Unit 5 - A2: Structure, reactions & properties of commercially important organic compounds

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1. THE BASIC CONCEPTS OF ORGANIC CHEMISTRY

1.1 Introduction

Organic chemistry is the study of compounds containing carbon. Organic chemistry affects our every-day life; from the medicines we take to clothes, food and cosmetics.

The first thing to notice about every carbon atom in the molecules above is that they:

- form 4 covalent bonds. This is because carbon is in group 4 of the periodic table and therefore has 4 outer electrons.
- Carbon can form single, double or triple bonds and even forms rings.
- Each hydrogen forms 1 bond to another atom.
- each oxygen forms 2 single bonds or 1 double bond) with 2 lone pairs remaining (O is in group 6 of the periodic table).

Q. Correct the following structures?

Hydrocarbon: a compound that contains carbon and hydrogen ONLY.

\[ \text{e.g.} \]

The hydrocarbon could either be aliphatic (straight chain that is either branched or un-branched) or alicyclic (carbon atoms are in a ring). It can also be aromatic – contains at least one benzene ring.

Saturated: a compound containing single bonds only / no double bonds

Unsaturated: a compound containing at least one carbon-carbon multiple bond (e.g. C=C)

Q. Draw an example of a saturated and a unsaturated aliphatic hydrocarbon.
1.2 Functional groups

**Functional group:** the part of a molecule that is responsible for its chemical reactions.

*Saturated hydrocarbons* have little reactivity; it is the **functional group** that is responsible for the **reactions** of a compound. Molecules with the *same* functional group react in the *same* way.

![Molecular structures of alkane, alkene, alcohol, and haloalkane](image)

**Q.** Spot functional groups in the following molecules.

![Functional groups in molecules](image)

**Q.** Explain why the following two molecules react similarly during chemical reactions.

![Similar molecules reacting](image)

**Q.** Draw a molecule containing at least 3 different functional groups and get it checked by a peer.

1.3 Homologous series

**Homologous series:** a series of organic compounds that have the same functional group and each successive member differs by $\text{–CH}_2$

A **homologous series** is a family of compounds of the *same functional group* (and therefore similar chemical properties), with each member just differing by *one carbon and two hydrogen’s* ($\text{–CH}_2$).

- Homologous series of the **alkanes**:

  ![Molecular structures of alkanes](image)

  **General formula** of the alkanes $= \text{C}_n\text{H}_{2n+2}$
- Homologous series of the **alkenes**:

\[
\begin{align*}
\text{C}_2\text{H}_4 & \quad \text{C}_3\text{H}_6 & \quad \text{C}_4\text{H}_8 \\
\end{align*}
\]

*General formula of the alkenes = C\textsubscript{n}H\textsubscript{2n}*

Q. Use the general formula for alkanes and alkenes to fill in the blanks in the table below

<table>
<thead>
<tr>
<th>No. of C atoms</th>
<th>Alkane name</th>
<th>Alkane formula</th>
<th>Alkene name</th>
<th>Alkene formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Methane</td>
<td>CH\textsubscript{4}</td>
<td>Methene</td>
<td>/</td>
</tr>
<tr>
<td>2</td>
<td>Ethane</td>
<td>C\textsubscript{2}H\textsubscript{6}</td>
<td>Ethene</td>
<td>C\textsubscript{2}H\textsubscript{4}</td>
</tr>
<tr>
<td>3</td>
<td>Propane</td>
<td>C\textsubscript{3}H\textsubscript{8}</td>
<td>Propene</td>
<td>C\textsubscript{3}H\textsubscript{6}</td>
</tr>
<tr>
<td>4</td>
<td>Butane</td>
<td></td>
<td>Butene</td>
<td>C\textsubscript{4}H\textsubscript{8}</td>
</tr>
<tr>
<td>5</td>
<td>Pentane</td>
<td></td>
<td>Pentene</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Hexane</td>
<td></td>
<td>Hexene</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Heptane</td>
<td></td>
<td>Heptene</td>
<td></td>
</tr>
</tbody>
</table>

Q. Draw cyclopropane, cyclobutane and cyclopentane and determine the general formula for cycloalkanes. Which other functional group has the same general formula?

1.4 Nomenclature

All of the molecules that we have met so far have specific names that have been assigned following a set of rules outlined by the International Union of Pure and Applied Chemistry (IUPAC).

The names of organic molecules can be broken down into three main parts:

- **Prefix**
  - Added before the stem
- **Stem**
  - Indicates the number of carbon atoms in the longest chain
- **Suffix**
  - Added after the stem
  - Identifies the functional group
When naming a given molecule, the very first thing that you should do is to count the number of carbon atoms in the longest continuous chain in the molecule to find the stem.

<table>
<thead>
<tr>
<th>Number of C atoms</th>
<th>Stem</th>
<th>Alkyl group*</th>
<th>Formula of alkyl group</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Meth-</td>
<td>Methyl</td>
<td>-CH₃</td>
</tr>
<tr>
<td>2</td>
<td>Eth-</td>
<td>Ethyl</td>
<td>-C₂H₅</td>
</tr>
<tr>
<td>3</td>
<td>Prop-</td>
<td>Propyl</td>
<td>-C₃H₇</td>
</tr>
<tr>
<td>4</td>
<td>But-</td>
<td>Butyl</td>
<td>-C₄H₉</td>
</tr>
<tr>
<td>5</td>
<td>Pent-</td>
<td>Pentyl</td>
<td>-C₅H₁₁</td>
</tr>
<tr>
<td>6</td>
<td>Hex-</td>
<td>Hexyl</td>
<td>-C₆H₁₃</td>
</tr>
<tr>
<td>7</td>
<td>Hept-</td>
<td>Heptyl</td>
<td>-C₇H₁₅</td>
</tr>
<tr>
<td>8</td>
<td>Oct-</td>
<td>Octyl</td>
<td>-C₈H₁₇</td>
</tr>
<tr>
<td>9</td>
<td>Non-</td>
<td>Nonyl</td>
<td>-C₉H₁₉</td>
</tr>
<tr>
<td>10</td>
<td>Dec-</td>
<td>Decyl</td>
<td>-C₁₀H₂₁</td>
</tr>
</tbody>
</table>

*Removing a H atom from an alkane gives you an alkyl group. After you identify the stem, you need to spot any alkyl groups on the molecule that you are naming. Can you spot the alkyl groups below?

Once you have identified the stem, follow the rules below to finish naming your molecule:

1. **Number the carbon atoms in the longest chain** in such a way so that any alkyl groups or functional groups are on the lowest numbered carbon atom. Functional groups take priority over alkyl groups when numbering.

2. Identify the functional group(s) and add any prefix or suffix (see the table below).

<table>
<thead>
<tr>
<th>Functional group</th>
<th>Prefix</th>
<th>Suffix</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkane</td>
<td>Use the word ‘cyclo’ for cyclic alkanes and list any alkyl groups, with their position on the carbon chain first, in alphabetical order.</td>
<td>-ane</td>
</tr>
<tr>
<td>Alkene</td>
<td>-ene</td>
<td>Include the position of the alkene before ‘-ene’</td>
</tr>
<tr>
<td>Haloalkane</td>
<td>-Fluo/-chlor/-bromo/-iodo</td>
<td>Include the position of the halogen before the prefix.</td>
</tr>
<tr>
<td>Alcohol</td>
<td>-ol</td>
<td>Include the position of the alcohol before ‘-ol’</td>
</tr>
</tbody>
</table>

3. List any alkyl groups or halogens in alphabetical order in the prefix.
4. Use the words ‘di’ for two of the same groups, ‘tri’ for three of the same groups, tetra for four.

5. Separate numbers with a comma(,) and numbers from letters with a hyphen(-).

6. Remove the final ‘e’ from the parent alkane if the suffix starts with a vowel.

**Worked examples:**

<table>
<thead>
<tr>
<th>Structure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Diagram" /></td>
<td>The stem is <strong>pent-</strong> and the molecule is an alkane. The suffix for alkens is –<strong>ane</strong> so the name is <strong>pentane</strong>.</td>
</tr>
<tr>
<td><img src="image2" alt="Diagram" /></td>
<td>The stem is <strong>prop-</strong> and the molecule is an alkane, so the suffix is –<strong>ane</strong>, hence <strong>propane</strong>. However, there is a methyl group attached to carbon 2 (you number the chain so that alkyl groups or functional groups end up on the lowest numbered carbon atom). Alkyl groups are added as a prefix to alkanes. Separate numbers from letters with a ‘-’ so the name is <strong>2-methylpropane</strong>.</td>
</tr>
<tr>
<td><img src="image3" alt="Diagram" /></td>
<td>The stem is <strong>pent-</strong> and the molecule is an alkane, so <strong>pentane</strong>. However, there are two different alkyl groups attached; a <strong>methyl on carbon 2</strong> and an <strong>ethyl on carbon 3</strong>. You must list the different alkyl groups in alphabetical order. Separate numbers from letters with a ‘-’ so the name is <strong>3-ethyl-2-methylpentane</strong>.</td>
</tr>
<tr>
<td><img src="image4" alt="Diagram" /></td>
<td>The stem is <strong>pent-</strong> and the molecule is an alkane, so <strong>pentane</strong>. There are two <strong>methyl</strong> groups; one on carbon 2 and another on carbon 3. Use the word ‘di’ for two of the same groups. Remember to separate number from letters with a ‘-’. The name is <strong>2,3-dimethylpentane</strong>.</td>
</tr>
<tr>
<td><img src="image5" alt="Diagram" /></td>
<td>The stem is <strong>but-</strong> and the molecule contains an alkene functional group, so the suffix is –<strong>ene</strong>, hence <strong>butene</strong>. You must state the position of the functional group; number the carbon atoms so that the functional group is between the lowest numbered carbon atoms. In this example, the double bond is between carbons 1 and 2. Use the lowest number in the name. For alkenes, the number is placed before the suffix ‘ene’. Separate numbers from letters with a ‘-’ so the name is <strong>but-1-ene</strong>.</td>
</tr>
<tr>
<td><img src="image6" alt="Diagram" /></td>
<td>The stem is <strong>prop-</strong> and the molecule contains an alcohol functional group, so the suffix is –<strong>ol</strong>, which is added to the end of the parent alkane, hence <strong>propanol</strong>. However, the suffix ‘ol’ starts with a vowel, so remove the final ‘e’ from the parent alkane. This gives <strong>propanol</strong>. You must include the position of the alcohol before the suffix. Remember to separate number from letters with a ‘-’. The name is <strong>propan-2-ol</strong>.</td>
</tr>
<tr>
<td><img src="image7" alt="Diagram" /></td>
<td>The stem is <strong>but-</strong> and the molecule contains two alcohol functional groups, so the suffix is –<strong>diol</strong>, which is added to the end of the parent alkane (use the word ‘di’ for two of the same groups). The name is <strong>butane-2,3-diol</strong>. Note that we kept the final ‘e’ from the parent alkane because the suffix, ‘diol’, does not start with a vowel.</td>
</tr>
</tbody>
</table>
Q. Circle the mistakes in the following names.

2-methylhexane   pentane-2-methyl   1-methyl hexane   butane-1-ene

Q. Name / draw the following molecules.

1. ........................................ 2. propane  3. ........................................

4. 2,2-dimethylbutane  5. .............................. 6. pent-1-ene

7. .............................. 8. ethene  9. ..............................

10. cyclopropane  11. .............................. 12. ..............................

13. .............................. 14. 2,2-dibromopropane  15. ..............................
<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>16. ..................................</td>
<td>17. propan-1-ol</td>
<td>18. ..................................</td>
</tr>
<tr>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
</tr>
<tr>
<td>19. ..................................</td>
<td>20. ethane-1,2-diol</td>
<td>21. ..................................</td>
</tr>
<tr>
<td><img src="image4.png" alt="Image" /></td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
<tr>
<td>22. 2-chloroethanol</td>
<td>23. .........................</td>
<td>24. 2-methylpropan-2-ol</td>
</tr>
</tbody>
</table>

### 1.5 Types of formula

- **General formula**: the simplest algebraic formula for a member of a homologous series.
- **Molecular formula**: the actual number of atoms of each element in a compound. You can use the general formula to work this out e.g. butane is C4H10.
- **Displayed formula**: Shows the relevant positioning of all the atoms in a molecule and **all** of the bonds between them (this is what we have been using all along). E.g. butane:

  ![Image](image7.png)

- **Structural formula**: Shows the **minimal detail for the arrangement of atoms** in a molecule, without showing the bonds between them. If a side chain that is attached to the longest carbon chain contains more than one atom then use **brackets** around it. E.g. butane is CH₃CH₂CH₂CH₃.
- **Skeletal formula**: A simplified organic formula with hydrogen atoms removed leaving behind just the **carbon skeleton** (drawn as a zigzag) and the **functional group(s)**. There is a carbon atom where two lines meet and also at the end of each line. The bond to the functional group is included as are all of the atoms that make up the functional group. E.g. butane is shown below:

  ![Image](image8.png)
Q. Fill in the blanks for the different types of formulae shown in the table below.

<table>
<thead>
<tr>
<th>Displayed formula</th>
<th>Molecular formula</th>
<th>Structural formula</th>
<th>Skeletal formula</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Displayed formula 1" /></td>
<td>C₅H₁₂</td>
<td>CH₃CH₂CH₂CH₂CH₃</td>
<td></td>
</tr>
<tr>
<td><img src="image2" alt="Displayed formula 2" /></td>
<td></td>
<td>CH₃CH₂CH(CH₃)CH₂CH₃</td>
<td></td>
</tr>
<tr>
<td><img src="image3" alt="Displayed formula 3" /></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><img src="image4" alt="Displayed formula 4" /></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><img src="image5" alt="Displayed formula 5" /></td>
<td></td>
<td>CH₃CH(CH₃)CH₂CH=CH₂</td>
<td></td>
</tr>
<tr>
<td><img src="image6" alt="Displayed formula 6" /></td>
<td></td>
<td>CH₂BrCH₂CH(CH₃)CH(CH₃)CH₂Cl</td>
<td></td>
</tr>
<tr>
<td><img src="image7" alt="Displayed formula 7" /></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

L3 Applied Science
Unit 5: Organic Chemistry

9
1.6 Bond strength, length, angle and shapes

C=C and C≡C bonds are flat (planar) but around a C-C there is a 3D shape. Use a one bold wedge and one dashed line for 2 of the bonds coming from the C atom when there are single bonds. You must be able to recall the shape names, angles around the C atoms and the relative strength and length.

<table>
<thead>
<tr>
<th>Bond</th>
<th>No. of electrons</th>
<th>Examples</th>
<th>Shape &amp; angle</th>
<th>Strength &amp; length</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C (sp(^3))</td>
<td>2</td>
<td></td>
<td>Tetrahedral, 109.5°</td>
<td></td>
</tr>
<tr>
<td>C≡C (sp(^2))</td>
<td>4</td>
<td></td>
<td>Trigonal planar 120°C</td>
<td></td>
</tr>
<tr>
<td>C≡C (sp)</td>
<td>6</td>
<td>H-C≡C-H</td>
<td>Linear 180°C</td>
<td></td>
</tr>
</tbody>
</table>

Q. Challenge: draw 3D representations for the following molecules

<table>
<thead>
<tr>
<th>2-methylprop-1-ene</th>
<th>Methylbenzene</th>
</tr>
</thead>
</table>
1.7 Isomerism

There are two types of isomerism; **structural isomerism** and **stereoisomerism**.

**Structural isomerism** exists when two or more different molecules contain the same number and type of atoms, but they are arranged in **different** ways.

**Structural isomers**: compounds with the same molecular formula but with a different structure

Q. Work out the molecular formula for the two molecules below. What do you notice?

![Molecular structures](image)

**Note**: structural isomerism can occur in three ways:

- **Chain isomerism** – when the difference is the chain being **branched** or **un-branched**.

![Chain structures](image)

- **Positional isomerism** – when the difference is the **position** of the **functional group**.

![Positional structures](image)

- **Functional group isomerism** – when the difference is the **functional group present**.

![Functional group structures](image)

**Working out structural isomers for a compound**:

*Hint* – it will be easier if you work with skeletal formulae throughout when trying to determine all of the possible structural isomers for a compound.

- Draw out the **straight chain** form of your compound.

- See how many **branched isomers** you can draw by **removing one carbon** from the end of the molecule and placing it further along the chain.

- **Repeat the above**, but this time **removing two carbons** from the end of the molecule and using both carbons to produce branched isomers. Keep going until you have all the possibilities.

- If you have **functional groups** present, e.g. an OH group, then for each branched isomer of the main chain that you draw, place the functional group in as many **different positions** as possible.

- See if you can form a **different functional group** with the atoms that you have present.
Q. Draw out all of the possible structural isomers for butane.

Q. CHALLENGE: Draw out all of the possible structural isomers for pentane.

Q. CHALLENGE: Draw out all of the possible structural isomers for hexane.

Q. CHALLENGE: Draw out all of the possible structural isomers for 1-bromobutane.

Q. CHALLENGE: Draw out all of the possible structural isomers for butan-1-ol.
In **stereoisomerism**, the atoms that make up the isomers are joined up in the same order, but they have a different arrangement in *space*. This is best seen by building models of the relevant alkenes.

**Q.** Build the models of but-2-ene (below left). Explain what you notice about the C=C bond. Are the two models the same? Extension: compare this to the models of butane (below right). Are these two the same? What are the H-C-H bond angles in alkanes and alkenes?

![Models of Butane and But-2-ene](image)

**Stereoisomers:** compounds with the same structural formula but with a different arrangement of the atoms in space.

Because the two molecules of but-2-ene are different (yes, they do have the same structural formula, but we saw from the models we built that the atoms are arranged *differently in space*), we need to come up with labels for each one. Chemists use the labels **Z** or **CIS** (when the two H atoms are on the same side of the double bond) and **E** or **TRANS** (when the two H atoms are on opposite sides of the double bond).

**For a molecule to have E/Z stereoisomerism, it must have:**

- A C=C bond, which restricts rotation
- Two different groups attached to each carbon in the C=C bond
Q. Draw the displayed formulae for the \( E/Z \) stereoisomers of 1,2-dichloroethene.

Q. Draw the displayed formula for but-1-ene. Explain why this molecule does not have \( E/Z \) isomers.

Q. Draw the skeletal and displayed formulae for the \( E/Z \) stereoisomers of \( \text{CH}_3\text{CH=CHCH}_2\text{CH}_3 \). Include in your answer the definition of \( E/Z \) stereoisomerism and explain why this molecule has \( E/Z \) stereoisomers.

2. Alkanes
2.1 Introduction

The alkanes are saturated organic compounds. Alkanes are found in crude oil – they are separated out using fractional distillation. Cracking and combustion of alkanes are important industrially (see later).

**Q. The general formula** for the alkanes is: ………………………………………………………………………………………………………

**Q.** Draw the skeletal formula for the following alkanes:

<table>
<thead>
<tr>
<th>Alkane</th>
<th>Formula</th>
<th>Boiling point</th>
<th>State at RT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>CH₄</td>
<td>-162</td>
<td>gas</td>
</tr>
<tr>
<td>Ethane</td>
<td>C₂H₆</td>
<td>-89</td>
<td>gas</td>
</tr>
<tr>
<td>Propane</td>
<td>C₃H₈</td>
<td>-42</td>
<td>gas</td>
</tr>
<tr>
<td>Butane</td>
<td>C₄H₁₀</td>
<td>0</td>
<td>gas</td>
</tr>
<tr>
<td>Pentane</td>
<td>C₅H₁₂</td>
<td>36</td>
<td>liquid</td>
</tr>
<tr>
<td>Hexane</td>
<td>C₆H₁₄</td>
<td>69</td>
<td>liquid</td>
</tr>
<tr>
<td>Heptane</td>
<td>C₇H₁₆</td>
<td>98</td>
<td>liquid</td>
</tr>
<tr>
<td>Octane</td>
<td>C₈H₁₈</td>
<td>126</td>
<td>liquid</td>
</tr>
<tr>
<td>Nonane</td>
<td>C₉H₂₀</td>
<td>151</td>
<td>liquid</td>
</tr>
<tr>
<td>Decane</td>
<td>C₁₀H₂₂</td>
<td>174</td>
<td>liquid</td>
</tr>
</tbody>
</table>

Boling point increases as the chain length increases
Straight chain alkanes have a higher boiling point than branched chain alkanes because straight chain alkanes can get closer together, so there are more points of contact and therefore temporary dipole-induced dipole forces are stronger between straight chain alkanes. Branched chain alkanes have a lower boiling point for the opposite reason. Branched chains cannot come as close together, so there are less points of contact which results in weaker temporary dipole-induced dipole forces between branched chain molecules.

Q. Draw a diagram to show the points of contact between straight chain / branched molecules.

<table>
<thead>
<tr>
<th>Between straight chain</th>
<th>Between branched chains</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Q. Explain why the straight chain isomer of octane has a higher boiling point than any of its branched chain structural isomers. How would the boiling point of this straight chain isomer of octane compare with the boiling point of pentane?

2.3 Cracking of alkanes

Crude oil contains a mixture of hydrocarbons, including the saturated alkanes. The mixture of hydrocarbons is separated using the process of fractional distillation. Fractional distillation works because the different chain length hydrocarbons have different boiling points due to a difference in the strength of temporary dipole-induced dipole forces between the molecules. Once the straight chain alkanes have been separated from crude oil by fractional distillation, they are then cracked into shorter chain alkanes.
Cracking converts long chain alkanes into shorter chain alkanes and alkenes. The C-C bond can break anywhere, so a variety of alkanes and alkenes are produced randomly. Cracking is important industrially because shorter chain alkanes ignite more easily and make more efficient fuels than the longer chain alkanes in crude oil, of which there is a surplus. The alkenes also produced in cracking are important building blocks for other chemicals so are also in high demand. Cracking can be achieved in two ways in the petrochemical industry:

(i) Thermal cracking – this process uses high temperatures of 450°C – 750°C and high pressures of up to 70 atmospheres. This process gives high numbers of alkenes. Higher temperatures mean that the chain breaks near to its end, giving a high proportion of short chain alkenes.

(ii) Catalytic cracking – this process uses zeolite catalysts with temperatures of 500°C and low pressures. This process produces alkanes with between 5-10 carbon atoms and also branched alkanes and aromatic hydrocarbons such as benzene.

Examples of equations showing cracking are below:

\[
\text{Cracking of } \text{C}_{10}\text{H}_{22} \rightarrow \text{C}_8\text{H}_{18} + \text{C}_2\text{H}_4
\]

\[
\text{Cracking of } \text{C}_{10}\text{H}_{22} \rightarrow \text{C}_7\text{H}_{16} + \text{C}_3\text{H}_6
\]

Q. Write equations to show the cracking of:

(a) Nonane.

(b) Octane.

Q. Explain what conditions a petrochemical company would need if they wanted to produce a high proportion of short chain alkenes from cracking long chain hydrocarbons. Why would they want to produce alkenes?
2.4 Combustion of alkanes

Cracking produces shorter chain alkanes which are used as fuels. **Combustion** of alkanes is important industrially for producing energy. Alkanes react with oxygen, O$_2$, to produce a large amount of energy, water and either carbon monoxide or carbon dioxide. A large amount of energy is released because strong covalent bonds are broken.

In a **plentiful supply of oxygen**, alkanes undergo **complete combustion** to produce CO$_2$ and H$_2$O.

*Hint: when writing out these combustion equations, balance the atoms in the following order – C, H, then O. You may use fractions for O$_2$. E.g.*

\[
\text{CH}_4 + 1\frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O}
\]

When there is a **limited supply of oxygen**, alkanes undergo **incomplete combustion** to form CO and H$_2$O. E.g.

\[
\text{CH}_4 + \text{O}_2 \rightarrow \text{CO} + 2 \text{H}_2\text{O}
\]

**Q.** Write out equations to show the **complete** combustion of:

(a) Butane.

...............................................................................................................................

(b) Octane.

...............................................................................................................................

(c) Propane.

...............................................................................................................................

**Q.** Write out equations to show the **incomplete** combustion of:

(a) Butane.

...............................................................................................................................

(b) Octane.

...............................................................................................................................

(c) Decane.

...............................................................................................................................
2.5 Halogenation of alkanes by radical substitution

The alkanes are very un-reactive molecules. However, in addition to combustion reactions, the alkanes also react with halogens in the presence of UV light or high temperatures of 300°C. The reaction taking place is a substitution reaction; a H atom in the alkane is substituted by a halogen atom (Br or Cl). The equation below shows the overall equation for the reaction of methane with chlorine. The reaction taking place is far more complex that suggested by the overall equation. The actual reactions taking place can be broken down into three parts (the mechanism) – initiation, propagation and termination steps.

\[
\text{CH}_4 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{HCl}
\]

**Radical**: a species with an unpaired electron

**Homolytic fission**: a covalent bond breaks and one electron goes to each atom

1. **Initiation** – The halogen (Cl₂ or Br₂) breaks down into two radicals when exposed to UV light via homolytic fission. Only a few radicals need to be formed for the next steps to take place.

\[
\text{Cl}_2 \rightarrow 2 \text{Cl}^\cdot
\]

2. **Propagation** – There are two steps that take place, with radicals on both sides of each equation. In the first step, the hydrocarbon reacts with the halogen radical produced earlier, with the halogen radical removing a H atom (to form HCl or HBr and a hydrocarbon radical). In the second step, the hydrocarbon radical reacts with any remaining halogen molecules (those that did not undergo homolytic fission earlier) to remove a Cl or Br atom to replace the H atom which was lost earlier. At this stage, the substitution of a H atom on the alkane for a Cl or Br atom is complete. However, a Cl· or Br· is also regenerated (in other words, the Cl· or Br· are acting as a catalyst) so that the reaction continues and more alkane molecules undergo a substitution reaction.

\[
\begin{align*}
\text{CH}_4 + \text{Cl}^\cdot & \rightarrow \text{CH}_3^\cdot + \text{HCl} \\
\text{CH}_3^\cdot + \text{Cl}_2 & \rightarrow \text{CH}_3\text{Cl} + \text{Cl}^\cdot
\end{align*}
\]

3. **Termination** – Any two radicals combine to form a molecule. The reaction therefore stops.

\[
\begin{align*}
\text{Cl}^\cdot + \text{Cl}^\cdot & \rightarrow \text{Cl}_2 \\
\text{CH}_3^\cdot + \text{Cl}^\cdot & \rightarrow \text{CH}_3\text{Cl} \\
\text{CH}_3^\cdot + \text{CH}_3^\cdot & \rightarrow \text{C}_2\text{H}_6
\end{align*}
\]

Note that the formation of C₂H₆ is not shown in the overall equation. Radicals are highly reactive species and it is difficult to control these reactions. This always leads to a mixture of products formed when radicals are involved (so this is certainly not a good way to make haloalkanes!). As a matter of fact, if there is any remaining Cl· once the desired product has already formed (CH₃Cl) then multi-substitution can occur. The CH₃Cl can react with more Cl· to form CH₂Cl₂, CHCl₃ or even CCl₄. There are also lots of termination steps where other products can form (e.g. C₂H₆), and the products of these termination steps may also go on to react with more Cl· to form other halogenated products.
Q. Fill in the gaps for the free radical substitution mechanism of butane with bromine.

1. Initiation: ........................................................................................................

2. Propagation: \[ \text{C}_4\text{H}_{10} + \ldots \rightarrow \text{C}_4\text{H}_9^+ + \ldots \]

\[ \text{C}_4\text{H}_9^+ + \ldots \rightarrow \ldots + \ldots \]

3. Termination: \[ \text{Br}^- + \text{Br}^- \rightarrow \ldots \]

\[ \text{C}_4\text{H}_9^+ + \text{Br}^- \rightarrow \ldots \]

\[ \text{C}_4\text{H}_9^+ + \text{C}_4\text{H}_9^+ \rightarrow \ldots \]

Q. Fill in the gaps for the free radical substitution mechanism of hexane with chlorine.

Overall equation: ........................................................................................................

1. Initiation: ........................................................................................................

2. Propagation: \[ \text{C}_6\text{H}_{14} + \ldots \rightarrow \ldots + \ldots \]

\[ \text{C}_6\text{H}_{13}^+ + \ldots \rightarrow \ldots + \ldots \]

3. Termination: \[ \text{Cl}^- + \text{Cl}^- \rightarrow \ldots \]

\[ \text{C}_6\text{H}_{13}^+ + \text{Cl}^- \rightarrow \ldots \]

\[ \text{C}_6\text{H}_{13}^+ + \text{C}_6\text{H}_{13}^+ \rightarrow \ldots \]

How many different structural isomers of chlorohexane, \( \text{C}_6\text{H}_{13}\text{Cl} \), can be formed in this reaction?

Q. Write out the mechanism, naming all steps, for the reaction of propane with Br\(_2\) under UV light.
3. Alkenes

3.1 Introduction

The alkenes are unsaturated organic molecules. They are more reactive than alkanes and undergo addition reactions (see later).

Q. The general formula for the alkenes is: .................................................................

Q. Draw the skeletal formula for the following alkenes:

- propene
- Z-pent-2-ene
- cyclobutene
- E-pent-2-ene

Q. Suggest the bond angles around the carbon atoms in alkenes and alkanes.

3.2 Bonding in alkenes

There are two types of bonds in alkenes; Pi bonds (\(\pi\) bonds) and sigma bonds (\(\sigma\) bonds). Single bonds are called \(\sigma\) bonds. Once the three \(\sigma\) bonds have been made around the carbon atoms in alkenes, there is one remaining electron in a \(p\)-orbital (carbon is in group 4 in the \(p\)-block of the periodic table). These \(p\)-orbitals overlap sideways to make the second bond between the carbon atoms, a \(\pi\) bond.

Orbital overlap model: sideways overlap of two \(p\) orbitals on each carbon atom leads to formation of a \(\pi\) bond above and below the plane of the molecule.
3.3 Reactivity of alkenes

Alkenes are more reactive than alkanes due the presence of the extra electrons in the C=C bond and also due to the π bond strength; the π bond is weaker than a σ bond. During a reaction, the π bond breaks and the σ bond stays intact. Alkenes undergo addition reactions.

<table>
<thead>
<tr>
<th>Bond type</th>
<th>Strength / kJmol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–C</td>
<td>347</td>
</tr>
<tr>
<td>C= C</td>
<td>612</td>
</tr>
</tbody>
</table>

Q. Use the data in the table to calculate the strength of a π bond between two carbon atoms. Compare this to the strength of a σ bond between two carbon atoms.

Q. Write an equation using displayed formulae for the addition of molecule X-Y into ethene.

3.4 Addition reactions of alkenes

- Alkenes undergo an addition reaction with halogens (Cl₂, Br₂, I₂) at room temperature to form haloalkanes.

H H  C=C   Br₂ → H H  C C ≡ C H Br Br

Note – you can test for the presence of alkene by addition of bromine water, there is a colour change from orange to colourless.

- Alkenes undergo an addition reaction with hydrogen halides (HBr, HCl, HI) at room temperature to form haloalkanes. Watch out for unsymmetrical alkenes – more than one product is possible depending on which carbon the hydrogen and the halogen atoms are placed.

H H  C≡C  H Br → H H  C C ≡ C H H Br H
H H  C≡C  H H Br → H H  C C ≡ C H H Br + H C ≡ C H H

two structural isomers possible with an unsymmetrical alkene
- Alkenes undergo an **addition reaction with concentrated sulfuric acid** \((H_2SO_4)\) under **cold conditions** to form alkyl hydrogensulfates. Watch out for **unsymmetrical alkenes – more than one product is possible** depending on which carbon the H and the \(OSO_3H\) atoms are placed.

- Alkenes undergo an **addition reaction with steam** \((H_2O(g))\) at **high temperatures** with a phosphoric acid \((H_3PO_4)\) catalyst. Watch out for **unsymmetrical alkenes – more than one product is possible** depending on which carbon the H and the OH atoms are placed.

\[
\begin{align*}
\text{propene} + \text{Cl}_2 & \quad \xrightarrow{H_2O, \ H_3PO_4} \quad \text{two structural isomers possible with an unsymmetrical alkene} \\
\text{E-but-2-ene} + \text{I}_2 & \\
\text{hex-1-ene} + \text{HBr} & \\
\text{cyclohexene} + \text{HCl} & \\
\text{E-but-2-ene} + \text{H}_2\text{SO}_4 &
\end{align*}
\]

**Q.** Write equations for the following addition reactions, identifying where two products are possible:

i) propene + Cl₂

ii) \(E\)-but-2-ene + I₂

iii) hex-1-ene + HBr

iv) cyclohexene + HCl

v) \(E\)-but-2-ene + H₂SO₄
vi) but-1-ene + H₂SO₄

vii) Z-but-2-ene + steam

viii) 2-methylprop-1-ene + steam (skeletal formula)

3.5 Electrophilic addition mechanism

**Heterolytic fission:** covalent bond breaks, both electrons go to the same atom.
**Curly arrow:** shows the movement of a pair of electrons.
**Nucleophile:** donates a pair of electrons.
**Electrophile:** accepts a pair of electrons.

How do the addition reactions actually happen step by step, i.e. what is the mechanism for the addition reactions of the alkenes? Because the C=C bond of alkenes is a region of high electron density, the alkene acts as a nucleophile (donates a pair of electrons) when the π bond breaks during reactions. The pair of electrons go into making a new σ bond with an electrophile (the species which accepts the pair of electrons). We show this movement of a pair of electrons with curly arrows. The curly arrow mechanism for the addition of HBr to ethene is shown below. HBr is acting as an electrophile (it accepts the pair of electrons from ethene, the nucleophile) and this reaction is called an electrophilic addition reaction. You shall only be asked to draw the electrophilic addition mechanism for the addition of halogens, hydrogen halides and sulfuric acid to alkenes. The mechanism for the addition of steam and hydrogen gas to alkenes is completely different and is not on your specification.

- For hydrogen halides and sulfuric acid, the H atom is less electronegative than the halogen or the O atom and the molecule is polar due to the permanent dipoles. The electron pair in the π bond of the alkene is attracted to the slightly positive H atom.
- The movement of electrons from the π bond in the alkene towards the H atom is shown by a curly arrow which MUST start at the π bond and go directly towards the H atom. The π bond is broken and the pair of electrons is used to make a new C-H bond.
- Simultaneously, the H-Br or H-O (in sulfuric acid) bond breaks heterolytically, with the electron pair in the H-Br or H-O bond going to the more electronegative Br or O atom.
- This creates a carbocation intermediate (carbon with a positive charge) and a bromide ion.
- Tertiary carbocations are more stable than secondary, which are more stable than primary carbocations – use this rule to predict which one will form if the alkene is unsymmetrical.
- Finally, the positively charged carbocation intermediate attracts the lone pair of electrons on the bromide ion towards itself, once again the movement of the pair of electrons is shown by a curly arrow staring DIRECTLY at the lone pair on the bromide and going straight towards the positively charged carbon in the carbocation intermediate to make a new C-Br or C-O bond.

For addition of halogens, the electron dense alkene repels the electrons in the Br atom closest to the alkene, making it slightly positive.

Q. Draw the curly arrow mechanism for the electrophilic addition of Br₂ to Z-but-2-ene. Label the electrophile, nucleophile, carbocation intermediate and state the type of bond fission taking place.

Q. Draw the curly arrow mechanism for the electrophilic addition of HCl to cyclopentene. Label the electrophile, nucleophile, carbocation intermediate and state the type of bond fission taking place.
Q. Draw the curly arrow mechanism for the electrophilic addition of H$_2$SO$_4$ to Z-but-2-ene. Label the electrophile, nucleophile, carbocation intermediate and state the type of bond fission taking place.

Q. The addition of HBr and H$_2$SO$_4$ to the unsymmetrical alkene 2-methylprop-1-ene leads to the formation of two different products. Carefully draw the curly arrow mechanism for each reaction and explain which is the major product formed.

i) 2-methylprop-1-ene with HBr

ii) 2-methylprop-1-ene with H$_2$SO$_4$
3.6 Radical polymerisation of alkenes

Polymers are long chain molecules made from alkene monomers. The main use is as plastics. The alkene monomers are unsaturated but the polymer is saturated due to the breaking of the π bond that was present in the alkene monomer. One method of making polymers is via the free radical polymerisation of alkene monomers. The overall equation is shown below.

\[
\begin{align*}
\text{ethene} & \quad \rightarrow \quad \text{poly(ethene)} \\
\text{H} & \quad \text{C} &= \text{C} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\text{H} & \quad \text{C} &= \text{C} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\end{align*}
\]

Poly(ethene) is produced by the addition reaction of ethane monomers at 200°C in the presence of a small amount of oxygen. The steps are summarised below:

1. **Initiation:** the ethene reacts with some oxygen to produce an organic peroxide. Peroxides contain a oxygen-oxygen single bond (O-O) which can break easily to give radicals, represented by \( \text{Ra} \cdot \).

2. **Propagation:** The free radical, \( \text{Ra} \cdot \), reacts with an ethene molecule to form a longer free radical. One electron from the radical and one electron from the π bond in the alkene made the new bond with the radical. The other electron in the π bond returns to the other carbon atom that was part of the alkene, so only a single bond now exists between the C atoms (saturated). In the next step, the longer radical reacts with more ethane molecules to make an even longer radical. The steps repeat themselves, building a long polymer.

\[
\begin{align*}
\text{Ra} \cdot + \text{CH}_2=\text{CH}_2 & \rightarrow \text{RaCH}_2\text{CH}_2 \cdot \\
\text{RaCH}_2\text{CH}_2 \cdot + \text{CH}_2=\text{CH}_2 & \rightarrow \text{RaCH}_2\text{CH}_2\text{CH}_2\text{CH}_2 \cdot \\
\end{align*}
\]

And so on…

3. **Termination:** Two free radicals combine to make a final molecule that is not a radical, as the free electron on both radicals have joined together to make a single bond. The reaction stops as no more free radicals have been made. Because chain termination is a random process, poly(ethene) of varying lengths will be made. The sample will contain a mixture of molecules of different sizes.

\[
\begin{align*}
\text{Ra}(\text{CH}_2)_m \cdot + \text{Ra}(\text{CH}_2)_n \cdot & \rightarrow \text{Ra}(\text{CH}_2)_m(\text{CH}_2)_n \text{ Ra}
\end{align*}
\]

Q. Cover up the equations above and see if you can write the equations for steps 2 and 3 from memory:
Q. Write the overall equation for the radical polymerisation of propene

Q. Explain why organic peroxides are important in the radical polymerisation of alkenes.

3.7 Benzene

Benzene is not an alkene – the Kekule structure with alternating double and single bonds has been disproven. Benzene contains a delocalised ring of electrons and has different reactivity to alkenes – it is a different functional group. All of the bond lengths are equal, in between C-C and C=C bonds, due to the delocalised ring of electrons. The strength of the bonds between the carbon atoms in benzene is also in between the strength of typical C-C and C=C bonds. The bond angles are the same as with alkenes – 120°.

Benzene is a planar cyclic molecule with bond angles of 120°. Each carbon has 3 sigma (σ) bonds (1 bond to H and two bonds to other C atoms). The fourth electron of each carbon is contained in a p orbital. The p orbitals overlap sideways above and below the plane of the ring to form π bonds. The electrons are delocalised about the ring. The delocalisation of the electrons leads to further stability of benzene meaning that it does not readily take part in addition reactions with halogens or hydrogen halides like typical alkenes because then this extra stability would be lost.