

GCE MARKING SCHEME

CHEMISTRY AS/Advanced

SUMMER 2013

GCE CHEMISTRY - CH4

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Q.1	(a)	(i)	(2-)Methylpropan-2-ol	[1]
		(ii)	30.1 / 30	[1]
		(iii)	(Concentrated) sulfuric acid / phosphoric acid / aluminium oxide / pumice	[1]
		(iv)	CH ₃ H CH ₃ H (with or without p)	
			(with or without n)	[1]
		(v)	H H OH H H-C-C-C'-C-H H H H H H (1) for structure, (1) for asterisk	[2]
			(,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	
		(vi)	I acidified potassium dichromate / H ⁺ , Cr ₂ O ₇ ²⁻ (aq)	[1]
			II ethanal has a C = O bond at 1650-1750 cm ⁻¹ (metaldehyde does not have this bond) (1)	
			metaldehyde has a C – O bond at 1000-1300 cm ⁻¹ (ethanal does not have this bond) (1)	[2]
	(b)	(i) R e	eagent 2,4-dinitrophenylhydrazine / 2,4-DNP OR iodine / NaOH or KI / NaOCI (1))
		O	bservation yellow / orange / red precipitate OR yellow precipitate (1)	[2]
		(ii) Re	eagent ethanol / sulfuric acid OR NaHCO ₃ OR Ag ⁺ /NH ₃ / Tollens'	(1)
		O	bservation sweet smelling liquid OR effervescence OR silver mirror (1)	[2]
			Total	[13]

Q.2	(a)	React with iron(III) chloride solution Purple solution with phenol, no reaction with methyl propenoate			
		OR			
		W	t with aqueous bromine / bromine water //hite precipitate with phenol (and bromine decolourised), bromine decolourised ith methyl propenoate		
		(1) for reagent and (1) for observation with compound	[2]	
	(b)	(i)	It absorbs all colours except yellow / absorbs the blue end of the spectrum and reflects yellow – do not accept 'emits'	[1]	
		(ii)	Tin / iron and concentrated hydrochloric acid	[1]	
	(c)	(i)	Moles of 2,4-dinitrophenol = $7.36/184 = 0.040$ (1)		
			Moles of 2,4-dinitrophenyl ethanoate = $7.91/226 = 0.035$ (1)		
			Percentage yield = $0.035 \times 100 / 0.040 = 87.5 / 88 \%$ (1)	[3]	
		(ii)	R _f value is given by distance travelled by the 2,4-dinitrophenol distance travelled by the solvent front (1)		
			=	[2]	
	(d)	(i)	Nickel / platinum	[1]	
		<i>(</i> **)	TI 011		

(ii) The –OH groups are able to hydrogen bond with water (1) but these are a very small part of the 'urushiol' molecule (1) [2]

Total [12]

Q.3 (a) (i) 48.5 / 49 % [1]

(ii) Find a use for the calcium sulfate [1]

(b) Total volume of aqueous sodium hydroxide needed = $\underline{26.40 \times 250} = 264.0 \text{ cm}^3$ (1) 25.00

from the graph this is equivalent to 0.011 mole of the acid (1)

$$\therefore M_r \text{ of the acid} = \underbrace{\text{mass}}_{\text{no. of moles}} = \underbrace{2.31}_{0.011} = 210 \quad (1)$$

$$C_6H_8O_7$$
. $n H_2O = 210$
 \uparrow
 $192 \therefore n = 18$ (1)

since M_r of water is 18 n = 1 (1)

(c) The two 'ends' of the double bond have different groups bonded to the carbon atoms (of the double bond) / they have different structural formulae, so cannot be stereo / geometric isomers [1]

(d) eg sodium ethanoate / ethanoic acid (1) methane (1) [2]

(e)
$$C_5H_6O_5 \rightarrow CH_3COCH_3 + 2CO_2$$
 [1]

(f)

(g) (Fractional) distillation / (preparative) gas chromatography / HPLC [1]

(h) (i) eg An optically active isomer that will rotate the plane of polarised light
/ an isomer with a chiral centre [1]

(ii) An equimolar mixture of both enantiomers (that has no apparent effect on the plane of polarised light) [1]

Total [15]

[1]

Q.4 (a) Benzene is a compound whose molecules contain six carbon atoms bonded in a (hexagonal) ring (1)

All the carbon to carbon bond lengths are equal / intermediate (1)

Each carbon atom is bonded to two other carbon atoms and a hydrogen atom (1) by σ -bonds (1)

All the $C - \hat{C} - C$ angles are the same / 120° (1)

The remaining p electron of each carbon atom / overlap of p orbitals forms a delocalised cloud of electrons / π -system (1) above and below the plane (1)

Credit can be gained from labelled diagram

[Candidates can gain a maximum of (4) for this part]

This delocalisation increases the **stability** (1) of the molecule and this stability is maintained by benzene undergoing substitution reactions in preference to addition reactions (that would destroy the delocalised system)

The π -cloud is **electron rich** and will be attracted to electron deficient electrophiles (1) [Candidates can gain (2) for this part]

QWC Selection of a form and style of writing appropriate to purpose and to complexity of subject matter (1)

Legibility of text; accuracy of spelling, punctuation and grammar; clarity of meaning. (1)

QWC [2]

[6]

catalyst eg AlCl₃ (anhydrous) (1)

[2]

(c) (There are two environments for the protons), the 3 aromatic protons at ~6.8 δ (i) and the 9 methyl / aliphatic protons at \sim 2.3 δ (1) (1)

These give a peak area of 3:9, ie.1:3

These environments are separate / discrete (1) therefore no splitting pattern

[3]

(ii) Dissolve in the minimum volume (1)

Of hot water (1)

(Filter hot) (1)

Cool (1)

Filter (1)

Dry (1)

(up to 4 max but candidates must give the first two points in order to gain full credit)

[4]

(iii)

$$-$$
 O $CH_2 - CH_2 - O - C$ CH_3 CH_3

[1]

(iv) Reagent **S** is alkaline potassium manganate(VII) (1)

> Reagent T is eg hydrochloric acid (1)

[2]

Total [20]

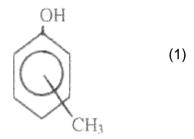
Q.5 (a) (i) The **nitrogen atom** has a **lone pair** of electrons making it an electron pair donor / proton acceptor

[1]

(ii) Compound **L** must contain the grouping -N-C (1

The nitrogen atom must be bonded directly to the ring as a (primary) aromatic amine is formed on hydrolysis (1)

As the hydrolysis compound is a phenol (and has an OH group directly bonded to the ring) a methyl group must also be bonded directly to the ring, as the molecular formula is C_7H_8O / the compound has the structure



The compound is likely to be an amide, as these are hydrolysed by bases to amines (1)

A suggested formula is

$$H$$
 CH_3
(1)

which is $C_9H_{11}NO$, an isomer of cathinone / has M_r of 149(1)

[6]

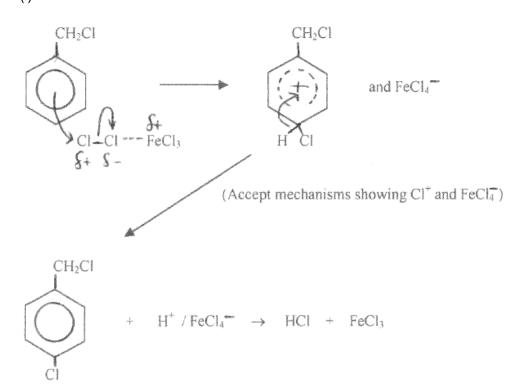
QWC Information organised clearly and coherently, using specialist vocabulary where appropriate QWC [1]

(b) (i)

(ii)

OR

(c) (i)



Correct catalyst (1)

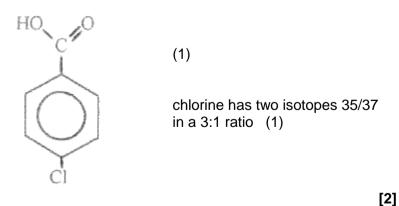
Correct curly arrows and polarisation / formation of Cl⁺ (1)

Wheland intermediate (1) Production of HCl and regeneration of FeCl₃ (1) [4]

(ii) Volume of sodium hydroxide solution needed (1)
How long to reflux (1) [2]

(iii) The aromatic C – CI bond is stronger than the aliphatic C – CI bond (1) This is because a p-electron(s) of the chlorine atom in the aromatic compound becomes part of / incorporated into the delocalised π system of the ring (1) [2]

(iv)



Total [20]