ANDERSON SERANGOON JUNIOR COLLEGE JC1 H2 CHEMISTRY <u>HYDROCARBONS: ALKANES</u>

Lecture Outline

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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 their catalytic removal
 - (ii) gases that contribute to enhanced greenhouse effect
- (e) recognise that petroleum, a chemical feedstock, is a finite resource and the importance of recycling

References

- 1. Chemistry for Advanced Level, Peter Cann, 2002
- 2. Chemistry, The Molecular nature of Matter and Change, Silberberg, 2003
- 3. Chemistry (2nd edition). Chris Conoley and Phil Hill
- 4. Chemistry in Context. Hill & Holman
- 5. Understanding Chemistry for Advanced Level. Ted Lister, Janet Renshaw

1. Introduction

Hydrocarbons

- Hydrocarbons are compounds containing <u>only hydrogen and carbon</u>, and are obtained from crude oil, a fossil fuel.
- □ It is a major energy source.
- Alkanes constitute the major part of crude oil. Alkanes are transformed into feedstock for the chemical industry and fuels in internal combustion engines, jet engines and power stations (See Section 8). Huge fractions of energy we use come from combustion of alkanes.



<u>Alkanes</u>

- □ Alkanes are <u>saturated hydrocarbons</u>. All the carbon atoms are joined by <u>single</u> covalent bonds only.
- □ Each C atom is sp³ hybridised, tetrahedrally surrounded by H and other C atoms.
- □ Alkanes can exist as <u>straight chains</u>, <u>branched chains</u>, and <u>rings</u>.
- □ Saturated hydrocarbons with one or more rings of carbon are known as <u>cycloalkanes</u>.
- General formula:
 - for open-chain (i.e. straight-chain and branched-chain) alkanes: C_nH_{2n+2} ,
 - for cycloalkanes: C_nH_{2n} ; where n equals the number of carbon atoms.
- □ If a hydrogen atom is removed from an alkane, the partial structure that remains is called an alkyl group (*usually denoted as R*, *R*' *etc.*).

Examples of straight-chain and branched-chain alkanes

n	Condensed structural formula	Displayed formula	3–D structure	Skeletal formula	Alkyl (replace –ane with –yl)
1	CH₄ methane	H H-C-H H	H H 109.5°		–CH₃ methyl
2	CH₃CH₃ ethane	H H H-C-C-H H H			–CH₂CH₃ ethyl
3	CH₃CH₂CH₃ propane	$\begin{array}{cccc} H & H & H \\ H & - & - & - \\ H & - & - & - \\ - & - & - & - \\ H & - & H \end{array}$			–CH ₂ CH ₂ CH ₃ propyl
4	CH ₃ CH ₂ CH ₂ CH ₃ butane	H H H H H-C-C-C-C-H H H H H			–CH ₂ CH ₂ CH ₂ CH ₃ butyl
	CH ₃ CH(CH ₃) ₂ 2–methylpropane	H H H H H H C C C H H H H H H H H H			CH₃CH(CH₃)CH₂– 2–methylpropyl
5	CH₃(CH₂)₃CH₃ pentane	н н н н н н с с с с с с н н н н н н н н н н			CH ₃ (CH ₂) ₃ CH ₂ – pentyl

n	Molecular formula	Displayed formula	Skeletal formula	Ball–and–stick model
3	C₃H₅ Cyclopropane	H H H H	\bigtriangleup	ಿ ಕ್ ಿ ಕೆ ಿ ತಿ
4	C₄H₃ Cyclobutane	H H H-C-C-H H-C-C-H H-C-C-H H H		
5	C₅H₁₀ Cyclopentane			
6	C ₆ H ₁₂ Cyclohexane			

Examples of cycloalkanes (isomeric with alkenes i.e. same general formula)

2. Nomenclature using the IUPAC system

2.1 Nomenclature for Straight–Chain Alkanes

The IUPAC system is the most common method used for naming most organic compounds. Straightchain alkanes have IUPAC names as shown below. Each member has a suffix '**ane**'.

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

Alkane	Structural formula	Skeletal formula
propane	CH ₃ CH ₂ CH ₃	\langle
butane	CH ₃ CH ₂ CH ₂ CH ₃	\sim
hexane	CH ₃ (CH ₂) ₄ CH ₃	$\overline{}$
octane	CH ₃ (CH ₂) ₆ CH ₃	

2.2 Nomenclature for Branched–Chain Alkanes

In the IUPAC nomenclature, every name consists of:



Steps in naming alkanes:

Step		Example
1	Identify the parent chain [longest continuous carbon chain] and use it with the suffix.	$CH_2-CH_2-CH_3$ CH_3-CH_2-C-CH_2-CH_3 H
		longest chain is hexane
2	Identify the substituent/side chain, if any (prefix).	1 ethyl group
3	Number the carbon chain. Assign lowest possible numbers to the group(s) cited as prefix .	$\begin{array}{c} & \overset{4}{\text{CH}_2}-\overset{5}{\text{CH}_2}-\overset{6}{\text{CH}_3}\\ & \overset{ }{\text{CH}_3}-\overset{ }{\text{CH}_2}-\overset{-}{\text{C}}-\overset{-}{\text{CH}_2}-\overset{-}{\text{CH}_3}\\ & \overset{3}{\text{H}}\\ & \text{H}\\ \end{array}$ Ethyl group on C3
4	Use commas to separate numbers. Use hyphens to separate numbers and words.	3–ethylhexane [prefix]–parent–suffix

Note: (For multiple, different types of substituents)

- 1. For compounds with different multiple substituents, we number the carbon chain to give the substituents the lowest number at the first point of difference.
- If two or more alkyl groups are attached to the parent chain, they are named in <u>alphabetical</u> order.
 E.g. (1) butyl (2) ethyl (3) methyl (4) propyl

Which is correct? [Circle it]



- 3. If the same alkyl group occurs more than once, the prefixes <u>di, tri, or tetra</u> etc. are used to indicate the number of groups.
 - E.g.

$\begin{array}{c} CH_3\\CH_3CH_2CH_2\overset{I}{-} \overset{I}{C} \overset{I}{-} CH_3\\\overset{I}{H} \end{array}$	$\begin{array}{c} CH_3\\CH_3CH_2CH_2\overset{ }{-} \overset{ }{CH_3}\\ \overset{ }{CH_3}\\CH_3\end{array}$	$\begin{array}{ccc} CH_3 & CH_3 \\ & \\ CH_3 - C - CH_2 - C - CH_3 \\ \\ CH_3 & H \end{array}$
2-methylpentane	2,2–dimethylpentane	2,2,4-trimethylpentane

Note: (For naming of cycloalkanes)

1. Use the cycloalkane as the parent chain.

2. Number the carbons of the cycloalkane to give the substituents the lowest number at the first point of difference. Hence, the correct name for the following example is **1–ethyl–3–methylcyclohexane**.



€*<u>Exercise 1</u>

1. Write the IUPAC names of the following compounds.



2. Write the structural formula for the following compounds.



3. Physical properties

Alkanes contain C–C and C–H bonds. As the difference in electronegativity between C and H atoms is negligible (refer to the Pauling Electronegativity Values), the C–H bond is essentially non–polar and alkanes are **essentially non–polar** with the following physical properties.

3.1 Boiling point / volatility

- Alkanes have relatively low boiling points (or high volatility).
- **Table below shows 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.	remarks
methane	CH₄	-182	-162	gas	gas	The C ₁ to C ₄ straight–
ethane	CH₃CH₃	-183	-89	gas	gas	colourless gases at
propane	$CH_3CH_2CH_3$	-188	-42	gas	gas	room temperature.
butane	CH ₃ (CH ₂) ₂ CH ₃	-138	-0.5	gas	gas	
pentane	CH3(CH2)3CH3	-130	36	0.626	liquid	The C ₅ to C ₁₇ alkanes
hexane	CH ₃ (CH ₂) ₄ CH ₃	-95	69	0.659	liquid	of increasing viscosity.
heptane	CH3(CH2)5CH3	-91	98	0.684	liquid	The neuroining ellipse
octane	CH ₃ (CH ₂) ₆ CH ₃	-57	126	0.703	liquid	containing 18 carbon
nonane	CH3(CH2)7CH3	-53	151	0.718	liquid	atoms or more are
decane	CH ₃ (CH ₂) ₈ CH ₃	-30	174	0.730	liquid	temperature.
undecane	CH3(CH2)9CH3	-26	196	0.740	liquid	
icosane	CH ₃ (CH ₂) ₁₈ CH ₃	37	343	0.789	solid	

□ For straight chain alkanes, the boiling point increases (and volatility decreases) steadily as the number of carbon atoms increases.

Reason:

Larger alkanes have <u>more electrons</u> and therefore <u>stronger instantaneous dipole</u><u>-induced dipole</u> <u>attractions</u> exist <u>between the alkane molecules</u>. <u>More energy</u> is needed to overcome these attractions between the molecules, resulting in a higher boiling point (and lower volatility) as the number of carbon atoms in alkanes increases. Branched chain alkanes have <u>lower boiling point</u> (and higher volatility) than their corresponding straight chain alkane. The greater the degree of branching in the isomer, the lower is its boiling point.

 $E.g. C_5H_{12}$

 $CH_3CH_2CH_2CH_2CH_3$

pentane boiling point: 36°C CH₃ | CH₃—C—CH₃ | CH₃

2,2–dimethylpropane boiling point: 10°C

Reason:

Branched molecules are <u>more compact</u> with a <u>smaller surface area</u> for <u>instantaneous</u> <u>dipole–induced dipole (id–id)</u> forces of attraction <u>between molecules</u> and hence <u>less energy</u> is needed to overcome the <u>weaker intermolecular forces</u>, resulting in a lower boiling point.

●^{*}<u>Exercise 2</u>

Predict, with reasons, which compound has a lower boiling point.



Compound _____ has a lower boiling point.

Since both molecules have the <u>same electron cloud size</u>, compound ____ with <u>shorter carbon chain length</u> <u>will be more compact</u>, resulting in <u>smaller surface area</u> for <u>instantaneous dipole –induced dipole forces</u> <u>of attraction between the molecules</u>. <u>Lesser energy</u> is needed to overcome the <u>weaker intermolecular</u> <u>forces of attraction</u>, resulting in a lower boiling point.

3.2 Solubility

Alkanes are soluble in <u>non-polar solvents</u> such as benzene.

Big idea: polar solute tends to dissolve in polar solvents while non–polar solute tends to dissolve in non–polar solvent.

The instantaneous dipole–induced dipole interaction between alkane molecules and the non–polar solvent molecules <u>releases sufficient energy</u> to <u>overcome</u> the <u>instantaneous dipole–induced dipole</u> <u>attractions</u> between the alkane molecules as well as that between the solvent molecules.

Alkanes are insoluble in water and other highly – polar solvents such as ethanol.

The instantaneous dipole–induced dipole interaction between alkane molecules and the water molecules <u>does not release sufficient energy</u> to <u>overcome</u> the <u>stronger hydrogen bonds</u> between the water molecules and the <u>instantaneous dipole–induced dipole attractions</u> between the alkane

Note: If solute is **soluble** in solvent \Rightarrow 'Energy released during formation of solute–solvent interaction > Energy taken in to overcome solute–solute and solvent–solvent interaction'

Exercise 3

Do fatty acids with long carbon chains usually dissolve in water? Why or why not?

- 1. No. because fatty acid is organic and water is not.
- 2. No, because fatty acid is non-polar and water is polar.
- 3. Yes, because the oxygen on the fatty acid is attracted to the hydrogen of water.
- 4. Yes, because the oxygen on the fatty acid is more electronegative than the carbon, making it having a partial positive charge.

3.3 Density

- □ Alkanes are less dense than water.
- **D** The density of alkanes increases with increasing molecular size.
- □ For larger molecules, the <u>strength of instantaneous dipole–induced dipole attractions between</u> <u>molecules increases</u>, which causes the alkanes to be <u>more closely–packed</u> per unit volume.

4. Isomerism in alkanes (Recap from Introduction to Organic Chemistry)

4.1 Constitutional (or structural) isomerism

- Constitutional (or structural) isomerism occurs when compounds have the <u>same molecular formula</u> but <u>different structural formulae</u>.
- From butane onwards, alkanes have constitutional isomers due to the branching of the hydrocarbon chains.

molecular formula	constitutional isomers					
C_4H_{10}	CH ₃ CH ₂ C	CH_2CH_3 CH_3	CH_3 CH_3 — C — CH_3 H 2-methylpropane			
		H CH ₃	CH ₃			
C_5H_{12}	CH ₃ CH ₂ CH ₂ CH ₂ CH ₃	CH3—Ċ—Ċ—CH3 H H	$CH_3 - CH_3 = CH_3 CH_3$			
	pentane	2-methylbutane	2,2-dimethylpropane			

4.2 Stereoisomerism

Stereoisomerism occurs when compounds have the same molecular formula and structural formula but differ in the way in which their atoms are arranged in 3D space relative to one another.

(a) Enantiomerism (a.k.a optical isomerism in the previous A-level syllabus)

- Some branched-chain alkanes display enantiomerism. This is because they contain a <u>chiral carbon</u> centre and hence can <u>exist as a pair of enantiomers</u>, which are <u>non-superimposable mirror images</u> of each other.
 - E.g.: 3-methylhexane displays enantiomerism.



(b) Cis-trans isomerism

- □ Some cycloalkanes display **cis-trans isomerism**. This is because the ring structure <u>restricts the free</u> <u>rotation</u> of the bonds in the ring.
 - E.g.: 1,2-dimethylcyclopentane displays cis-trans isomerism.



5. Chemical reactivity of alkanes

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Alkanes are generally unreactive. They are inert towards <u>most bases, acids, oxidising and reducing</u> <u>agents</u>.

Reasons:

- <u>Strong</u> C–C and C–H covalent bonds which are difficult to break under ordinary conditions.
- Both C–C bonds and C–H bonds can be considered as <u>non–polar bonds</u> because carbon and hydrogen are very similar in electronegativity. Hence, there is a lack of <u>electron rich or electron</u> <u>deficient sites</u> on the alkane molecule. The non–polar nature of the alkanes makes them <u>unreactive</u> to <u>polar reagents and ions</u>.
- Hence, reactions of alkanes require a fairly high temperature and/or a photochemical initiator.

6. Chemical reactions of alkanes

6.1 Cracking

- □ Cracking is the process whereby long-chain alkanes is split into shorter-chain alkanes and alkenes, with the use of heat or catalysts.
- Cracking is very important in the petroleum industry in breaking down large hydrocarbons into <u>smaller</u> <u>hydrocarbons</u>, (notably from gasoline and refinery gas fractions) which burn more easily as fuels. See Section 8.
- □ Cracking tends to produce **branched–chain** alkanes rather than straight–chained alkanes, hence providing petrol of higher octane rating.

(i) Thermal cracking

- □ Used to produce organic chemicals (feedstock) for the petrochemical industry.
- **Conditions**: <u>Heat with steam at high temperature and pressure</u>
- □ Products include a <u>high percentage of alkenes</u>.
- During thermal cracking, very <u>little rearrangement</u> of the chains occurs compared to catalytic cracking.
 - E.g. $C_{12}H_{26} \longrightarrow CH_3CH_2CH_2CH_2CH_3 + 3 CH_2=CH_2$ dodecane hexane ethene

(ii) Catalytic cracking

- **\square** Used to produce petrol (C₅ to C₁₀) and aromatic hydrocarbons.
- **Catalyst**: <u>zeolites (mixture of Al_2O_3 and SiO_2)</u>.
- **Conditions**: <u>high temperature and pressure</u>
- □ Products include branched–chain alkanes (desirable components of high octane petrol) and alkenes.

E.g.
$$C_{12}H_{26} \longrightarrow$$

dodecane
 $CH_3 CH_3$
 $| | | CH_3CHCH_2CH_2CHCH_3$
branched chain C₈H₁₈

Г

• CH₃CH₂CH=CH₂ but–1–ene

6.2 Combustion (SDL)

Alkanes react with <u>excess oxygen</u> to form <u>carbon dioxide and water</u> only. The complete combustion is a highly exothermic process.

General equation:

$$C_nH_{2n+2} + \frac{3n+1}{2}O_2 \rightarrow nCO_2 + (n+1)H_2O$$

Example: Complete combustion of ethane gas

$$C_2H_6(g) + \frac{7}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O(I)$$

□ In a limited supply of oxygen, C, CO and H₂O are formed. Example: Incomplete combustion of methane gas

$$CH_4(g)$$
 + $\frac{3}{2}O_2(g) \rightarrow CO(g)$ + $2H_2O(I)$

$$CH_4(g) \ + \ O_2(g) \ \rightarrow \ C(s) \ + \ 2H_2O(l)$$

6.3 Free-radical substitution (Halogenation)

- \Box Alkanes react with halogens such as $Cl_2(g)$ or $Br_2(I)$ to give halogenoalkanes.
- **The hydrogen atom(s) in the alkane is substituted by the halogen atom(s) during the reaction.**

$$R-H + X_2 \xrightarrow{UV \text{ light}} R-X + H-X$$

R denotes the rest of the molecule

Reagents and conditions: limiting $Cl_2(g)$ or $Br_2(I)$, in the presence of ultraviolet (UV) light

7. Chemical reactions of alkanes

7.1 Understanding the Basics

(a) Free radical

- □ A free radical is an atom or group of atoms that has an <u>unpaired electron</u> in its outer shell. (i.e. has an odd number of electrons).
- Radicals are <u>highly reactive</u> and they readily form bonds with other atoms or molecules to regain their full octet of electrons.
- **They are formed as intermediates in the halogenation of alkanes.**
- □ Radicals have the same number of protons as electrons, so they are <u>electrically neutral</u>.

e.g.



□ Methyl radical and ethyl radical are examples of alkyl radicals.

(b) Homolytic fission (applicable in FRS of alkanes / alkylbenzenes)

□ Homolytic fission (or homolysis) is a type of bond breaking process where each of the atom involved in forming the bond acquires one of the two bonding electrons, thus forming free radicals.

We use the **'half arrow'** notation ['I to illustrate the movement of <u>a single electron in the</u> <u>bond</u> during homolytic fission. The 'tail' of the arrow shows where the single electron comes from and the arrow 'head' shows where the electron ends up.

e.g.



- radicals are formed
- 1 electron of the C-H bond moves towards the C atom and the other towards the H atom
- the dot beside each atom represents the unpaired electron that the atom has gained from the shared pair in the bond

(c) Heterolytic fission (applicable in other mechanisms from alkenes onwards)

Heterolytic fission (or heterolysis) is another type of bond breaking process where the splitting of a bond gives an <u>unequal share</u> of bonding electrons to each particle.

We use the **'full arrow'** notation [**'**] to illustrate the movement of the **bonded pair of electrons** from the position at the 'tail' of the arrow to the position at the 'head'.

e.g.



- ions are formed
- the 2 electrons in the C-Cl bond move towards the Cl atom and become a lone pair on it
- C now has 1 less e⁻ than proton, hence charge +1
 C*l* now has 1 more e⁻ than proton, hence charge -1
- □ The 'full arrow' and 'half arrow' notations are used to show the movement of a pair of electrons and a single electron respectively. The arrows illustrate the movement of electrons as bonds between atoms are broken and formed. You are expected to be able to interpret and use these curly arrow notations to represent the movement of electrons in organic reaction mechanisms.

? <u>Exercise 5</u>

Which of the following bonds is most likely to be first broken down heterolytically during a chemical reaction?

- 1. C–H bond
- 2. C-C bond
- 3. C–Cl bond
- 4. C=C bond

Reason: Since C-Cl is a polar bond, it will tend to cleave heterolytically. (Non–polar bonds like C–C and C–H bonds tend to cleave homolytically.)

(d) Classification of hydrogen and carbon atoms

- □ If a hydrogen atom is removed from an alkane, the partial structure that remains is called an alkyl group (*usually denoted as R, R' etc.*).
- □ Each removal of a hydrogen atom leads to a greater degree of alkyl substitution. There are four possible degrees of alkyl substitution for carbon and it is denoted primary (1°), secondary (2°), tertiary (3°) and quaternary (4°).



<u>4°</u> carbon

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



How many tertiary hydrogens are there in $C/CH_2C(CH_3)_2CH(CH_3)C(CH_3)_3$?

Draw out the partial displayed formula to aid in your visualisation.

7.2 Free-radical substitution mechanism

Using the reaction between methane and chlorine as an example, the overall equation for the reaction is:

$$CH_4 + Cl_2 \xrightarrow{UV \text{ light}} CH_3Cl + HCl$$

□ The mechanism involves three distinct stages.

Important	Stage 1	Initiation	$Cl \longrightarrow Cl$ UV light $2 \cdot Cl$
	Stage 2	Propagation	• Cl + $CH_4 \rightarrow •CH_3$ + HCl • CH_3 + $Cl_2 \rightarrow CH_3Cl$ + $•Cl$
	Stage 3	Termination (any 2)	• $Cl + \bullet CH_3 \rightarrow CH_3Cl$ $2 \bullet Cl \rightarrow Cl_2$ $2 \bullet CH_3 \rightarrow CH_3CH_3$

Stage 1: Initiation

□ Under ultraviolet light, the <u>homolytic fission</u> of C*l*–C*l* bond takes place and two chlorine free radicals, •C*l*, are formed.



Note:

- (Recall) Homolytic fission: A type of bond breaking process where each of the atom involved in forming the bond acquires one of the two bonding electrons forming radicals. This takes place in the presence of UV light.
- The reaction between methane and chlorine does not proceed in the dark at room temperature because there is not enough energy available to break bonds and start the reaction.
- The C*l*–C*l* bond is easier to break than the C–H bond. Therefore, chlorine molecules are supplied with the energy necessary to split them into atoms by breaking the C*l*–C*l* bond, but not the C–H bond.

 $\begin{array}{ll} Cl_2 \rightarrow 2Cl \bullet & \Delta H = +244 \text{ kJ mol}^{-1} \\ CH_4 \rightarrow \bullet CH_3 + \bullet H & \Delta H = +410 \text{ kJ mol}^{-1} \end{array}$

• Information on the wavelength of light corresponding to the energy required to initiate the reaction can be given in the question [*refer to N2017/III/4(c)*].

Stage 2: Propagation

□ The highly reactive chlorine free radical, on colliding with alkanes such as methane, abstracts a hydrogen atom to produce HC*l* and a methyl radical, \bullet CH₃.

•
$$C_l + H - C - H \longrightarrow OC - H + HC_l$$

H H H H H H $\Delta H = -21 \text{ kJ mol}^{-1}$

□ The methyl radical reacts further with another chlorine molecule.

$$\begin{array}{c} H \\ \bullet C \\ \bullet C \\ H \end{array} + Cl \\ H \end{array} + Cl \\ Cl \\ H \end{array} \rightarrow Cl \\ H \\ H \\ H \end{array} + \bullet Cl \\ \Delta H = -96 \text{ kJ mol}^{-1}$$

- □ The product, <u>chloromethane</u> is produced and <u>a chlorine free radical is regenerated</u>.
- This step leads to a <u>chain reaction</u> since the chlorine free radical formed can react as in the first propagation step.

Note:

- The reaction only requires a flash of ultraviolet light rather than prolonged radiation.
- Since the Cl- radical is <u>regenerated</u> in the propagation step, the generation of Cl- radical is only required initially to start a <u>chain reaction</u>.

Stage 3: Termination

- □ When <u>any two free radicals collide</u>, the unpaired electrons pair up to form a <u>stable</u> product. This <u>terminates the chain reaction</u>.
- Possible termination equations:

Note:

- Termination reactions are highly exothermic as they involve bond formation only.
- As the concentration of free radicals at any one time in the reaction is very small, the likelihood of two radicals colliding is small.
- <u>Trace amounts of ethane</u> are formed as by-products in this case.

7.3 Free-radical substitution in organic synthesis

This is <u>not a good method</u> to prepare halogenoalkanes, as it is very hard to control the reaction resulting in a mixture containing other by–products such as <u>different</u> halogen–substituted alkanes.

Formation of multi-substituted by-products

- □ A free radical is highly reactive and can react with almost any molecule in the reaction mixture.
- □ The chloromethane formed can undergo further substitution via the same mechanism to yield multi–substituted halogenoalkanes in the propagation stage.

C	$l \bullet + CH_3Cl$	\rightarrow	• CH_2Cl + HCl
•	$CH_2Cl + Cl_2$	\rightarrow	CH_2Cl_2 + Cl_{\bullet}
			dichloromethane is produced
Cl	• + CH ₂ C <i>l</i> ₂	\rightarrow	•CHC l_2 + HC l
•	$CHCl_2 + Cl_2$	\rightarrow	$CHCl_3 + Cl \bullet$
			trichloromethane is produced

Note:

- Further substitution can be minimised by using a <u>large excess</u> of CH₄ to yield chloromethane as the major product. This reduces the probability of the chlorine radical from colliding with a monochlorinated methane which will lead to multi–substituted product.
- Alternatively, controlling the proportion of the reactants (alkane and halogen) and the time allowed for the reaction will also improve the purity of the reaction mixture.

7.4 Reactivity of halogens with alkanes

Halogen	Reaction with alkanes
F ₂ (g)	Reacts explosively with alkanes
Cl ₂ (g)	Both can react with alkanes in the presence of UV light (or heat).
Br ₂ (I)	Br ₂ reacts less readily than chlorine.
(both reagents can be dissolved in inert solvents like CCl ₄)	Both have <u>no reaction</u> with alkanes in <u>dark conditions</u> (or at room temperature).
I ₂ (s)	No reaction with alkanes

(* Why is there a trend in reactivity of halogens with alkanes? Hint: try calculating the ΔH_r for the halogenation reactions for each type of halogen used)

<mark>♦ FYI</mark>							
ΣBE(t	bond bre	eaking)	-	ΣBE(bond formation) =		ion) =	∆ <i>H</i> r / kJ mol ^{−1}
С–Н	+	X–X		C–X	+	H–X	
CH ₄ (+410)	+	F ₂ (+158)		CH₃–F (+485)	+	H–F (+562)	-479
CH₄ (+410)	+	Cl ₂ (+244)		CH₃–C <i>l</i> (+340)	+	H–C <i>l</i> (+431)	-117
CH ₄ (+410)	+	Br ₂ (+193)		CH₃–Br (+280)	+	H–Br (+366)	-43
CH₄ (+410)	+	I ₂ (+151)		CH ₃ –I (+240)	+	H–I (+299)	+22

●* Exercise 7

Ethane and chlorine react when irradiated with ultraviolet light. The following equation gives the first stage of the reaction.

 $CH_3CH_3 + Cl_2 \rightarrow CH_3CH_2Cl + HCl$ reaction 1

- (a) (i) Write the equation for the step which initiates this reaction.
 - (ii) Write two equations for the propagating steps.
 - (iii) What is the intermediate organic species for the reaction?

●* Exercise 8

The reaction conditions for the following transformation are correct. True / False



Reason:

●* Exercise 9

Which of the following reaction is a propagation step in the reaction of methane with chlorine in the presence of ultraviolet light?

Extension

Why is it unlikely for reaction described in **D** to occur in the first propagation step?

The first propagation step can be predicted by simple bond energy calculations. Reaction described in C involves the <u>formation</u> of a <u>stronger H–C/ bond</u> (–431 kJ mol⁻¹), which is <u>more exothermic</u> and hence, energetically more favorable than the <u>formation of a C–C/ bond</u> (–340 kJ mol⁻¹) in **D**. Moreover, <u>H radicals are highly unstable, and energetically unfavourable</u> for the reaction in **D** to occur.

7.5 Halogenation of higher alkanes (using CH₃CH₂CH₃ and Cl₂ as example)

When propane reacts with chlorine, a mixture of two monochlorinated propane is produced i.e. 1–chloropropane and 2–chloropropane.



This is because the chlorine atom can abstract either one of the *primary* hydrogen atoms or *secondary* hydrogen atoms in the propagation step, before forming 1–chloropropane and 2–chloropropane respectively.

Abstraction of

1° hydrogen: $C_{l} \bullet + CH_3 - CH_2 - CH_3 \longrightarrow CH_3 - CH_2 - CH_2 + HC_l$ 2° hydrogen: $C_{l} \bullet + CH_3 - CH_2 - CH_3 \longrightarrow CH_3 - CH_3 - CH_3 + HC_l$

Assuming that the abstraction of a 1° hydrogen and of a 2° hydrogen are both <u>equally likely</u>, the ratio of 1–chloropropane : 2–chloropropane in the product mixture should also be 3 : 1, because the ratio of 1° hydrogen atoms : 2° hydrogen atoms is 6 : 2 = 3 : 1.

●* Exercise 10

Pentane was reacted with limited chlorine in the presence of *uv* light.

Assuming that only mono-chlorination takes place and the reaction occurs at the same rate at all carbon atoms, predict the ratio of the products obtained.

	1–chloropentane	:	2-chloropentane	:	3-chloropentane
Α	3	:	2	:	1
В	1	:	2	:	3
С	1	:	3	:	2
D	3	:	1	:	2



7.6 Relative rate of substitution

In the bromination of $CH_3CH_2CH_3$, the expected ratio of the product mixture of $CH_3CH_2CH_2Br$ and $CH_3CH(Br)CH_3$ are expected to be 3 : 1. However, it was found that $CH_3CH(Br)CH_3$ is present in much greater amounts than expected. Why is that so?

Reason:

- The abstraction of hydrogen atoms on different carbon atoms is not equally likely due to electron–donating effect of the alkyl groups on the carbon with the unpaired electron.
- CH₃–CH–CH₃ radical has <u>two electron donating alkyl groups</u> on the carbon with the unpaired electron, which reduces its electron deficiency. It is therefore <u>more stable</u> than the CH₃–CH₂–CH₂ radical (which has only one alkyl group on the carbon with the unpaired electron).

 $\begin{array}{ccc} \mathsf{CH}_{3} & & \overset{\bullet}{\xrightarrow{}} & & \mathsf{CH}_{3} \\ & & & & \\ & & & \\ \mathsf{prop-2-yl\ radical} \\ (\mathsf{more\ stable}) \end{array} \qquad \begin{array}{c} \mathsf{CH}_{3}\mathsf{CH}_{2} & & \overset{\bullet}{\xrightarrow{}} \mathsf{CH}_{2} \\ & & \mathsf{prop-1-yl\ radical} \\ (\mathsf{less\ stable}) \end{array}$

• Since the secondary (2°) prop–2–yl radical is more stable, the 2° hydrogen atoms in propane are more likely to be abstracted, hence forming more CH₃CH(Br)CH₃ in the product mixture.

7.7 Relative Stability of radicals

The stability of alkyl radicals depends on the number of alkyl groups (R) attached to the carbon atom with the unpaired electron.

The carbon with the unpaired electron is electron–deficient. As alkyl groups exerts an electron–donating effect, the stability of an alkyl radical is enhanced by more alkyl groups attached to the carbon with the unpaired electron as its deficiency is reduced to a greater extent.

The following shows the relative stability of alkyl radicals.



In summary, you may use the following expression to determine the ratio of the products expected based on the information provided in the question.

To find the number of products expected for each type of H atom, you always use this expression.

no. of products		number of		relative rate of
formed	=	equivalent H atom	X	substitution

For questions where it was assumed to be equal rates, you can simplify the expression to

no. of products	_	number of		
formed	=	equivalent H atom		

(because relative rate of substitution = 1 for all types of H atom)

(FYI) Further reading

Why does alkyl group have a positive inductive effect (i.e. exert an electron-donating effect)?

While C–C bonds are non–polar due to the equal electronegativity of the 2 carbon atoms, there is a slight electronegativity difference between C and H such that a very small accumulation of bonding electrons around the C atom of a $-CH_3$ group occurs.

If its adjacent carbon atom is electron deficient in some way (for example, being surrounded by only 7 electrons, as in a radical), the $-CH_3$ group can partially compensate for this deficiency by acting as an electron 'reservoir' (exerts an electron–donating effect).

Therefore, the methyl radical is much less stable than a primary radical, which in turn is less stable than a secondary radical. A tertiary radical experiences an even greater stabilisation due to the inductive effect of three alkyl groups.

In addition, the carbon in alkyl group is sp^3 hybridised and has 25% s and 75% p character whereas the carbon with the unpaired electron is sp^2 hybridised which has 33% s and 67% p character. A sp^2 carbon has more s character than sp^3 carbon as s orbitals hold electrons closer to the nucleus than p orbitals



Thus, the bonding electrons are pulled more strongly towards a sp² carbon than sp³ carbon due to its greater s character which reduces the electron deficiency in the carbon with an unpaired electron.

8 Hydrocarbons as fuels (SDL)

- □ Principal sources of alkanes are natural gas and petroleum (also called crude oil).
- Natural gas contains mainly methane with small amounts of other gaseous alkanes such as ethane, propane and butane.
- 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.

(a) Fractional distillation of petroleum

<u>Fractional distillation</u> separates the components of petroleum based on their <u>different boiling points</u>. The different fractions obtained from crude oil are shown 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
				Light petroleum	20 – 60	$C_5 - C_6$	Solvent
	40-100	6 - 12	GASOLINE	Light naphtha	60 –100	C ₆ – C ₇	Solvent
	100-150	7 - 14	NAPHTHA	Gasoline (petrol)	30 – 200	C ₅ -C ₁₂	Fuel for internal combustion engine (cars etc.)
	150-200	11 - 15	KEROSINE	Kerosene (paraffin)	175 – 300	C ₁₂ -C ₁₈	Fuel for jet engines
	220-350	15 - 19	GAS 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
	> 350	20 - 30	LUBRICATING OIL				industrial furnaces, being introduced as a fine mist to help the oil to burn.
_ <u>_</u>	> 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.

Many of the fractions obtained from the distillation of crude oil are used as fuels such as petrol, kerosene and diesel. Combustion of alkanes as fuels can give rise to pollution problems.

9. Car engine gas emissions and the environmental consequences (SDL)

The combustion reactions in the car engines release a lot of heat causing the temperature to reach about 1000°C. Under these conditions, the gases in the petrol–air mixture react to give several products.

9.1 Pollutants arising from internal combustion engines

Carbon monoxide, CO

CO is formed from the <u>incomplete combustion</u> of fuels in car engines. CO is very toxic because it forms a stable compound with <u>haemoglobin</u>, resulting in <u>ineffective transporting of oxygen</u> around the body. This can cause dizziness, fatigue and even death.

□ Oxides of nitrogen, NO and NO₂

At <u>high temperatures</u> inside the engines, atmospheric nitrogen and oxygen react to form the oxides of nitrogen.

 $N_2(g)$ + $O_2(g) \rightarrow 2NO(g)$

NO gas readily oxidises in oxygen to form NO₂ gas.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

NO₂ is a brown pungent acidic gas which contributes to <u>acid rain</u>.

$$2NO_2(g) + H_2O \rightarrow HNO_2 + HNO_3$$

Nitrogen oxides can contribute to <u>photochemical smog</u> which causes respiratory problems in humans. Nitrogen dioxide exacerbates <u>acid rain</u> formation from sulfur dioxide by catalysing its oxidation to sulfur trioxide. Acid rain can cause corrosion of buildings, destroy crops and marine life.

Hence in the presence of water, $SO_3(g) + H_2O(I) \rightarrow H_2SO_4(aq)$ (acid rain)

Unburnt hydrocarbons

When oxygen is in limited supply in a car engine, unburnt hydrocarbons are present in the exhaust emissions. Unburnt hydrocarbons are <u>carcinogenic (cancer causing)</u> and contributes to photochemical smog (yellowish–white haze), which can bring about respiratory problems.

- Photochemical smog is formed by complex photochemical reactions involving nitrogen oxides, ozone and unburnt hydrocarbons.
- Some equations of photochemical reactions:
 Sunlight causes the photochemical decomposition of NO₂ into NO and O

$$NO_2 \rightarrow NO + O$$

O atoms are very reactive and will react with O_2 to form ozone.

$$0 + O_2 \rightarrow O_3$$

□ As photochemical reactions continue in the atmosphere, ozone levels increase. Small molecules combine to form larger ones and eventually tiny particles. The particles and the brown NO2 give the air a dirty and smoggy appearance.

9.2 Catalytic converters

- □ Catalytic converters employ metals such as platinum (Pt), palladium (Pd) and rhodium (Rh) as catalysts.
- Converts pollutant gases to harmless gases by redox reactions.
 - by Rh catalyst • CO(g) + NO(g) $\rightarrow \frac{1}{2} N_2(g) + CO_2(g)$
 - CO(g) + $\frac{1}{2}O_2(g) \rightarrow CO_2(g)$
 - CO(g) + $\frac{1}{2}O_2(g) \rightarrow CO_2(g)$ Unburnt hydrocarbons, C_xH_y + O₂ (g) $\rightarrow CO_2(g) + H_2O(g)$ by Pt and Pd catalyst

Note:

- \Box Lead in the form of $(CH_3CH_2)_4Pb$ is often added to petrol as an anti-knocking agent.
- □ It is critical to use unleaded petrol when a car is fitted with catalytic converters. Lead present in the exhaust gas will bind onto the catalyst surface and render it useless. This is known as catalytic poisoning.

9.3 Gases contributing to enhanced greenhouse effect

□ Carbon dioxide, CO₂

CO₂, a major greenhouse gas, is produced from burning of fossil fuels for heating, transport and generating electricity.

□ Methane, CH₄

Produced from more intensive agricultural activity, e.g. cattle-rearing

□ Water vapour, H₂O

If global warming increases, the warmer atmosphere absorbs more water vapour, which in turn leads to a greater greenhouse effect, increasing the global warming even more.

Consequences:

 \Box Increased greenhouse effect \Rightarrow global warming \Rightarrow melting icecaps, rising sea levels and climate changes

10. Conservation of finite resources (SDL)

(a) Petroleum as a finite resource

- Petroleum (or crude oil) is a natural source of hydrocarbons. It is perhaps the most important substance consumed in modern society.
- The fuels derived from petroleum form a large part of the world's total supplyof energy. Gasoline, kerosene, and diesel oil provide fuel for automobiles, aircraft, and ships. Fuel oil and natural gas are used to heat homes as well as to generate electricity.
- Petroleum serves as a source of basic raw materials (chemical feedstocks) for the chemical industry to produce useful products such as dyes, drugs, plastics, synthetic fibers and paints.
- Petroleum 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.
- Our dependence on petroleum becomes clear that we must not only find alternative sources of energy but also conserve the remaining limited oil reserves by recycling.

(b) Recycling

- □ To reduce our energy consumption and ease major environmental problems, it is important to preserve the Earth's natural resources by <u>recycling</u>.
- □ Benefits/Importance of recycling:
 - Reduces the need for raw materials and conserves new resources.
 - Reduces waste material to be disposed of which saves space in landfills and lowers disposal costs and in the process reduce air, water and land pollution caused by the disposal process.
 - Conserves energy as less energy is required to recycle materials than to produce it. This will
 reduce air pollution as less hydrocarbons are combusted to produce energy. Process of ores also
 require more energy as compared to the energy required in recycling.
 - Recycling protect the environment and can reduce global warming as less fossil fuel will be burned at power station and thus less CO₂ will be released into the atmosphere.
 - Recycling creates jobs and innovation.