9 Alkanes Tutorial

Isomerism

1. Draw structures for the following alkanes.
   (a) 4-ethyl octane
   (b) 3-ethyl-4,4-dimethylheptane
   (c) 1-ethyl-2,2-dimethylcyclohexane
   (d) 2,2,3-trimethylbutane

Free Radical Reactions

2. (a) Excess ethane is reacted with chlorine in the presence of UV light to form chloroethane. Write the balanced chemical equation for the overall reaction.
   (b) Write a series of equations, with appropriate labels, for all the steps in the mechanism for the above reaction.
   (c) The reaction produces small quantities of chlorinated butane. Suggest how these might arise.
   (d) How do you know that hydrogen radicals are not formed in the propagating steps?

2. (a) \( \text{CH}_3\text{CH}_3 + \text{Cl}_2 \rightarrow \text{CH}_3\text{CH}_2\text{Cl} + \text{HCl} \)
   (b) **Chain Initiation**
       \[ \text{Cl}_2 \xrightarrow{\text{UV light}} 2\text{Cl}\cdot \]

   **Chain Propagation**
   \( \text{Cl}\cdot + \text{CH}_3\text{CH}_3 \rightarrow \text{HCl} + \cdot\text{CH}_3\text{CH}_3 \)
   \( \cdot\text{CH}_3\text{CH}_3 + \text{Cl}_2 \rightarrow \text{CH}_3\text{CH}_2\text{Cl} + \text{Cl}\cdot \)

   **Chain Termination**
   \( \text{Cl}\cdot + \text{Cl}\cdot \rightarrow \text{Cl}_2 \)
   \( \cdot\text{CH}_3\text{CH}_3 + \text{Cl}\cdot \rightarrow \text{CH}_3\text{CH}_2\text{Cl} \)
   \( \cdot\text{CH}_3\text{CH}_3 + \cdot\text{CH}_3\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \)

   (c) \( \text{CH}_3\text{CH}_2\text{Cl} \) formed in the propagation step collides with \( \text{Cl}\cdot \) to form \( \cdot\text{CHC/CH}_3 \).
   \( \text{Cl}\cdot + \text{CH}_3\text{CH}_2\text{Cl} \rightarrow \text{HCl} + \cdot\text{CHC/CH}_3 \)
Chlorinated butane can be formed in the termination steps:

\[
2 \rightleftharpoons \text{CHClCH}_3 \rightarrow \text{CH}_3\text{CHClCHClCH}_3 \\
\rightleftharpoons \text{CH}_3\text{CH}_2 + \text{CHCl/CH}_3 \rightarrow \text{CH}_2\text{CH}_2\text{CHClCH}_3
\]

Chlorinated butane can also be formed when butane produced in the termination step reacts with the Cl\(\bullet\) radical in the reaction mixture.

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

(d) **Reason 1:**
If hydrogen radicals are formed, they may combine (in the terminating stage) to give \(\text{H}_2\). Since there are no traces of \(\text{H}_2\) in the final products, hydrogen radicals are not formed in the propagating steps.

**Reason 2:**
In the 1st propagating step, \(\text{C}_2\text{H}_6 + \text{Cl}\bullet \rightarrow \text{CH}_2\text{CH}_3 + \text{HCl}\)
\[
\Delta H = +410 - 431 = -21 \text{ kJ mol}^{-1}
\]
If \(\text{H}\bullet\) is formed, \(\text{C}_2\text{H}_6 + \text{Cl}\bullet \rightarrow \text{H}\bullet + \text{CH}_3\text{CH}_2\text{Cl}\)
\[
\Delta H = +410 - 340 = +70 \text{ kJ mol}^{-1}
\]
Thus hydrogen radicals are not formed since this process is energetically less favourable.

3. Write equations to show the mechanism of bromination of cyclohexane to give bromocyclohexane.

### Mechanism: free radical substitution

**Initiation**

\[
\text{Br} + \text{Br} \xrightarrow{\text{UV}} 2\text{Br}\bullet
\]

**Propagation**

\[
\begin{align*}
\text{C}_6\text{H}_12 + \text{Br}\bullet & \rightarrow \text{C}_6\text{H}_11\bullet + \text{HBr} \\
\text{C}_6\text{H}_11\bullet + \text{Br}_2 & \rightarrow \text{C}_6\text{H}_11\text{Br} + \text{Br}\bullet
\end{align*}
\]

**Termination**

\[
\begin{align*}
\text{Br}\bullet + \text{Br}\bullet & \rightarrow \text{Br}_2 \\
\text{C}_6\text{H}_11\bullet + \text{Br}\bullet & \rightarrow \text{C}_6\text{H}_11\text{Br}
\end{align*}
\]

**Note:**
- Cyclohexane, cyclohexyl radical and bromocyclohexane should be represented with skeletal structures instead of molecular formula such as \(\text{C}_6\text{H}_{12}\).
- All 3 equations should be written for the termination stage.
4 A and B are two structural isomers with the molecular formula C₄H₁₀.

When A reacts with chlorine gas in the presence of light, two monochlorinated alkanes C and D are formed. Only D contains a chiral carbon.
When B reacts with chlorine gas in the presence of light, two monochlorinated alkanes E and F are formed.

Identify compounds A, B, C, D, E and F by drawing their structural formulae.

| A | CH₃CH₂CH₃CH₃ | B | CH₃
|   | CH₃—CH—CH₃  |   | CH₃
| C | CH₃CH₂CH₂CH₂Cl/ | E and F | CH₃
|   | CH₃—CH—CH₂CH₃ |   | CH₃
|   | Cl/           |   | CH₃—CH—CH₂Cl/

5 When 2–methylpropane is reacted with chlorine, a mixture in which the major products are two monochlorinated alkanes is produced.

When 2–methylpropane reacts with chlorine gas in the presence of light and at 25°C, the following products are formed:

\[
\begin{align*}
\text{CH₃CH₃CH₃} & \quad \text{Cl}_2, \text{light} \\
\text{CH₃—CH—CH₃} & \quad \text{25°C} \\
\rightarrow & \quad \text{CH₃CH₃CH₂Cl/} + \text{CH₃CH₃CCl/}
\end{align*}
\]

63% 37%

Explain why the observed ratio of these two products is less than 9:1.

(N95/'S' paper/7(c) modified)

5 Let A be (CH₃)₂CHCH₂Cl/ and B be (CH₃)₃CCl/.

There are 9 primary H atoms and 1 tertiary H atom that can be substituted to form A and B respectively. Based on probability, the ratio of A:B is 9:1.

However, tertiary radical is more stable than primary radical and more likely to be formed so more B will be formed.

Hence the actual ratio of A:B is less than 9:1.

Note:
Unless required by the question, it is sufficient to consider either the probability factor or the stability of the alkyl radical to predict the ratio of products. Refer to Q8 (N07 P3 Q1e) in Self-practice questions.
By using the table of bond energies in the Data Booklet, estimate the enthalpy changes in the propagation steps of the reaction for the formation of chloromethane when methane and chlorine are irradiated with light at room temperature.

[The energy required to break the H–CH$_3$ bond is 434 kJ mol$^{-1}$.] Use your results to sketch an energy level diagram (reaction profile) for this reaction. (N95/'S' paper/7(b) modified)

Note: The initiation step is not included in the reaction profile because it is not necessary for each molecule of product formed as Cl• is regenerated in the propagation step.

$\text{CH}_4 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{HCl} \quad \Delta H = (+3) + (−96) = −93 \text{ kJ mol}^{-1}$
Self-practice Questions

GCE A-level Chemistry Paper

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Further-practice Questions

1 (i) \( \text{H}_3\text{C} \) \( \text{CH}_3 \) \( \text{CH}_3 \) \( \text{CH}_3 \) \( \text{CH}_3 \)

(ii) \( \text{CH}_3\text{CH}_2\text{C} \) \( \text{CH}_3 \) \( \text{(CH}_2\text{)}_2\text{CH}_3 \) \( \text{H} \) \( \text{CH}_3\text{(CH}_2\text{)}_2\text{C} \) \( \text{CH}_3 \) \( \text{(CH}_2\text{)}_4\text{CH}_3 \) \( \text{H} \) \( \text{CH}_2\text{CH}_3 \)

2 (a) Pentane has larger electron cloud \( \Rightarrow \) strength of dispersion forces increases
\( \Rightarrow \) more energy required to overcome stronger dispersion forces \( \Rightarrow \) boiling point increases.

(b) 
\( \text{CH}_3 \) \( \text{H}_3\text{C} \) \( \text{C} \) \( \text{CH}_2\text{CH}_3 \) \( \text{CH}_3 \)

2,2-dimethylbutane has a smaller surface area than hexane \( \Rightarrow \) reduced strength of dispersion forces \( \Rightarrow \) lower boiling point.