## GCE

## Chemistry A

H432/02: Synthesis and analytical techniques

Advanced GCE

Mark Scheme for Autumn 2021

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This mark scheme is published as an aid to teachers and students, to indicate the requirements of the examination. It shows the basis on which marks were awarded by examiners. It does not indicate the details of the discussions which took place at an examiners' meeting before marking commenced.

All examiners are instructed that alternative correct answers and unexpected approaches in candidates' scripts must be given marks that fairly reflect the relevant knowledge and skills demonstrated.

Mark schemes should be read in conjunction with the published question papers and the report on the examination.

1. Annotations

| Annotation | Meaning |
| :--- | :--- |
| A | Correct response |
| A | Incorrect response |
| BOD | Omission mark |
| CON | Benefit of doubt given |
| RE | Contradiction |
| SF | Rounding error |
| ECF | Error in number of significant figures |
| L1 | Learried forward 1 |
| L2 | Level 2 |
| L3 | Level 3 |
| NBOD | Nenefit of doubt not given |
| SEEN | Ignore |
| I |  |

2. Abbreviations, annotations and conventions used in the detailed Mark Scheme (to include abbreviations and subject-specific conventions)

| Annotation | Meaning |
| :---: | :--- |
| DO NOT ALLOW | Answers which are not worthy of credit |
| IGNORE | Statements which are irrelevant |
| ALLOW | Answers that can be accepted |
| () | Words which are not essential to gain credit |
| ECF | Underlined words must be present in answer to score a mark |
| AW | Alternative wording |
| ORA | Or reverse argument |


| Question | Answer | Marks | AO element | Guidance |
| :---: | :---: | :---: | :---: | :--- |
| 1 | C | 1 | AO2.1 | ALLOW 4 (This is the number of structural isomers) |
| 2 | B | 1 | AO1.2 |  |
| 3 | C | 1 | AO2.2 |  |
| 4 | C | 1 | AO2.6 |  |
| 5 | D | 1 | AO2.1 |  |
| 6 | B | 1 | AO1.2 |  |
| 7 | A | 1 | AO1.2 |  |
| 8 | C | 1 | AO2.1 |  |
| 10 | C | 1 | AO1.2 |  |
| 11 | D | 1 | AO2.1 |  |
| 12 | B | 1 | AO2.5 |  |
| 14 | B | 1 | AO2.1 |  |
| 15 | A | 1 | AO2.1 |  |
|  |  | 1 | AO1.1 |  |
|  | Total | 15 |  |  |


| Question |  |  | Answer | Marks | AO element | Guidance |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 16 | (a) | (i) | $\sigma$-bond: Overlap of orbitals between (bonding) atoms $\checkmark$ <br> $\pi$-bond: Sideways overlap of (adjacent) p-orbitals $\checkmark$ | 2 | $\begin{gathered} \mathrm{AO} 1.1 \\ \times 2 \end{gathered}$ | ALLOW labelled diagrams IGNORE the type of orbital for $\sigma$-bond DO NOT ALLOW pi-orbital |
|  |  | (ii) | $\begin{aligned} & \sigma \text {-bonds: } 9 \checkmark \\ & \pi \text {-bonds: } 2 \checkmark \end{aligned}$ | 2 | $\begin{gathered} \mathrm{AO} 1.2 \\ \times 2 \end{gathered}$ |  |
|  | (b) | (i) |  <br> Curly arrow from $\mathrm{C}=\mathrm{C}$ bond to H of $\mathrm{H}-\mathrm{Br} \checkmark$ DO NOT ALLOW partial charge on $\mathrm{C}=\mathrm{C}$ <br> Correct dipole shown on $\mathrm{H}-\mathrm{Br}$ AND curly arrow showing breaking of $\mathrm{H}-\mathrm{Br}$ bond $\checkmark$ | 4 | $\begin{gathered} \hline \mathrm{AO} 1.2 \\ \times 2 \\ \\ \mathrm{AO} 2.5 \\ \times 2 \end{gathered}$ | NOTE: curly arrows can be straight, snake like, etc. but NOT double headed or half headed arrows <br> 1st curly arrow must <br> - go to the H atom of $\mathrm{H}-\mathrm{Br}$ AND <br> - start from, OR be traced back to any point across width of $\mathrm{C}=\mathrm{C}$ <br> 2nd curly arrow must <br> - start from, OR be traced back to any part of ${ }^{\delta+} \mathrm{H}-\mathrm{Br}^{\delta-}$ bond AND <br> - go to $\mathrm{Br}^{\delta-}$ |



| Question |  | Answer | Marks | AO element | Guidance |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | (ii) | (major product forms from) most/more stable intermediate/carbocation <br> (major product forms from a) secondary carbocation <br> OR carbocation bonded to more C atoms / more alkyl groups OR carbocation bonded to fewer H atoms $\checkmark$ | 2 | AO1. 1 <br> AO1.2 | For carbocation, <br> ALLOW carbonium ion or cation <br> IGNORE descriptions of the major/minor product in terms of Markownikoff's rule e.g. H atom joins to C with most H <br> IGNORE references to stability of the product <br> ALLOW ORA, i.e. <br> (minor product forms from) least/less stable intermediate/carbocation <br> (minor product forms from a) primary carbocation <br> OR carbocation bonded to less $C$ atoms / less alkyl groups <br> OR carbocation bonded to more H atoms $\checkmark$ |
|  | (iii) | $3 \checkmark$ | 1 | A01.2 |  |
| (c) | (i) | Same structural formula <br> AND <br> Different arrangement (of atoms) in space <br> OR different spatial arrangement (of atoms) $\checkmark$ | 1 | AO1.1 | ALLOW structure/displayed/skeletal formula <br> DO NOT ALLOW same empirical formula OR same general formula <br> IGNORE same molecular formula <br> Reference to $E / Z$ isomerism or optical isomerism is not sufficient |
|  | (ii) | Student is not correct <br> AND <br> 2 groups on one carbon atom (of $\mathrm{C}=\mathrm{C}$ ) are the same OR <br> C-C bond can rotate $\checkmark$ | 1 | AO3.1 | DO NOT ALLOW one side of $\mathrm{C}=\mathrm{C}$ |


| Question |  | Answer | Marks | AO element | Guidance |
| :---: | :---: | :---: | :---: | :---: | :---: |
| (d) | (i) | 1 mark for each curly arrow $\checkmark \checkmark$ | 2 | $\begin{gathered} \mathrm{AO} 2.5 \\ \times 2 \end{gathered}$ | IGNORE any dipoles shown <br> NOTE: curly arrows can be straight, snakelike, etc. <br> but NOT half headed or double headed arrows <br> Curly arrow from $\mathrm{C}=\mathrm{C}$ bond must start from, OR be traced back to, <br> Lower left: any part of $\mathrm{C}=\mathrm{C}$ bond and go to C-C <br> Upper left: any part of $C=C$ bond and go to gap between $C=C$ and $C=C$ |
|  | (ii) |   | 2 | $\begin{gathered} \mathrm{AO} 3.2 \\ \times 2 \end{gathered}$ |  |
|  |  | Total | 17 |  |  |


| Question |  |  | Answer | Marks | AO element | Guidance |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 17 | (a) |  | Formation of Cl• $\mathrm{CClF}_{3} \rightarrow \mathrm{CF}_{3} \cdot+\mathrm{Cl} \cdot \checkmark$ <br> Breakdown of $\mathrm{O}_{3}$ $\begin{aligned} & \mathrm{Cl} \cdot+\mathrm{O}_{3} \rightarrow \cdot \mathrm{ClO}+\mathrm{O}_{2} \checkmark \\ & \cdot \mathrm{ClO}+\mathrm{O} \rightarrow \mathrm{Cl} \cdot+\mathrm{O}_{2} \checkmark \end{aligned}$ | 3 | AO2.5 <br> A01.1 <br> $\times 2$ | IGNORE dots for formation $\mathrm{C} / \bullet$, i.e. ALLOW CClF $_{3} \rightarrow \mathrm{CF}_{3}+\mathrm{Cl}$ <br> DO NOT ALLOW ECF <br> Dots required in this equation <br> IGNORE O $+\mathrm{O}_{3} \rightarrow 2 \mathrm{O}_{2}$ <br> ALLOW 1 mark if both equations are correct by atom but dot(s) missing or incorrect |
|  | (b) | (i) |  | 1 | AO2.5 | ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous <br> 'End bonds' MUST be shown <br> DO NOT ALLOW more than 1 repeat unit <br> IGNORE brackets <br> IGNORE $n$ |
|  |  | (ii) | More points of contact / more surface interaction (between molecules) <br> AND <br> Stronger/more dipole(-dipole) interactions <br> More energy needed to break the intermolecular forces $\checkmark$ | 2 | $\begin{gathered} \mathrm{AO} 2.1 \\ \times 2 \end{gathered}$ | Both answers need to be a comparison <br> IGNORE surface area ALLOW more electrons <br> ALLOW induced/permanent dipole interactions ALLOW London forces ALLOW van der Waals' forces (as permanent dipole-dipole and induced dipole-dipole interactions are present within this polymer) IGNORE IDID |



| Question |  |  | Answer | Marks | AO <br> element | Guidance |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 18 | (a) | (i) | Non-superimposable mirror images (about a chiral centre) $\checkmark$ | 1 | A01.1 |  |
|  |  | (ii) | Correct groups attached to chiral C of alanine seen once e.g. <br> Two 3D structures of alanine that are mirror images AND correct connectivity in both i.e. | 2 | $\begin{gathered} \mathrm{AO} 2.1 \\ \times 2 \end{gathered}$ | Each structure must have four central bonds with at least two wedges. <br> For bond into paper accept: <br> ALLOW two 3D structures with 2 groups swapped e.g. <br> IF $\mathrm{CH}_{3}$ is shown as ' R ' ALLOW 1 mark for two 3D structures with correct connectivity that are mirror images e.g. |


| Question |  | Answer | Marks | AO element | Guidance |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | (iii) | $4 \checkmark$ | 1 | AO2.2 |  |
| (b) |  |  | 7 | $\begin{gathered} \mathrm{AO} 1.2 \\ \times 4 \\ \\ \mathrm{AO} 2.5 \\ \times 3 \end{gathered}$ | ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous <br> ALLOW names of reagents <br> DO NOT ALLOW OH- for HObut ALLOW ECF for subsequent use in (b) <br> For hydrolysis, <br> ALLOW dilute acid <br> ALLOW alkaline conditions followed by protonation of carboxylate <br> i.e. $\mathrm{NaOH}(\mathrm{aq}) / \mathrm{OH}^{-}(\mathrm{aq})$ AND $\mathrm{H}^{+}(\mathrm{aq}) / \mathrm{HCl}(\mathrm{aq})$ <br> ALLOW HBr for $\mathrm{NaBr} / \mathrm{H}_{2} \mathrm{SO}_{4}$ |


| Question |  | Answer |  | Marks | AO | Guidance |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| (c) | (i) | $\mathrm{C}_{13} \mathrm{H}_{18} \mathrm{O}_{2} \checkmark$ |  | 1 | AO2.1 | ALLOW C, H and O in any order |
|  | (ii) | FIRST CHECK ANSWER ON THE ANSWER LINE If answer $=1.17 \times 10^{21}$ award 3 marks $\begin{aligned} & M(\text { ibuprofen })=206 \\ & n(\text { ibuprofen })=\frac{400 \div 1000}{206}=1.94 \times 10^{-3}(\mathrm{~mol}) \end{aligned}$ $\begin{aligned} \text { Number of molecules } & =1.94 \times 10^{-3} \times 6.02 \times 10^{23} \\ & =1.17 \times 10^{21} \text { to } 3 \mathbf{S F} \checkmark \end{aligned}$ |  | 3 | $\begin{gathered} \mathrm{AO} 2.2 \\ \times 3 \end{gathered}$ | ALLOW ECF from (c)(i) <br> Calculator: $1.941747573 \times 10^{-3}$ <br> ALLOW ECF from n(ibuprofen) <br> 3 SF essential |
| (d) | (i) |   |  | 2 | $\begin{gathered} \mathrm{AO} 3.2 \\ \times 2 \end{gathered}$ | IGNORE small slip in carbon chains <br> ALLOW |
|  | (ii) | More soluble in water $\checkmark$ |  | 1 | AO3.1 | Answer must be a comparison ALLOW dissolve faster/quicker IGNORE absorbed more quickly (given in question) |
|  |  |  | Total | 18 |  |  |




| Question | Answer | Marks | AO element | Guidance |
| :---: | :---: | :---: | :---: | :---: |
|  | There is a line of reasoning presented with some structure. The information presented is relevant and supported by some evidence. <br> Level 1 (1-2 marks) <br> Calculation of the mass of $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{CH}_{2} \mathrm{Cl}$ is partly correct OR <br> Attempts to calculate mass of $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{CH}_{2} \mathrm{Cl}$ but makes little progress <br> AND <br> Planned synthesis includes formation of the intermediate $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{CH}_{2} \mathrm{CN}$ with the reagent identified <br> OR <br> Planned synthesis includes both steps with some of the reagents identified <br> OR <br> Attempts equations for both steps but these may contain errors <br> OR <br> Describes one step of the synthesis with reagent(s) and equation mostly correct <br> There is an attempt at a logical structure with a line of reasoning. The information is in the most part relevant. <br> 0 marks <br> No response or no response worthy of credit. |  |  | Synthesis: reagents and conditions <br> Stage 1: Formation of intermediate, $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{CH}_{2} \mathrm{CN}$ <br> - Reagents: $\mathrm{CN}^{-}($(ethanol) <br> - Equation: <br> $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{CH}_{2} \mathrm{Cl}+\mathrm{CN}^{-} \rightarrow \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{CH}_{2} \mathrm{CN}+\mathrm{Cl}^{-}$ <br> OR $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{CH}_{2} \mathrm{Cl}+\mathrm{NaCN} \rightarrow \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{CH}_{2} \mathrm{CN}+\mathrm{NaCl}$ <br> (OR use of KCN) <br> Stage 2: Formation of A, $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{CH}_{2} \mathrm{COOH}$ <br> - Reagents: $\mathrm{H}^{+} / \mathrm{H}_{2} \mathrm{O}$ (ALLOW 'acid hydrolysis' <br> - Equation: <br> $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{CH}_{2} \mathrm{CN}+2 \mathrm{H}_{2} \mathrm{O}+\mathrm{H}^{+} \rightarrow \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{CH}_{2} \mathrm{COOH}+$ $\mathrm{NH}_{4}{ }^{+}$ <br> OR $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{CH}_{2} \mathrm{CN}+2 \mathrm{H}_{2} \mathrm{O}+\mathrm{HCl} \rightarrow \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{CH}_{2} \mathrm{COOH}+$ $\mathrm{NH}_{4} \mathrm{Cl}$ |
|  | Total | 18 |  |  |




| Question |  | Answer | Marks | AO element | Guidance |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  | DO NOT ALLOW mark for intermediate if phenolic $\mathrm{O}^{-}$ is missing <br> curly arrow must start from, OR be traced back to, any part of $\mathrm{C}-\mathrm{H}$ bond and go inside the 'hexagon' |
|  | (ii) | $\mathrm{OH}^{-}:$base $\checkmark$ <br> $\mathrm{CO}_{2}$ : electrophile OR electron pair acceptor $\checkmark$ | 2 | $\begin{gathered} \mathrm{AO} 2.1 \\ \times 2 \end{gathered}$ | ALLOW alkali IGNORE 'nucleophile', 'donates electron pair' <br> IGNORE lone pair acceptor (No lone pair involved) |
|  | (iii) | One ester link in organic product <br> Correct structure of organic product <br> Correct equation AND balanced $\checkmark$ | 3 | AO3.1 <br> AO3.2 <br> AO2.6 |  |


| Question |  | Answer | Marks | AO element | Guidance |
| :---: | :---: | :---: | :---: | :---: | :---: |
| (b) | (i) | Dissolve in hot water/solvent <br> Minimum amount of solvent <br> Cool AND Filter AND (leave to) dry $\checkmark$ <br> All three needed | 3 | $\begin{gathered} \mathrm{AO} 3.3 \\ \times 3 \end{gathered}$ | ALLOW any solvent <br> IGNORE <br> - Initial filtering <br> - hot filtration to remove insoluble impurities <br> DO NOT ALLOW adding of a drying agent (e.g. $\mathrm{MgSO}_{4}$ ) |
|  | (ii) |  <br> Molecular formula $=\mathrm{C}_{6} \mathrm{H}_{3} \mathrm{~N}_{3} \mathrm{O}_{7}$ <br> AND use of $M=229.0$ (directly linked to molecular formula) $\checkmark$ <br> Any trisubstituted $-\mathrm{NO}_{2}$ substituted phenol that is consistent with $M=229.0 \checkmark$ <br> Evidence for substitution <br> 2,4,6 OR 3,4,5 substituted phenol AND 4 peaks/ $C$ environments from ${ }^{13} \mathrm{C}$ NMR $\checkmark$ <br> 2,4,6 substituted phenol <br> AND directing effects of $-\mathrm{OH} \checkmark$ | 6 | AO 1.2 $\times 2$ <br> $\times 2$ <br> AO3.1 <br> AO3.2 <br> AO3.1 <br> $\times 2$ | ALLOW alternative approach for empirical formula and evidence that 229 is equal to $\mathrm{C}_{6} \mathrm{H}_{3} \mathrm{~N}_{3} \mathrm{O}_{7}$ <br> DO NOT ALLOW ECF from the empirical formula with the wrong molar ratio <br> 2,4,6 <br> $3,4,5$ <br> 2,4,6 |
|  |  | Total | 20 |  |  |



| Question | Answer | Marks | AO element | Guidance |
| :---: | :---: | :---: | :---: | :---: |
|  | There is an attempt at a logical structure with a line of reasoning. The information is in the most part relevant. <br> 0 marks <br> No response or no response worthy of credit. |  |  |  |
|  | Total | 6 |  |  |

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