Mark scheme - Alkanes

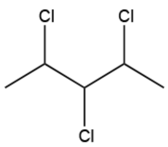
Question			Answer/Indicative content	Marks	Guidance
1		i	**Initiation** $Cl_2 \rightarrow 2Cl\cdot$ **AND** UV ✓ **Propagation** $C_4H_{10} + Cl\cdot \rightarrow C_4H_9\cdot + HCl$ ✓ $C_4H_9\cdot + Cl_2 \rightarrow C_4H_9Cl + Cl\cdot$ ✓	3 (AO1.1) (AO2.5) (AO2.5)	Dots **NOT** required for initiation **IGNORE** temperature **OR** pressure Dots **required** in each propagation equation **ALLOW** 1 mark for **BOTH** propagation equations with any dots missing or extra dots e.g. $C_4H_{10} + Cl \rightarrow C_4H_9 + HCl$ $C_4H_9\bullet + Cl_2\bullet \rightarrow C_4H_9Cl + Cl$ **DO NOT ALLOW** charges **<u>Examiner's Comments</u>** A minority of Many candidates scored all 3 marks for this part, showing that most had thoroughly learnt the mechanism for radical substitution. The equation and conditions for the initiation step were well-known but the equations for the propagation steps often included errors. It was common for dots to be omitted for some radicals and $C_4H_9Cl\cdot$, rather than $C_4H_9\cdot$, was often shown for one of the products in the first propagation stage. $H\cdot$ was then shown as the other product.
		ii	$C_4H_{10} + 10\ Cl_2 \rightarrow C_4Cl_{10} + 10\ HCl$ ✓	1 (AO2.6)	**ALLOW** structural formulae, e.g. $CH_3CH_2CH_2CH_3 + 10Cl_2$ $\rightarrow CCl_3CCl_2CCl_2CCl_3 + 10HCl$ **<u>Examiner's Comments</u>** Only the highest attaining candidates were able to write the correct equation. Although most candidates did identify the organic product as C_4Cl_{10}, the other product was usually seen as $5H_2$ rather than 10HCl.
		iii	$n(\mathbf{E}) = \frac{78.0}{32500} = 2.4(0) \times 10^{-3}$ (mol) ✓ $M(\mathbf{E}) = \frac{0.636}{2.4(0) \times 10^{-3}}$ **OR** 265 ✓ Molecular formula = $C_4H_4Cl_6$ ✓	3 (AO3.1×2) (AO3.2)	**ALLOW ECF** from incorrect n(**E**) **ALLOW ECF** from incorrect M(**E**) from n(**E**)

					--- **COMMON ERROR** $n(\mathbf{E}) = \frac{78.0}{24000} = 3.25 \times 10^{-3}$ (mol) ✗ $M(\mathbf{E}) = \frac{0.636}{3.25 \times 10^{-3}} = 195.69$ **OR** 196 ✓ *(3SF or more)* Molecular formula = $C^4H^6Cl^4$ ✓ **ALLOW ECF** for molecular formula but must be derived from a calculated value for *M*(**E**) **<u>Examiner's Comments</u>** A minority of This question discriminated very well. It was encouraging to see the number of candidates who used 32.5 dm^3 mol^{-1} as the molar gas volume under the experimental conditions to obtain 2.40×10^{-3} mol of gas. Many though used 24.0 dm3 mol^{-1} for RTP and obtained 3.25×10^{-3} mol. Error carried forward allowed such candidates to still secure the final 2 of the 3 marks available. Lower attaining candidates were unsure where to start and tried to do anything with the number provided. The result was often n unusable number.
			Total	**7**	
2	a		**Structural isomers:** *1 mark* Different structural formulae AND same molecular formula ✓ **Common molecular formula:** *1 mark* C_5H_{12} for all 3 hydrocarbons ✓	**5**	For 'structural': **ALLOW** different structure **OR** different displayed/ skeletal formula **DO NOT ALLOW** any reference to spatial/space/3D Same formula is **not** sufficient (no 'molecular') Different arrangement of atoms is **not** sufficient (no 'structure'/'structural') **ALLOW** 5 carbons and 12 hydrogens **ALLOW** for 2 marks: Different structural formulae **AND** same molecular formula ✓ of C_5H_{12} ✓

			Boiling point and branching: *1 mark* Boiling point decreases with more branching **OR** more methyl/alkyl groups/side chains **OR** shorter carbon chain ✓ **Branching and London forces:** *1 mark* *Could be seen anywhere within response* More branching gives less (surface) contact **AND** fewer/weaker London forces ✓ **Energy and intermolecular forces:** *1 mark* Less energy to break London forces/ intermolecular forces/intermolecular bonds/ ✓		**Comparisons** needed throughout **ORA** throughout **ALLOW** comparison between any alcohols, e.g. **A** is least branched and has highest b pt **C** is most branched and has lowest b pt **ALLOW** induced dipole(−dipole) interactions **IGNORE** van der Waals'/vdw forces **ALLOW** SA for surface area **ALLOW** 'harder to overcome intermolecular forces **ALLOW** more energy to separate the molecules **IGNORE** just 'bonds' ***intermolecular/London forces*** *required* **Examiner's Comments** This question discriminated well and resulted in a full range of marks. Most candidates were aware that structural isomers have different structural formulae but the same molecular formulae. It was common though for candidates to refer to different arrangements of atoms in space, clearly confusing with stereoisomerism. The best candidates used the structures (as in the question) to show that the common molecular formula was C5H12. Candidates were expected to link the amount of surface contact between molecules with induced dipole–dipole forces or London forces. 'Contact' or the name of the intermolecular forces was often omitted. Finally, candidates were expected to link the amount of branching to the strength of the intermolecular forces and the energy needed to change state. Lower ability candidates often let themselves down by being unable to construct a well-reasoned response. There was often a gulf between the clear responses of able candidates and those of lower ability candidates.
	b	i	Radical substitution ✓	**1**	**ALLOW** Free radical substitution **Examiner's Comments** Most candidates identified this reaction as radical substitution.

<table>
<tr><td></td><td></td><td>ii</td><td><table><tr><th>A</th><th>B</th></tr><tr><td>3 ✓</td><td>4 ✓</td></tr></table></td><td>2</td><td><u>Examiner’s Comments</u>

Most candidates achieved at least one mark, particularly for isomer A. Successful candidates often drew structures of the isomers alongside the table to help with their response.</td></tr>
<tr><td></td><td></td><td>iii</td><td>Structure of D

Structure of a trichloro isomer of A, e.g.

✓
ALLOW any trichloro isomer of A
CHECK carefully

Equation

$C_5H_{12} + 3Cl_2 \rightarrow C_5H_9Cl_3 + 3HCl$ ✓
Molecular formulae required

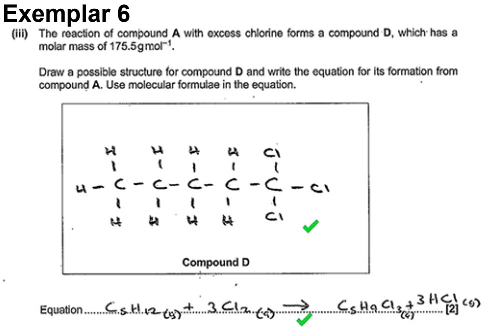
NO ECF from incorrect structure of D</td><td>2</td><td>ALLOW correct structural OR displayed OR skeletal formula OR mixture of the above (as long as unambiguous)

IGNORE molecular formula

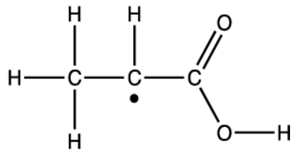
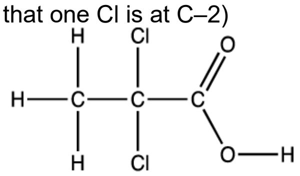
ALLOW multiples,
e.g. $2C_5H_{12} + 6Cl_2 \rightarrow 2C_5H_9Cl_3 + 6HCl$

<u>Examiner’s Comments</u>

Many candidates correctly drew the structure of compound D but comparatively few were able to construct a correct equation. For this equation, candidates needed to apply their knowledge and understanding of monosubstitution of alkanes to substitution of three H atoms by three Cl atoms. This task proved to be one of the most difficult questions on this paper. The exemplar shows an excellent response. The candidate has drawn a trisubstituted structure that fits the molar mass of 175.5 g mol^{-1} and a correct equation for its formation. Many attempts at this equation showed H2 as the second product rather than HCl.

Exemplar 6

(iii) The reaction of compound A with excess chlorine forms a compound D, which has a molar mass of 175.5 g mol^{-1}.
Draw a possible structure for compound D and write the equation for its formation from compound A. Use molecular formulae in the equation.
Compound D
Equation $C_5H_{12(g)} + 3Cl_{2(g)} \rightarrow C_5H_9Cl_{3(g)} + 3HCl_{(g)}$ [2]</td></tr>
</table>

			Total	10	
3		i	Ultraviolet (radiation)/UV ✓	1	**ALLOW** sunlight **IGNORE** temperature **Examiner's Comments** Most candidates scored this mark.
		ii	$CH_3CH_2COOH + Cl_2 \rightarrow CH_3CHClCOOH + HCl$ ✓	1	**ALLOW** $C_2H_5COOH + Cl_2 \rightarrow C_2H_4ClCOOH + HCl$ **ALLOW** $C_3H_6O_2 + Cl_2 \rightarrow C_3H_5ClO_2 + HCl$ **Examiner's Comments** Many candidates could write the overall equation but there was some confusion with propagation steps and some equations contained radicals or missed out HC*l* as a product.
		iii	one electron from the bond (pair) goes to each atom / chlorine/radical ✓	1	**ALLOW** the breaking of a covalent bond where each atom keeps one of the bonding electrons **IGNORE** particle for atom **ALLOW** one electron from the bond goes to each product / species **DO NOT ALLOW** molecule or compound for atom **IGNORE** homolytic fission equations **Examiner's Comments** Homolytic fission is described in the specification in terms of each bonding atom receiving one electron from the bonded pair forming two radicals. A large proportion of candidates failed to match the essential points in this definition.
		iv	*Propagation step 1* $Cl\cdot + CH_3CH_2COOH \rightarrow CH_3CHCOOH\cdot + HCl$ ✓ *Propagation step 2* $CH_3CHCOOH\cdot + Cl_2 \rightarrow CH_3CHClCOOH + Cl\cdot$ ✓	2	**ALLOW** 1. $Cl\cdot + C_3H_6O_2 \rightarrow C_3H_5O_2\cdot + HCl$ 2. $C_3H_5O_2\cdot + Cl_2 \rightarrow C_3H_5ClO_2 + Cl\cdot$ **ALLOW** dot at any position on the radical **ALLOW** 1 mark if both equations correct but any dots omitted from radicals **Examiner's Comments** Generally well answered. Candidates took note of the instruction in the question and it was very rare to see radicals without their unpaired electron.

		v	 ✓	**1**	Dot shown in correct position **ALLOW** –OH **Examiner's Comments** Unfortunately, candidates who were not able to attempt equations for the propagation steps in part (iv) were then unable to suggest the structure of the radical formed in the first step. Many candidates did not present a fully displayed formula. However, formulae showing –OH were given credit in this question.
		vi	Any structure with two or more Cl atoms on alkyl chain (provided that one Cl is at C–2)  e.g.✓	**1**	**ALLOW** correct structural **OR** skeletal **OR** displayed formula **OR** mixture of the above **DO NOT ALLOW** $C_3H_4Cl_2O_2$ **ALLOW** further substitution into any or all of the 4 positions occupied by H atoms in the alkyl group, provided that at least one Cl is at C–2 **Examiner's Comment:** Generally well answered but it was clear from some of the structures drawn that some candidates did not understand what is meant by further substitution.
			Total	**7**	
4			Alcohols have hydrogen bonds (and van der Waals' forces) ✓ Hydrogen bonds are stronger than van der Waals' forces (in alkanes) ✓	2	**ANNOTATE ANSWER WITH TICKS AND CROSSES** **ALLOW** reference to specific compounds e.g. comparing methane and methanol Second marking point requires **BOTH** types of intermolecular forces in response i.e comparison of hydrogen bonds **AND** van der Waals is **essential** **DO NOT ALLOW** the second mark for a comparison of van der Waals' and hydrogen bonds between alcohols and water **ALLOW** more energy required to break hydrogen bonds than van der Waals' forces

					ALLOW it is harder to overcome the hydrogen bonds than van der Waals' forces **IGNORE** more energy is needed to break bonds **Examiner's Comments** Many candidates attributed the difference in boiling point between alkanes and alcohols to the relative strength of hydrogen bonds compared with van der Waals' forces. Weaker responses simply identified alcohols as being able to form hydrogen bonds, but failed to compare these with van der Waals' forces.
			Total	**2**	
5		i	$C_8H_{18} + 12½O_2 \rightarrow 8CO_2 + 9H_2O$ ✓	1	**ALLOW** multiples e.g. $2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O$ **IGNORE** state symbols **Examiner's Comments** Almost all candidates could provide a correctly balanced equation for the complete combustion of octane.
		ii	(n(C_8H_{18}) burned) = 0.32 (mol) ✓ (n(CO_2) from complete combustion) = 2.56 **or** 2.6 mol **OR** (ratio nCO_2 / nC_8H_{18}) = 7.8(125) **OR** (n C_8H_{18} produce 2.5 mol CO_2) = 0.31(25) ✓	2	**DO NOT ALLOW ECF** from an incorrect moles of octane **DO NOT ALLOW ECF** from incorrect ratio from equation in **(i)** **ALLOW** the following alternate methods --- **Method 1** (mass CO_2 produced) = 110 g ✓ (mass CO_2 from complete combustion) = 8 × 0.32 × 44 = 112.64 **or** 112.6 **or** 113 g ✓ --- **Method 2** (n C_8H_{18} to produce 2.5 mol CO_2) = 0.31(25) ✓

					(mass of octane required to produce 2.50 mol CO_2) = 35.6 **OR** 35.63 **OR** 35.625 g ✓ **Examiner's Comments** Candidates coped well with this unfamiliar question. Almost all candidates recognised the need to calculate the number of moles of octane combusted and received the first mark. The majority of candidates were able to process this to show that 2.56 moles of carbon dioxide should have been produced. It was encouraging to see a range of alternative approaches adopted by candidates. For example, some used the calculated moles of octane and the amount of CO_2 given in the question to show that the reacting ratio was less than 8. The mark scheme allowed full marks for all valid responses.
			Total	**3**	
6	a	i	(series of compounds with the) same functional group **OR** same / similar chemical properties **OR** same / similar chemical reactions ✓ each **successive/subsequent** member differing by CH_2 ✓	2	**IGNORE** references to physical properties **IGNORE** has same general formula (in question) **DO NOT ALLOW** have the same empirical formula **OR** have the same molecular formula **Examiner's Comments** Many candidates were able to score both marks by specifying the same functional group and that each successive member varies by a CH_2 group. Some responses were imprecise and referred to just members differing by CH_2 group.
		ii	C_nH_{2n} ✓	1	**Examiner's Comments** Most candidates were able to state the general formula for the cycloalkanes.
		iii	More carbons (in ring) **OR** more (surface area of) contact **AND**	2	**Both answers need to be comparisons** **ALLOW** ORA throughout **ALLOW** has more electrons **OR** larger (carbon) ring **OR** higher molecular mass **IGNORE** bigger molecule **IGNORE** chain instead of ring **DO NOT ALLOW** 'more contact between

<table>
<tr><td></td><td></td><td></td><td>more van der Waals forces
OR stronger van der Waals forces ✓

More energy needed to break the intermolecular forces ✓</td><td></td><td>atoms'

ALLOW 'VDW' for van der Waals
'More intermolecular forces' is not sufficient

ALLOW it is harder to overcome the intermolecular forces
ALLOW intermolecular bonds / van der Waals bonds
ALLOW more energy is needed to separate molecules
IGNORE more energy is needed to break bonds

Examiner's Comments

This was a well answered question and many candidates could relate the difference in boiling point to the increase in points of contact and stronger van derWaals' forces. A significant number of candidates referred to the breaking of bonds rather than intermolecular forces.</td></tr>
<tr><td></td><td>b</td><td></td><td>tetrahedral ✓

four bonding pairs repel OR four bonds repel ✓</td><td>2</td><td>Mark each point independently

IGNORE surrounded by four atoms
IGNORE four areas of electron charge repel
IGNORE four electron pairs repel (one could be lp)
DO NOT ALLOW atoms repel

Examiner's Comments

Most candidates were able to state the shape required. Explanations for the bond angle often focused on the four bond pairs around the carbon atom, however candidates did not always refer to repulsion between these electron pairs.</td></tr>
<tr><td></td><td>c</td><td>i</td><td><table><tr><th>Step</th><th>Equation</th></tr><tr><td>Initiation
(1 mark)</td><td>$Br_2 \rightarrow 2Br\bullet$ ✓</td></tr><tr><td>Propagation
(2 marks)</td><td>$C_6H_{12} + Br\bullet \rightarrow C_6H_{11}\bullet + HBr$ ✓

$C_6H_{11}\bullet + Br_2 \rightarrow C_6H_{11}Br + Br\bullet$ ✓</td></tr><tr><td>Termination
(2 marks)</td><td>$C_6H_{11}\bullet + Br\bullet \rightarrow C_6H_{11}Br$

$C_6H_{11}\bullet + C_6H_{11}\bullet \rightarrow C_{12}H_{22}$

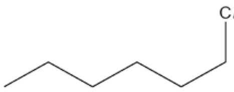
$Br\bullet + Br\bullet \rightarrow Br_2$</td></tr></table></td><td>5</td><td>IGNORE state symbols

IGNORE dots

If an incorrect hydrocarbon with six C atoms is used:
DO NOT ALLOW any marks for the propagation steps but
ALLOW ECF for termination steps (i.e. 3 max)

Examiner's Comments</td></tr>
</table>

			<table><tr><td></td><td>**Two** correct ✓ All **three** correct ✓✓</td></tr></table>		This question required candidates to apply their knowledge of the radical substitution mechanism and those who had prepared well scored full marks. A common misconception was to have hydrogen radicals being formed and reacted in propagation and termination steps.
		ii	The breaking of a (Br-Br) bond **AND** forms (two) radicals **OR** the breaking of a (Br-Br) bond **AND** one electron (from the bond pair) goes to each atom / bromine ✓	1	**ALLOW** 'the breaking of a covalent bond' **ALLOW** the splitting of the bond in bromine **ALLOW** the breaking of a covalent bond where each atom keeps one of the bonding electrons **IGNORE** particle for atom **ALLOW** one electron goes to each product / species **DO NOT ALLOW** molecule or compound for atom **IGNORE** homolytic fission equations **Examiner's Comments** This question was better attempted than in previous sessions. Although many candidates were able to identify that radicals were formed, a significant number did not refer to the breaking of the covalent bond in Br_2.
	d	i	$C_6H_{12} + 2Br_2 \rightarrow C_6H_{10}Br_2 + 2HBr$ ✓	1	**ALLOW** molecular formula only. **Examiner's Comments** This question proved quite difficult for the vast majority of candidates who failed to apply their knowledge of radical substitution to an unfamiliar example. The most common incorrect answer was $C_6H_{12} + Br_2 \longrightarrow C_6H_{10}Br_2 + H_2$.
		ii	1,1-dibromocyclohexane **OR** 1,2-dibromocyclohexane **OR** 1,3-dibromocyclohexane **OR** 1,4-dibromocyclohexane ✓	1	Locant numbers **MUST** lowest possible e.g. **DO NOT ALLOW** 2,4-dibromocyclohexane etc. **IGNORE** structures **Examiner's Comments** Candidates were required to name one of the dibromocyclohexane compounds that could be formed from cyclohexane and the more able candidates were able to apply their understanding of nomenclature successfully. Common incorrect responses included straight chain dibromo compounds e.g. 1,2—dibromohexane and incorrect use

					of locant numbers e.g. 2,3— dribromocyclohexane.
			Total	**15**	
7		i	any mono or multiple substituted chlorohexane − e.g.  (1)	1	
		ii	(because) substitution can replace any H atom / multiple substitution *owtte* (1)	1	**ignore** vague statements about free radical reactions being random **allow** termination can join alkyl radicals to form larger hydrocarbons *owtte*
			Total	**2**	
8		i	CO is toxic	1	**allow** responses linked to effect of CO in blood
		ii	*Calculation:* *n*(butane) = 600/58.0 = 10.34 (mol) **AND** *n*(O_2) required = 6.5 × 10.34 = 67.2 (mol) (1) *n*(O_2) consumed = 1.50 × 10^3 / 24.0 = 62.5 (mol) **OR** volume O_2 required for complete combustion = 67.2 × 24.0/1000 = 1.61 m^3 (1) *Conclusion:* incomplete combustion / stove not safe to use **AND** 62.5 < 67.2 **OR** 1.61 > 1.50 (1)	3	using 1 : 6.5 ratio **allow** number rounding to 67
			Total	**4**	
9		i	Overlap of orbitals directly between the bonding atoms	1	**allow** a correct diagram
		ii	120° **AND** trigonal planar	1	**allow** planar triangle
			Total	**2**	
10			Initiation $Cl_2 \rightarrow 2Cl\cdot$ (1) Propagation $C_2H_6 + Cl\cdot \rightarrow C_2H_5\cdot + HCl$ (1) $C_2H_5\cdot + Cl_2 \rightarrow C_2H_5Cl + Cl\cdot$ (1) Termination $Cl\cdot + Cl\cdot \rightarrow Cl_2$	5	If the structure of the ethyl radical is drawn, the lone electron must be attached to a C atom

			OR $C_2H_5\cdot + Cl\cdot \rightarrow C_2H_5Cl$ **OR** $C_2H_5\cdot + C_2H_5\cdot \rightarrow C_4H_{10}$ (1) Initiation, propagation, termination used in correct context (1)		
			Total	**5**	