GCE 2004
June Series

ASSESSMENT and QUALIFICATIONS ALLIANCE

Mark Scheme

Chemistry
(Subject Code CHM3/W)

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CHM3/W Introduction to Organic Chemistry

SECTION A

Question 1

(a) (i) $C_6H_{12}O_6 \longrightarrow 2C_2H_5OH + 2CO_2$ 1
(Or CH_3CH_2OH)
(Ignore state symbols in the equation)

(ii) Fermentation 1

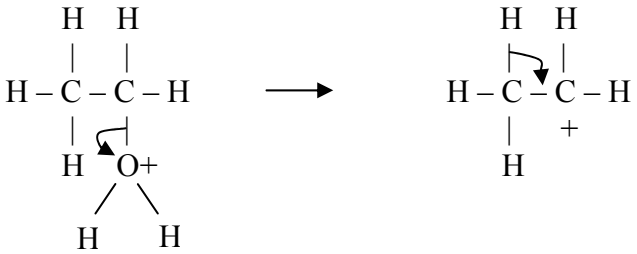
(b) (i) $C_2H_5OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O$ 1
(Or C_2H_6O or CH_3CH_2OH)

(ii) CO or carbon monoxide or C or carbon ONLY 1

(iii) $2CO + 2NO \longrightarrow 2CO_2 + N_2$ 1
OR $2NO \longrightarrow N_2 + O_2$
OR $2NO + C \longrightarrow N_2 + CO_2$
OR $C_8H_{18} + 25NO \longrightarrow 8CO_2\ 12½N_2 + 9H_2O$
(In equation 2, allow additional O_2 on both sides of the equation)

(c) Elimination 1
(Penalise additional words such as "electrophilic")

M1 structure of protonated alcohol *(allow $CH_3CH_2\overset{+}{O}H_2$)* 1



M2 arrow to show breakage of C – O bond on protonated alcohol 1

M3 structure of carbocation *(allow $CH_3\overset{+}{C}H_2$)* 1

M4 arrow from <u>correct</u> C – H bond on carbocation 1

(penalise 'sticks' once only for <u>structures</u> M1 and M3)
(synchronous mechanism using correct structure required for M1, loses M3)

(d) Silver OR silver-based 1
(NOT silver oxide)

$H_2C{=}CH_2 + \frac{1}{2}O_2 \longrightarrow H_2C\overset{O}{\diagup\diagdown}CH_2$ M1 balanced equation with O_2 1

M2 correct structure for epoxyethane 1

(Allow $CH_2{=}CH_2$ or C_2H_4 in the equation)
(Credit the structure of epoxyethane independently)
(Credit M1 provided O_2 has been used and the atoms balance, but the structure is poor e.g. C_2H_4O or CH_2OCH_2 but NOT CH_3CHO)

Total 13

Question 2

(a) (i) Electrophilic addition 1
(Both words required)

(ii) M1 the reaction to form 1-bromopropane goes *via* the primary carbocation OR 1^o carbocation 1

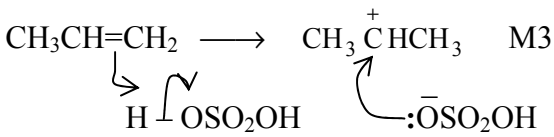
OR *via* $CH_3CH_2\overset{+}{C}H_2$
M2 primary carbocations are less stable than secondary carbocations. 1

(Credit converse arguments for M1 and M2 i.e. the reaction to form 2-bromopropane goes via the secondary carbocation , M1, and secondary carbocations are more stable than primary carbocations, M2)
(Accept the use of "carbonium ions" as an alternative to carbocation)

(b) M1 NaOH OR KOH OR correct name 1
M2 aqueous or solution in water *(ignore heat, reflux etc.)* 1
(Penalise M1 for hydroxide ion alone, but mark on and credit M2)
(Credit M2 ONLY for H_2O as reagent and heat / warm / T=50 to 100^oC)
(NaOH(aq) scores M1 and M2 provided it is not contradicted)
(Penalise M2 if NaOH(aq) followed by concentrated or ethanol)
(Penalise M1 and M2 if followed by acid)

(c) Ethanolic OR alcoholic OR CH_3CH_2OH / CH_3OH solvent OR aqueous ethanol/alcohol 1
OR higher temperature *(must be comparative)*
(Ignore heat or heat under reflux)
(Credit part (c) independently from part (b))
(Penalise "ethanoic")

(d) (i) Secondary OR 2^o 1

(ii) 

M3 structure of carbocation

M1 arrow from double bond to H of H – O bond
M2 arrow from bond to oxygen atom to show H – O bond breakage
M4 arrow from lone pair of electrons to carbon atom of carbocation

(Penalise M1 if arrow goes to H_2SO_4 or to formal positive charge on H, but ignore partial charges on sulphuric acid unless wrong)
(Credit M2 for H^+ ion)
(For M4, accept negative charge anywhere on the ion)

(iii) Catalyst ONLY 1
(Ignore homogeneous, heterogeneous)

Total 12

Question 3

(a) (i) Potassium (OR sodium) dichromate(VI) OR correct formula OR potassium manganate(VII) — 1

(Oxidation state not needed, but must be correct if included)
(Penalise errors in the formula or oxidation state, but mark conditions)

Acidified OR H_2SO_4 / HCl *(NOT with $KMnO_4$)* / H_3PO_4 / HNO_3 — 1

(Ignore heat or reflux)
(Credit "acidified" as part of reagent)

Oxidation or redox — 1

(ii) $NaBH_4$ OR $LiAlH_4$ OR H_2/Ni — 1

$CH_3COCH_3 + 2[H] \longrightarrow CH_3CH(OH)CH_3$ — 1

(Credit H_2 in the equation if H_2 has been chosen as reagent)

(b) (i)

```
CH3CH2C = O
        |
        H
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— 1

(Structure must show aldehyde structure)
(Credit C_2H_5 as alternative to CH_3CH_2)

(ii)

M1	Tollens' reagent OR ammoniacal silver nitrate OR $AgNO_3 + NH_3$	OR Fehling's solution	OR acidified potassium dichromate	1
M2	stays colourless	stays blue	stays orange	1

(Provided reagent is correct, credit "no reaction", "no change", "nothing", "no observation" for M2)

M3	silver mirror / deposit OR black / grey precipitate	red / brown / orange precipitate / solid	goes green	1

(Credit other correct reagents and observation)
(For M1, penalise $AgNO_3$ alone, penalise $Ag(NH_3)_2^+$, penalise "potassium dichromate", etc., but, in each case, mark on and credit correct M2 and M3)
(If totally wrong reagent or no reagent, CE = no marks for M1,M2 or M3)

Total 9

Question 4

(a) (i) (Free) radical substitution 1
(Both words needed)

(ii) M1 initiation ONLY 1
M2 ultra-violet light OR sunlight OR $1000^{o}C \geq T \geq 450^{o}C$ 1
(Ignore reference to temperature if included with uv light)
(Penalise "high temperature" for M2)

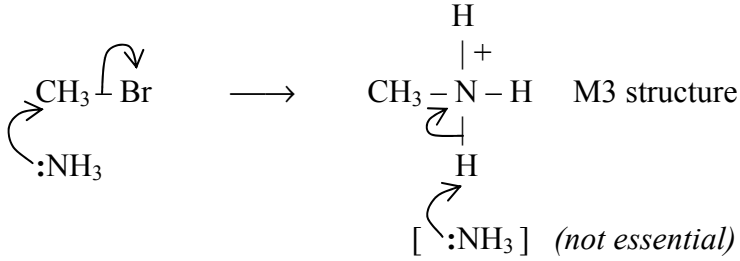
(iii) $2CH_3^{\bullet} \longrightarrow C_2H_6$ 1
(OR CH_3CH_3 as alternative to C_2H_6)

(iv) $CH_3Br + Br_2 \longrightarrow CH_2Br_2 + HBr$ 1

(b) (i) Electron pair donor 1
OR species with an electron pair able to form a covalent bond.

(ii) Methylamine 1
(Credit "aminomethane")

(iii)



M3 structure 1
(not essential)

M1 arrow to show breakage of C – Br bond 1
M2 arrow from lone pair on N of NH_3 to form bond with C 1

M4 arrow from bond of N – H to N atom of $CH_3\overset{+}{N}H_3$ 1

(Ignore partial charges on haloalkane but penalise if incorrect)

(Accept $CH_3\overset{+}{N}H_3$ for M3)
(Full credit for carbocation mechanism; M1 for C – Br bond breakage and M2 for lone pair attack on carbocation)
(Second mole of ammonia not essential to mechanism for full credit)

Total 11

SECTION B

Question 5

(a) M1 separation depends on boiling point QoL 1

M2 <u>boiling point</u> depends on size of molecules / M_r /chain length / intermolecular forces. 1

M3 <u>specified</u> temperature gradient or difference (stated or explained) on column / tower 1

M4 lower M_r / lower b.p. / more volatile / shorter chains / smaller fractions or molecules / lighter fractions or molecules at the top of the column. QoL 1

(or converse at the bottom of the column)

(Penalise M1 if bonds are broken or cracking is mentioned / discussed.)

(Penalise M4 if the candidate refers to polymers)

(b) M1 process 1 is <u>thermal</u> cracking 1

(ONLY award M1 if linked to Process 1 or clearly included in part b)

M2 any temperature (or range) in the range 400 – 900 ^{o}C OR <u>high</u> T 1

(ignore pressure)

M3 (free) radical intermediates / molecules / mechanism. 1

(Credit reference to homolysis)

(Penalise radical substitution)

(ONLY award M2 and M3 if linked to Process 1 or clearly included in part b)

$C_{13}H_{28} \longrightarrow C_6H_{14} + C_3H_6 + 2C_2H_4$

M4 correct formula for <u>both</u> alkenes 1

M5 correct balanced equation 1

(Credit M4 and M5 independently wherever the equation occurs in either part (b) or part (c) recording the marks in part b)

(c) M1 process 2 is <u>catalytic</u> cracking 1
(ONLY award M1 if linked to Process 2 or clearly included in part (c))

M2 carbocation or carbonium ion intermediates 1

(ONLY award M2 if linked to Process 2 or clearly included in part (c)
(Award one mark if <u>both</u> Process 1 and Process 2 are referred to as cracking reactions OR the two process names are the wrong way)

M3 C_5H_{12} could be $(CH_3)_2CHCH_2CH_3$ OR $(CH_3)_3CCH_3$ 1
M4 <u>correct</u> name i.e. 2-methylbutane or 2,2-dimethylpropane 1

(Numbers are not essential in the names, but if used they must be correct)

M5 C_6H_{12} could be one <u>structure</u> of cyclohexane OR methylcyclopentane etc. correct structure drawn 1

(Credit M3, M4 and M5 independently wherever they occur in part (b) or part (c) recording the marks in part (c)

(d)

Equation $n\ H_2C{=}CHCH_3 \longrightarrow -(CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}})-_n$ 1

(Equation must show n and be balanced with a clear structure for the polymer showing the single bond between each C atom in the chain and extending through the brackets)
(Credit $nCH_2{=}CHCH_3$ OR nC_3H_6 in the equation)

Total 15

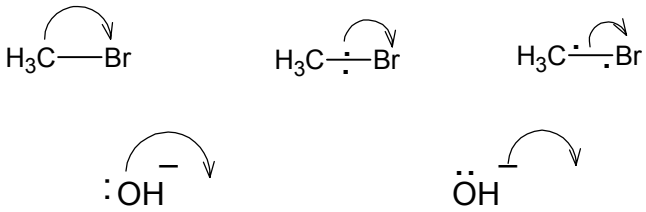
Some general principles applied to the marking of CHM3/W papers

Errors which should be penalised

Each of the following illustrates an error which should be **penalised once only** per script.
On the second occasion that the **same error** is repeated, the mark should be awarded and the tick annotated **RE** (repeat error).

Mechanisms

1. Curly arrows should originate either from a lone pair of electrons or from a bond. Each of the following representations should be **penalised once only** per script.



2. The absence of a radical dot in a free radical substitution should be **penalised once only** per script.

Structures

1. Bonds should be drawn clearly between the relevant atoms. By way of illustration, each of the following representations should be **penalised once only** per script.

(accept up to the mid-point)

2. Formulae for specific compounds which should be **penalised**.

CH_3COH	for	ethanal
CH_2OCH_2 or CH_2CH_2O	for	epoxyethane
CH_3CH_2HO or $OHCH_2CH_3$	for	ethanol

(N.B. specific exceptions may be made in the context of balancing equations)

3. The use of 'sticks' in structures should be **penalised once only** per script.

Names
As a general principle, non-IUPAC names or incorrect spelling or incomplete names should be **penalised once only** per script. Some illustrations are given here. *(N.B. specific exceptions may be made at individual standardising meetings)*

but-2-ol
2-hydroxybutane all should be **butan-2-ol**
butane-2-ol
2-butanol

2-methpropan-2-ol should be **2-methylpropan-2-ol**

2-methylbutan-3-ol should be **3-methylbutan-2-ol**

3-methylpentan both should be **3-methylpentane**
3-mythylpentane

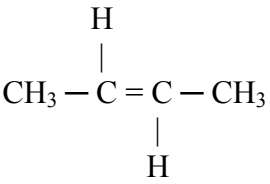
<u>Some general guidance on organic structures</u>

Each of the following **should be given credit** as alternatives to correct structures.

$CH_2 = CH_2$ for ethene

$CH_3CHOHCH_3$ for propan-2-ol

CH_2OHCH_2OH for ethane-1,2-diol

 for *trans* but-2-ene