) Name the following organic compounds using the IUPAC system.

(i) CH_3 (ii) CH_3 CH_3 CH_3 $CH_3-CH-CH_2-CH-CH_3$ $CH_3-C-CH_2-CH_2CH_2CH_3$ CH_2CH_3 CH_2CH_3 H

2 Cycloalkanes

- Saturated hydrocarbons that **contain a ring of carbon atoms** are called cycloalkanes.
- General formula is C_nH_{2n}.
 E.g.



• Chemical behaviour of cycloalkanes is similar to the open-chain alkanes.

Making Thinking Visible

Question: Why is it not necessary to name methylcyclopentane as 1–methylcyclopentane?

- **Answer:** Only one substituent on cyclopentane. Hence, position number is not required as there is no distinction between the carbon atoms.
- **Question:** Why is 1,2–dimethylcyclohexane not named as 3,4–dimethylcyclohexane or 5,6–dimethylcyclohexane?

Answer: The position numbers are chosen to be as low as possible.

You can now attempt Tutorial Questions: Q1 – Q3

3 Physical Properties

- I. Solubility, Density and Viscosity
- Alkanes are non-polar. They are insoluble in polar solvents such as water but soluble in non-polar solvents, such as benzene, ether (e.g. dimethyl ether, CH₃-O-CH₃) and CCl₄.

Reason: Alkanes do not dissolve in water since the energy released from the weaker permanent dipole–induced dipole interactions between the polar water molecules and non–polar alkane molecules is insufficient to overcome the stronger hydrogen bonding between the water molecules.

- Alkanes float on top of water and thus are **less dense than water**.
- Viscosity (more viscous, less fluid) of liquid alkanes increases with increasing molecular mass as long molecules have stronger instantaneous dipole–induced dipole interactions (due to greater number of electrons).
- II. Boiling and Melting Points

(i) Straight chain alkanes

• At room temperature and atmospheric pressure, first four alkanes (C₁–C₄) are gases; next thirteen alkanes (C₅–C₁₇) are liquids; C₁₈ or more are solids.

Reason: Boiling point increases with number of carbon atoms as more energy is required to overcome the **increasing strength of instantaneous dipole-induced dipole interactions** due to **increasing number of electrons**.

- Melting point increases in a zig-zag pattern as intermolecular forces in a crystal depend on the size of the molecules and how well they are packed into the solid lattice.
- (ii) Branched chain isomers
 - It has a lower boiling point than the straight chain isomer.

Reason: Branched molecules are **more spherical**, hence **less surface area of contact between molecules**, resulting in a **decrease in strength of instantaneous dipole–induced dipole interactions**.

• Effect of branching on packing and on melting point is irregular.

4 Preparation

Reduction of Alkenes

Reagent: H₂ gas

Condition: Ni catalyst, heat

OR

Pt or Pd catalyst



where R', R", R", R"": H or alkyl groups (can be the same or different)

5 Reactions

Candidates should be able to: (a) explain the general unreactivity of alkanes, including towards polar reagents

• Alkanes form the **backbone structure of organic compounds**, where other functional groups are bonded and thereby giving rise to specific reactivity.

E.g.: CH₃CH₂CH₃ CH₃CH₂CH₂**OH** CH₃CH₂CH₂**C***I* propane **(alkane)** propan–1–ol **(alcohol)** 1–chloropropane **(halogenoalkane)**

- Due to difference in electronegativities between elements, regions of high (δ–) and low (δ+) electron densities are introduced with addition of functional groups (e.g. C^{δ+}-Cl^{δ-} and C^{δ+}=O^{δ-}).
- However, due to the relatively non-polarity of the C-H bond in alkanes since C and H have similar electronegativities, electrons in the C-H and C-C bonds are shared equally by the bonding atoms.
- Hence, none of the atoms in an alkane has any significant charge to attract charged species like H⁺, OH⁻ and MnO₄⁻. This renders alkanes to be unreactive towards polar reagents (e.g. H^{δ+}Cl^{δ-}) and ions.

5.1 Combustion

Candidates should be able to: (b) describe the chemistry of alkanes as exemplified by the following reactions of ethane:

(i) combustion

5.11 Limited supply of oxygen

Incomplete combustion produces CO (or C) and H₂O.

E.g. $CH_3CH_3 + 5/2 O_2 \rightarrow 2CO + 3H_2O$ $CH_3CH_3 + 3/2 O_2 \rightarrow 2C + 3H_2O$

5.12 Unlimited supply / excess of oxygen

Complete combustion produces CO₂ and H₂O.

E.g. $CH_3CH_3 + 7/2 O_2 \rightarrow 2CO_2 + 3H_2O$

Note:

- Reaction is **exothermic**. The greater the number of carbon atoms, the more energy produced but the greater the amount of oxygen needed for complete combustion.
- Ease of burning accounts for the use of many alkanes as fuels.
- Methane (natural gas or cooking gas) burns with a clean blue flame tinged with a little yellow. Very little 'soot' (carbon) is formed. Burning of higher alkanes gives rise to sooty flames.
- The complete combustion of hydrocarbons can be expressed with a general equation:

$$C_{x}H_{y} + (x + \frac{y}{4})O_{2} \rightarrow xCO_{2} + (\frac{y}{2})H_{2}O$$

Amount of CO_2 and H_2O produced can be measured and the composition of hydrocarbon can be calculated.

Making Thinking Visible

Question: Why is it the combustion of alkanes exothermic?

Answer: Stronger bonds in CO₂ and H₂O are formed and weaker C–H bonds in alkanes are broken.

Question: Why does the burning of higher alkanes give rise to sooty flames?

Answer: Higher alkanes contain more carbon atoms which need more oxygen to burn. However, oxygen is limited and incomplete combustion is more likely to take place leading to formation of soot which is carbon.

5.2 Formation of Halogenoalkanes

Candidates should be able to:

- (b) describe the chemistry of alkanes as exemplified by the following reactions of ethane:
 - (ii) free–radical substitution by chlorine and by bromine

Alkanes react with halogens (Cl_2 or Br_2) to produce halogenoalkanes via **free-radical substitution** under **UV light** or under **high temperature** or **heat**. One or more of the hydrogen atoms in the alkane can be substituted by the halogen atoms.



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5.21 Free-radical substitution mechanism

- (c) describe the mechanism of free-radical substitution with particular
 - reference to the initiation, propagation and termination reactions
 - Chain reaction involving three basic steps:
 - 1. Initiation
 - 2. Propagation
 - 3. Termination
- E.g. Chlorination of ethane via free-radical substitution mechanism.

 $CH_3CH_3 + Cl_2 \rightarrow CH_3CH_2Cl + HCl$

1. Initiation: UV light, high temperature or heat provides energy for homolytic cleavage of C/–C/ bond to generate free radicals, C/•.



2. Propagation: A Cl- radical is consumed in one step and another Clradical is generated in another step to keep the chain reaction going.

(a)
$$CH_3CH_3 + Cl \bullet \rightarrow CH_3CH_2 + HCl$$

(b) $Cl_2 + CH_3CH_2 \rightarrow CH_3CH_2Cl + Cl \bullet$

radicals used and then regenerated

Together, these two propagation steps consume one CH_3CH_3 and one Cl_2 , and produce one HCl and one CH_3CH_2Cl , giving the following net reaction: $CH_3CH_3 + Cl_2 \rightarrow CH_3CH_2Cl + HCl$

When one more H atom in CH_3CH_3 is substituted by Cl, step (a) is repeated again and then step (b) and so forth. With each repetition of step (b), a chlorine–substituted molecule is formed.

3. Termination: Free radicals are consumed but not generated.

Possible chain-terminating steps are:

 $\begin{array}{l} \mathsf{C}/\bullet + \mathsf{C}/\bullet \to \mathsf{C}/_2\\ \mathsf{C}\mathsf{H}_3 \overset{\bullet}{\mathsf{C}}\mathsf{H}_2 + \mathsf{C}\mathsf{H}_3 \overset{\bullet}{\mathsf{C}}\mathsf{H}_2 \to \mathsf{C}\mathsf{H}_3\mathsf{C}\mathsf{H}_2\mathsf{C}\mathsf{H}_2\mathsf{C}\mathsf{H}_3\\ \mathsf{C}\mathsf{H}_3 \overset{\bullet}{\mathsf{C}}\mathsf{H}_2 + \mathsf{C}/\bullet \to \mathsf{C}\mathsf{H}_3\mathsf{C}\mathsf{H}_2\mathsf{C}/\end{array}$

radicals removed

Overall:

 $CH_{3}CH_{3} + Cl_{2} \xrightarrow{\text{UV light}} CH_{3}CH_{2}Cl + HCl$

Note:

- (i) A single free radical (once formed) can produce a large number of product molecules by **chain reaction** sequence.
- (ii) **Reaction does not stop at monosubstitution.** More than one hydrogen atom in an alkane can be replaced by chlorine with the formation of HC*l*.

E.g. Chlorination of CH₄ via free–radical substitution mechanism.

$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$	(monosubstitution)
$CH_{3}Cl + Cl_{2} \rightarrow CH_{2}Cl_{2} + HCl$	(disubstitution)
$CH_2Cl_2 + Cl_2 \rightarrow CHCl_3 + HCl$	(trisubstitution)
$CHCl_3 + Cl_2 \to CCl_4 + HCl$	(tetrasubstitution)

Hence, the reaction is not 'clean', meaning it does not give a single organic product but a mixture of products.

- (iii) Ethane and higher alkanes give rise to isomeric halogen derivatives when more than one hydrogen atom is substituted.
 - E.g. There are two dichloroethanes, CH₂C/CH₂C/ and CH₃CHC/₂, formed from the substitution of ethane with Cl₂. This is typical of reactions of alkanes as there is little difference between the strengths of the differently situated C–H bonds.

Making Thinking Visible

- **Question:** Why does **monosubstituted** ethane, CH₃CH₂C*l*, predominate if **excess of ethane** is used?
- **Answer:** In the propagation step, there is a higher probability for the C/• radical to collide with a CH_3CH_3 molecule rather than with a CH_3CH_2Cl molecule. Thus, considerable amount of CH_3CH_2Cl will be formed first. $CH_3CH_3 + Cl_2 \rightarrow CH_3CH_2Cl + HCl$
- Question: Why does more highly substituted ethane, such as CCl₃CCl₃, predominate if excess of Cl₂ is used?
- Answer: All the hydrogen atoms in ethane can be substituted by chlorine atoms when excess Cl_2 is used. $CH_3CH_3 + 6Cl_2 \rightarrow CCl_3CCl_3 + 6HCl$

Self-practice 2 (Check your answers on SLS Alkanes Lesson 2)

Write equations to show the mechanism of

 $CH_3CH_2CH_3 + 2Br_2 \rightarrow CH_3CHBrCH_2Br + 2HBr$

Mechanism:

Initiation:

Propagation:

Termination:

5.22 Reactivity of halogens

Reactivity of halogens with alkanes to form halogenoalkanes (RX) decreases down Group 17: $F_2 > Cl_2 > Br_2 > I_2$

F₂: Reaction proceeds with explosive violence, hence cannot be used in laboratory.Cl₂ and Br₂: Reaction occurs under UV light, high temperature or heat

I₂: Least reactive as iodine does not react with alkanes to any extent.

E.g 1: For CH₄ + Cl₂ \rightarrow CH₃Cl + HCl $\Delta H_{rxn 1}$ 1st propagation step: CH₄ + Cl• \rightarrow CH₃ + HCl $\Delta H_{1(1st)}$ $\Delta H_{1(1st)} = BE(C-H) - BE(H-Cl)]$ = 410 - 431 = -21 kJ mol⁻¹ 2nd propagation step: CH₃ + Cl₂ \rightarrow CH₃Cl + Cl• $\Delta H_{1(2nd)}$ $\Delta H_{1(2nd)} = BE(Cl-Cl)] - [BE(C-Cl)$ = 244 - 340 = -96 kJ mol⁻¹ $\Delta H_{rxn 1} = \Delta H_{1(1st)} + \Delta H_{1(2nd)}$ = -21 - 96 = -117 kJ mol⁻¹

E.g 2: For CH₄ + Br₂ \rightarrow CH₃Br + HBr $\Delta H_{rxn 2}$ 1st propagation step: CH₄ + Br• $\rightarrow CH_3$ + HBr $\Delta H_{2(1st)}$ $\Delta H_{2(1st)} = BE(C-H) - BE(H-Br)]$ = 410 - 366 = +44 kJ mol⁻¹ 2nd propagation step: $CH_3 + Br_2 \rightarrow CH_3Br + Br_ \Delta H_{2(2nd)}$ Δ $H_{2(2nd)} = BE(Br-Br)] - [BE(C-Br)$ = 193 - 280 = -87 kJ mol⁻¹ Δ $H_{rxn 2} = \Delta H_{2(1st)} + \Delta H_{2(2nd)}$ = 44 - 87 = -43 kJ mol⁻¹

Reasons:

As shown by the above examples, as the **atomic radius of halogen X increases** down the group, the energy released in the formation of H–X bond in the first propagation step is **less** than the energy needed to break C–H **bond**. Hence, the **first propagation step** is **increasingly endothermic** and there is **decreasing ease of substitution** since ΔH_{rxn} becomes less **exothermic** down the group.

You can now attempt Tutorial Questions: Q4 – Q5

5.23 Rate of substitution at 1°, 2° and 3° carbon atoms

In **higher alkanes**, the substitution of hydrogen atoms at different carbon atoms leads to different products.

E.g. When butane undergoes **monochlorination**, there are two possibilities for the substitution to take place as shown below.



Note: Classification of carbon atoms

Carbon atoms are classified as being 1°, 2° or 3° carbon, by the number of carbon atoms directly bonded to it.

1° carbon	2º carbon	3º carbon	4° carbon
c c	C-C-C	C-C-C	C C C C C C C
Bonded to	Bonded to	Bonded to	Bonded to
one other	two other	three other	four other
C atom	C atoms	C atoms	C atoms

Making Thinking Visible

Question: How is the expected yield of 1–chlorobutane and 2–chlorobutane in the monochlorination of butane obtained?

Answer: Butane has 10 hydrogen atoms. Based on probability factor, hydrogen atoms at any 6 positions around primary (1°) carbon atoms and any 4 positions around secondary (2°) carbon atoms can be substituted by halogen atoms. The expected ratio of 1-chlorobutane to 2-chlorobutane formed is 60% : 40%.



Question: Why is there is a discrepancy between the expected ratio and the ratio of the monochlorinated products obtained experimentally?

Answer: The 2° alkyl radical, which is more stable than the 1° alkyl radical, is formed preferentially. Hence, the rate of substitution of hydrogen atom at 2° carbon atom is higher than that at 1° carbon atom. With larger amount of 2° radicals formed, they will react with Cl₂ to form 2–chlorobutane (CH₃CH₂CHC/CH₃) as the major product.



Alkyl groups, R, exert electron donating inductive effect and they can stabilise a carbon radical by increasing the electron density on the electron deficient carbon atom carrying the odd electron. The more alkyl groups bonded to this carbon, the less reactive and more stable the radical. This explains why the tertiary radical is more stable than the secondary or primary radical that has fewer alkyl groups.

You can now attempt Tutorial Questions: Q6 – Q7

6 Petroleum and its Environmental Consequences

Candidates should be able to:

- (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

Petroleum is a finite resource. At some point in the future the supply of oil in the Earth's crust will be exhausted. In addition to being essential for current transportation technologies, most products manufactured today, from clothing to automobiles to medical supplies, are derived from petroleum–based products. Hence, it is important to recycle as much as we can.

6.1 Environmental Pollutants

To achieve maximum power, the internal combustion engine is normally run on an air– fuel mixture which is 10–20% richer in fuel than the stoichiometric mixture. Hence, car exhausts emissions contain the following pollutants.

- Carbon monoxide due to incomplete combustion of fuel. CO combines with haemoglobin in blood and reduces the oxygen–carrying ability of the haemoglobin. This can lead to oxygen starvation and eventual death.
- Oxides of nitrogen, NO and NO₂, formed from the reaction of nitrogen and oxygen in the car's engine. These oxides cause smog and acid rain. High levels of NO and NO₂ damage plant life. NO₂ also contributes to the formation of acid rain which damages vegetation, buildings and water bodies.
- Unburnt hydrocarbons due to incomplete combustion of fuel. In strong sunlight it becomes smog and can cause lung damage.

6.2 Use of Catalytic Converter

In many countries, pollution from motor cars is being reduced by fitting a platinum catalyst converter onto the motor car exhausts. It catalyses the oxidation of CO and unburnt hydrocarbons to CO_2 and H_2O by oxides of nitrogen, NO and NO_2 which are reduced to harmless N_2 and O_2 . The catalytic converter can be 'poisoned' by lead deposits on the catalyst's surface which block the sites for reactions to take place. Thus, lead–free petrol should be used.

E.g. hydrocarbons + oxides of nitrogen \rightarrow carbon dioxide + water + nitrogen 2CO + 2NO \rightarrow 2CO₂ + N₂

6.3 Enhanced Greenhouse Effect

The enhanced greenhouse effect is the direct result of human activities. Processes such as the burning of fossil fuels, industrial operations and forest clearing increase the amount of carbon dioxide, methane and oxides of nitrogen in the atmosphere. Chlorofluorocarbons, or CFCs, are also potent greenhouse gases, and as an added danger, they also destroy the ozone layer. In the upper atmosphere, CFCs produce C/ where it catalyses the conversion of ozone into O_2 . Ozone absorbs uv radiation better than does O_2 , so its depletion allows more of this high energy radiation to reach the Earth's surface.

Ultimately, more greenhouse gases means more infrared radiation trapped and held, which gradually increases the temperature of the Earth's surface and the air in the lower atmosphere. The atmosphere is now trapping more heat that would otherwise have escaped to space. This enhancement of the greenhouse effect is causing global warming. Of all the greenhouse gases released by man–made processes, carbon dioxide is the largest individual contributor to the enhanced greenhouse effect, accounting for about 60% of the increase in heat trapping.