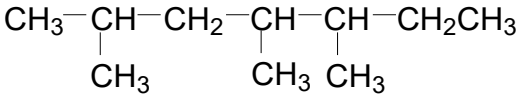
Raffles Institution
Year 5 H2 Chemistry 2025

Tutorial 10: Hydrocarbons – Alkanes (Suggested Answers)

Self-Check Questions – Suggested Answers

1 (a) (i) 3,3-diethyl-4-methylheptane
(ii) 4-ethyl-2,2,3,6-tetramethyloctane
(iii) 3-ethyl-2,7-dimethyloctane
(iv) 2,2,5-trimethylheptane
(v) 3,3,4-triethylhexane

(b) (i) 2,4,5-trimethylheptane



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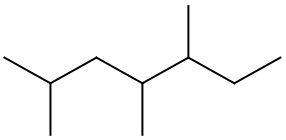
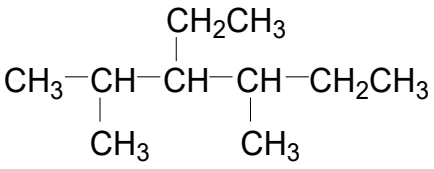


(ii) 3-ethyl-2,4-dimethylhexane



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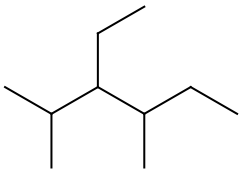


2 The given compounds have **simple molecular structures** and can be arranged in the following order of increasing boiling point:

2-methylpentane < hexane < 3,3-dimethylpentane < 2-methylhexane < heptane

i.e. (e) < (d) < (c) < (a) < (b)

Comparing (c), (a) and (b) vs (e) and (d)

- (c), (a) and (b) are seven-carbon alkanes while (e) and (d) are six-carbon alkanes. (c), (a) and (b) have more electrons per molecule and hence, larger and more polarisable electron clouds than (e) and (d). Hence, the instantaneous dipole-induced dipole interactions in (c), (a) and (b) are stronger and more heat is required for boiling these alkanes, resulting in them having a higher boiling point than (e) and (d).

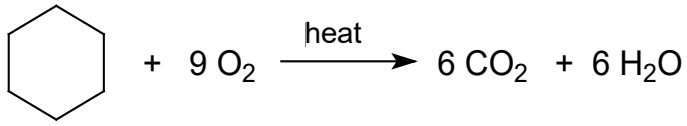
Comparing (c), (a) and (b)

- the degree of branching decreases from (c) to (a) to (b)
- there is increasing surface area of contact between molecules from (c) to (a) to (b)
- strength of instantaneous dipole-induced dipole interactions increases from (c) to (a) to (b)
- higher boiling point from (c) to (a) to (b)

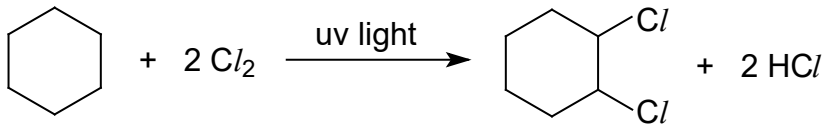
Comparing (e) and (d)

- the degree of branching decreases from (e) to (d),
- there is greater surface area of contact between molecules of (d),
- hence stronger instantaneous dipole-induced dipole interactions in (d)
- higher boiling point for (d)

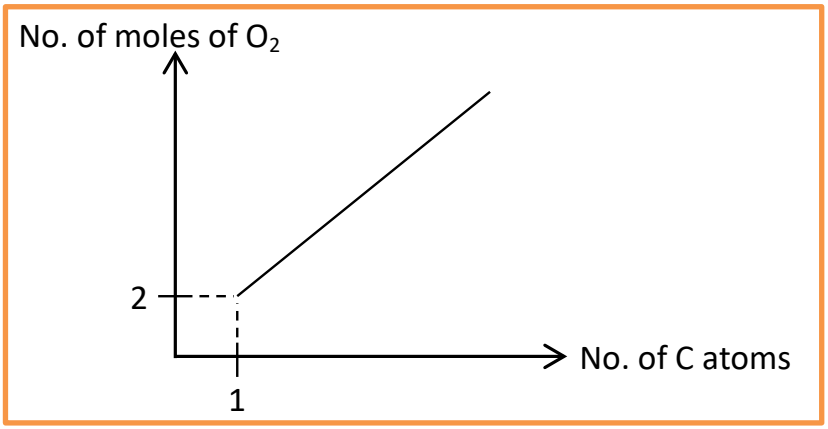
3 Reaction (1): **Combustion**



Reaction (2): **Free-radical substitution**



4 $C_nH_{2n+2} + \frac{3n+1}{2} O_2(g) \longrightarrow n\ CO_2(g) + (n+1)\ H_2O(l)$

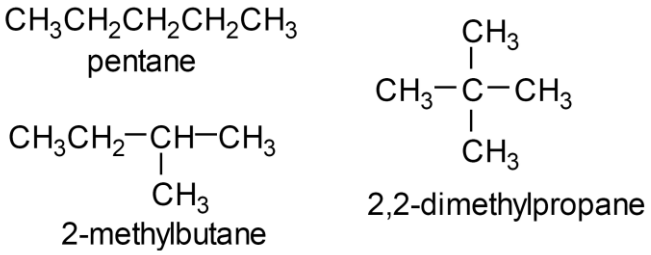


5(a) Volume of unreacted O_2 and CO_2 = 250 cm^3
Volume of unreacted O_2 = volume of residual gas (after shaking with NaOH) = 100 cm^3
Volume of CO_2 produced = 250 – 100 = 150 cm^3

	C_xH_y	+ (x + y/4)O_2(g)	→	xCO_2(g)	+ y/2 H_2O (l)
volume used/cm^3	30	340		-	-
volume reacted/cm^3	30	(340 -100) =240		(250 -100) =150	
volume ratio	1	: 8	:	5	
molar ratio	1	: 8	:	5	
molar ratio	1	: (x + y/4)	:	x	

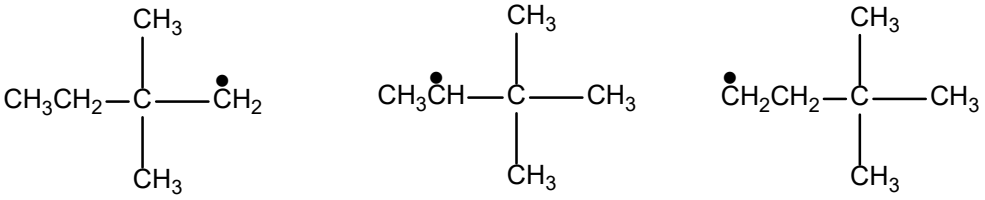
From the table, **x = 5**
And (x + y/4) = 8 ⇒ **y = 12**
Hence, the molecular formula of the hydrocarbon is **C_5H_{12}**.

5(b) • Possible isomers of the alkane:

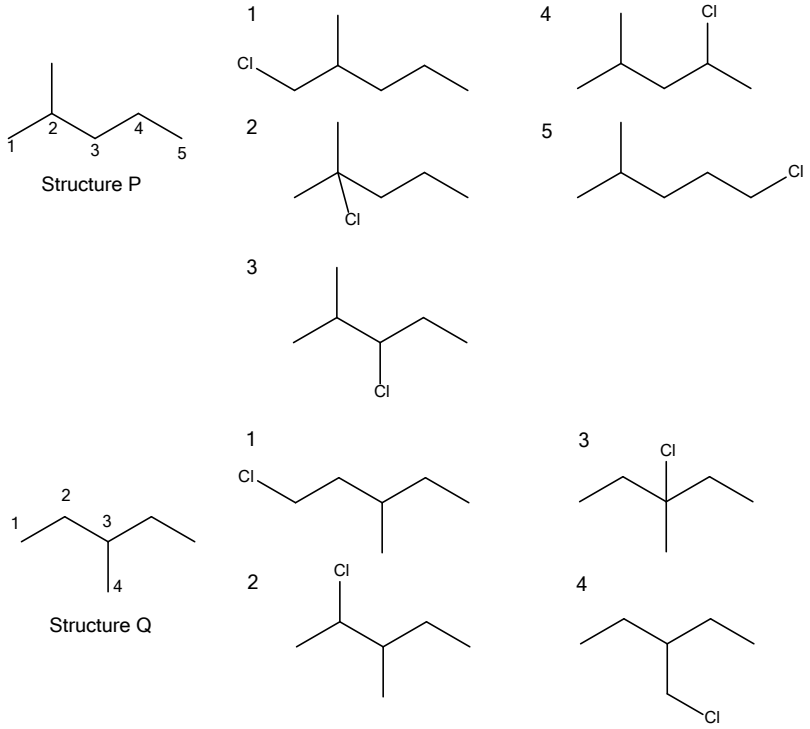


6 Answer : C

Possible answers:

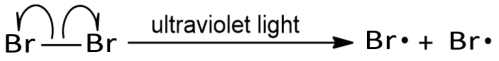


7 Answer : B

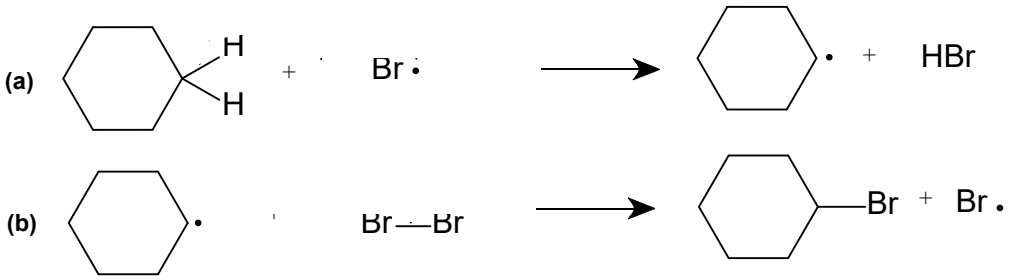


8 The mechanism is **<u>free-radical substitution</u>** which consists of the following steps:

<u>Step 1: Initiation</u>

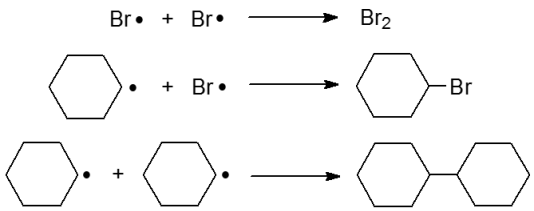


<u>Step 2: Propagation</u>



Then **(a), (b), (a), (b), …...**

<u>Step 3: Termination</u>



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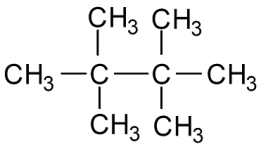
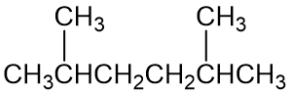
Practice Questions – Suggested Answers

9(a)(i)



9(a)(ii)



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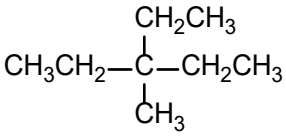
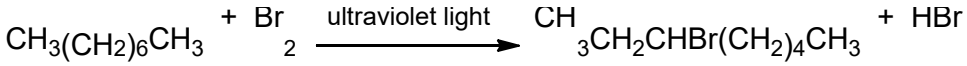


9(b)(i)



9(b)(ii) **Orange-red bromine is decolourised** and **white fumes of HBr** which turn damp blue litmus paper red are formed.

9(b)(iii) The mechanism is **free-radical substitution**

Step 1: Initiation

Step 2: Propagation

(a) $CH_3(CH_2)_6CH_3 + Br^{\bullet} \longrightarrow CH_3CH_2\dot{C}H(CH_2)_4CH_3 + HBr$

(b) $CH_3CH_2\dot{C}H(CH_2)_4CH_3 + Br_2 \longrightarrow CH_3CH_2CHBr(CH_2)_4CH_3 + Br^{\bullet}$

Then (a), (b), …

Step 3: Termination

$2Br^{\bullet} \longrightarrow Br_2$

$CH_3CH_2\dot{C}H(CH_2)_4CH_3 + Br^{\bullet} \longrightarrow CH_3CH_2CHBr(CH_2)_4CH_3$

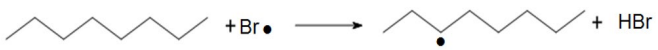
$2CH_3CH_2\dot{C}H(CH_2)_4CH_3 \longrightarrow CH_3CH_2CH(CH_2)_4CH_3$ (attached to) $CH_3CH_2CH(CH_2)_4CH_3$

Note: Skeletal formulae may be used.

Step 1: Initiation

Step 2: Propagation

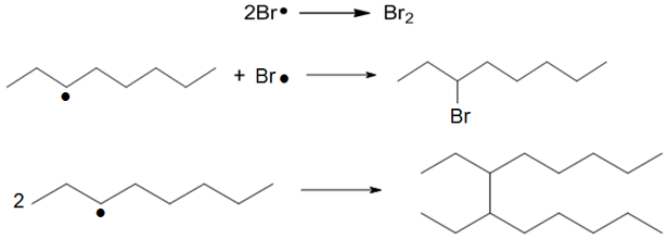
(a)



(b)

Then (a), (b), …

Step 3: Termination



9(b)(iv) A flash of ultraviolet light provides enough energy for some Br_2 molecules to undergo homolytic bond fission to form Br• radicals. Once the Br• radicals are generated in the initiation step, the **chain reaction is started** and the **propagation steps can proceed successively for many cycles un-aided**.

9(b)(v) Consider the 2 propagation steps:

(a) $CH_3(CH_2)_6CH_3 + Br^{\bullet} \longrightarrow CH_3CH_2\dot{C}H(CH_2)_4CH_3 + HBr$

(b) $CH_3CH_2\dot{C}H(CH_2)_4CH_3 + Br_2 \longrightarrow CH_3CH_2CHBr(CH_2)_4CH_3 + Br^{\bullet}$

Then (a), (b), …

The reaction is an example of homogeneous catalysis since the catalyst, Br•

- exists in the **same phase** (dissolved in inert solvent) as the two reactants, octane and Br_2.
- is consumed in one step and **regenerated** in another.

9(b)(vi) Use an excess of octane (or use a limiting amount of Br_2).

9(b)(vii) $CH_3(CH_2)_6CH_3 + I^{\bullet} \longrightarrow CH_3CH_2\dot{C}H(CH_2)_4CH_3 + HI$

ΔH reaction for the 1st propagation step = BE(C–H) – BE(H–I)= +410 – 299 = **+111 kJ mol^{-1}**

The first propagation step is **endothermic** due to the breaking of the relatively strong C–H bond and the formation of the weaker H–I bond. This makes it difficult for the chain propagation steps to occur. Thus, the formation of 3-iodooctane is energetically unfavourable.

10(a) Molar ratio of C to H in alkane **F** = $\frac{83.72}{12.0} : \frac{(100-83.72)}{1.0}$ = 6.977 : 16.28 = 1 : 2.33 = 3 : 7

Hence, the **empirical formula of F is C_3H_7**.

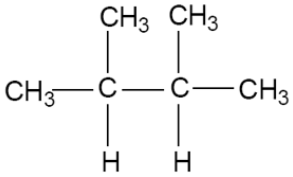
Let the molecular formula of **F** be $(C_3H_7)_m$, i.e. $C_{3m}H_{7m}$.
The general formula of an alkane is C_nH_{2n+2}.
In this case, 3m = n
and 7m = 2n + 2
Upon solving the simultaneous equations, m = 2
Hence, the **molecular formula of F is C_6H_{14}**.

Note #1:
- Can proceed by trial and error to find m.
- In this case, m ≠ 1 and m ≠3
- When m = 2, the molecular formula is C_6H_{14} which fits that of a six-carbon alkane.

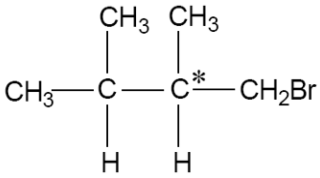
Note #2:
- Let **F** have n carbon atoms and have the general alkane formula, C_nH_{2n+2}.
- Then % of carbon (by mass) in **F** = $(\frac{12n}{14n+2}$ x 100) = 83.72
  Hence n = 6.06 = 6

Note #3:
- **F** is not a cycloalkane since percentage of carbon by mass in a cycloalkane is not 83.72%.

F undergoes **free-radical substitution** reaction with Br_2 to form only two mono-brominated products.
⇒ There are **2 types of H atoms** in a molecule of **F**.
⇒ **F** has to be

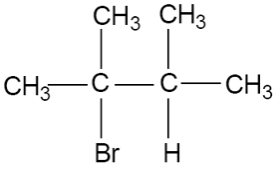


H is a mono-brominated product and is chiral.
⇒ **H** contains **a chiral carbon** atom.
⇒ **H** is

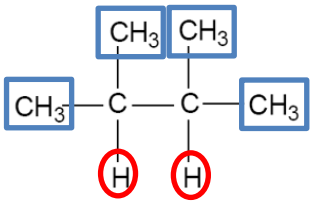


Note: ∗ denotes a chiral carbon atom

G is the other mono-brominated product.
⇒ **G** is



10(b)

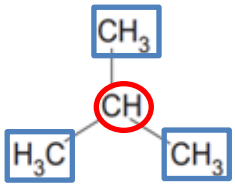


To form **G** from **F**, the Br atom can replace any one of the **2 tertiary hydrogen atoms** (denoted by the circle).
To form **H** from **F**, the Br atom can replace any one of the **12 primary hydrogen atoms** (denoted by the box).
Hence, based on probability factor (and assuming all the hydrogen atoms have the same reactivity), the approximate molar ratio in which **G** and **H** are formed = 2 : 12 = **1 : 6**

11(a) These reagents do not attack an alkane because

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

11(b)

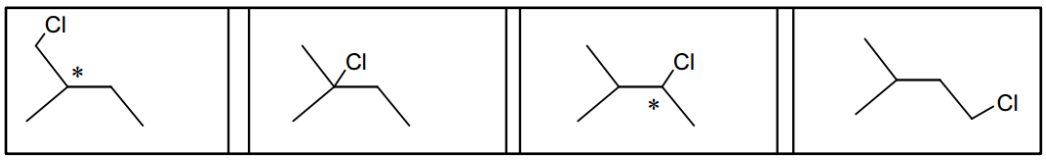


To form **A**, the C*l* atom can replace the only 1 tertiary H atom (denoted by the circle) in 2-methylpropane.
To form **B**, the C*l* atom can replace any one of the 9 primary H atoms (denoted by the box) in 2-methylpropane.

Note: In this example, substituting any primary H in 2-methylpropane results in the same product. This is only true because in this case, the primary H atoms are all equivalent.

Combining both the probability factor stated above and the given reactivity ratio factor, the relative ratio of **A** to **B** = (1)(21) : (9)(1) = 21:9 = **7:3**

11(c)



Total number of isomers: 6

12(a)(i) Secondary free radical is more stable than primary free radical. **[1]**

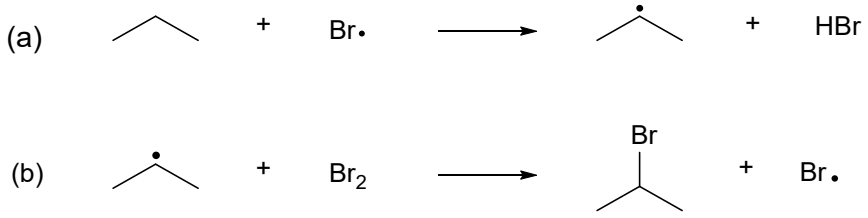
12(a)(ii) The free radical has a <u>C atom with an unpaired electron/is electron deficient</u>. Since a <u>secondary free radical</u> has <u>2 electron donating alkyl groups directly attached to this C atom compared to only one in a primary free radical</u>, the secondary radical is more stable. **[1]**

12(a)(iii) Homolytic fission of the C–H bond in $(CH_3)_2CH–H$ results in the formation of a <u>more stable secondary free radical, $(CH_3)_2\dot{C}H$</u>. **[1]**

12(b) Free radical substitution

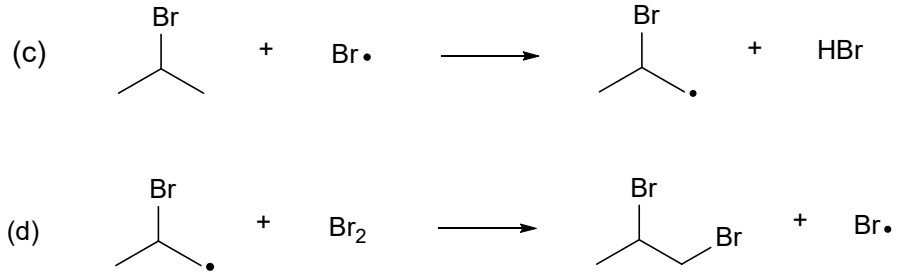
Initiation:

Propagation:



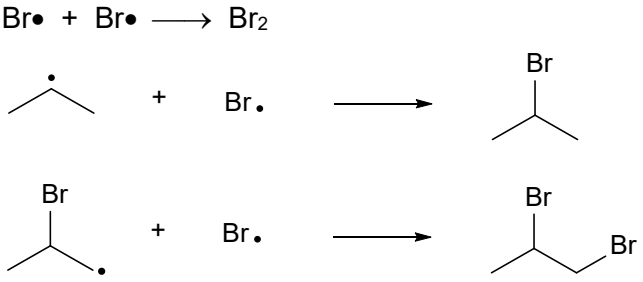
Then (a), (b), (a), (b), …
Propagation steps (a) and (b) give rise to many molecules of $CH_3CHBrCH_3$.

$CH_3CHBrCH_3$ can undergo further bromination via propagation steps **(c)** and **(d)** to form $CH_3CHBrCH_2Br$.



Then (c), (d), (c), (d), …

Termination:



Note: 1-bromopropane can also be formed first followed by 1,2-dibromopropane.