33. Carboxylic acids and derivatives

33.1 Carboxylic acids

Paper 4

Marking Scheme

Q1.

(a)	due to the electron-withdrawing effect/electronegative / –I effect of chlorine **AND** stabilising the anion / carboxylate ion **OR** weakening the O-H bond	**1**

Q2.

(b)	oxygen [1] acidified $KMnO_4$ [1]	**2**
(c)	C=O are electron withdrawing / electronegative [1] weakens O–H bond **OR** stabilises anion [1]	**2**

Q3.

(a)	**M1** benzoic acid > phenol > phenylmethanol **M2** / **M3** *Any two of:* • in benzoic acid negative inductive effect of C=O **AND** O-H bond is weakened **OR** due to delocalisation of minus charge by C=O / 2O carboxylate ion is stabilised • in phenol lone pair on oxygen is delocalised into the ring **AND** O-H bond is weakened • in phenyl methanol positive inductive effect of CH_2 group **AND** O-H bond is strengthened	**3**
(b)	<table><tr><th></th><th>benzoic acid</th><th>phenylmethanol</th><th>phenol</th></tr><tr><td>Na(s)</td><td>✓</td><td>✓</td><td>✓</td></tr><tr><td>NaOH(aq)</td><td>✓</td><td>×</td><td>✓</td></tr><tr><td>Na_2CO_3(aq)</td><td>✓</td><td>×</td><td>×</td></tr></table> Three correct for one mark, six correct for two marks, nine correct for three marks	**3**

Q4.

(a)	**M1** chloroethanoic acid > ethanoic acid > phenol > ethanol **M2** correct link of acidity once can be implied from M1 weakens O—H / carboxylate anion stabilised **M3** / **M4** explanation linked to structure • ($ClCH_2CO_2H$ > ethanoic acid) due to electronegative / electron withdrawing / negative inductive effect of Cl • (ethanoic acid > phenol) due to electronegative / electron withdrawing / negative inductive effect of COOH / C=O • (phenol > ethanol) due to lone pair of oxygen overlapping / delocalised into the ring • (ethanol weakest) alkyl group is electron donating / positive inductive effect two for one mark, four for two marks	**4**

(b)	• oxidation • (solution) decolourises **OR** purple → colourless / pale pink **OR** bubbles • $HOOCCOOH + [O] \rightarrow 2CO_2 + H_2O$ **OR** $5HOOCCOOH + 2MnO_4^- + 6H^+ \rightarrow 10CO_2 + 8H_2O + 2Mn^{2+}$ two for one mark, three for two marks	**2**

Q5.

(a)	**C** > **A** > **B** [1] chlorine and C=O are electronegative / withdraw charge **and** this causes greatest weakening of O–H bond or greatest stabilisation of the anion [1] 2nd oxygen / C=O is electronegative / withdraws charge **and** this weakens O–H bond or stabilises anion [1]	**3**

Q6.

(b)	M1: trend phenylethanoic acid > phenol > ethanol [1] M2: *why phenylethanoic acid is the strongest* • negative inductive electron withdrawing effect of C=O which weakens O-H bond / stabilises anion [1] M3: *why phenol is stronger than ethanol / weaker than phenylethanoic acid* • oxygen lone pair is delocalised into the ring system which weakens O-H bond / stabilises anion [1] M4: *why ethanol is the weakest* • electron donating alkyl / ethyl group which strengthens O-H bond / destabilises anion [1]	**4**

Q7.

(a)	**M1** 2-chloropropanoic acid > 3-chloropropanoic acid > propanoic acid [1] **M2** $CH_3CHClCO_2H$ / $ClCH_2CH_2CO_2H$ (are more acidic) as they contain an electronegative Cl atom so weaken O-H bond / stabilise carboxylate anion [1] **M3** $CH_3CHClCO_2H$ (is more acidic than $ClCH_2CH_2CO_2H$) as the Cl atom is closer to CO_2H so weaken O-H bond more / stabilise carboxylate anion more [1]	**3**

Q8.

(a)	ethanamide – ethanoic acid – trichloroethanoic acid [1] • ethanamide is neutral / not a proton donor • chlorine is electronegative / electron withdrawing [1] • O–H bond weakened / anion stabilised • correct statement linking acid strength to H^+ donation [1]	**3**
(b)(i)	methanoic acid [1]	**1**
(b)(ii)	methanoic and ethanedioic acids [1]	**1**

Q9.

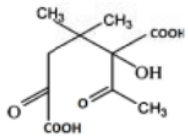
(e)(i)	acidified manganate(VII) or dichromate(VI)	**1**
(e)(ii)	carbon dioxide and water	**1**

(f)	**M1:** most acidic: hexanoic acid > phenol > hexan-1-ol :least acidic • the other O atom in CO_2H group of hexanoic acid **either** – withdraws charge from OH group **or** is electronegative **and** weakens O–H bond **or** – stabilises resultant anion/negative ion / $–CO_2^-$ group/carboxylate ion • benzene / aromatic / C_6H_5 ring in phenol <u>delocalises</u> **either** – lone pair on O atom **and** weakens O–H bond **or** – lone pair on resultant anion/negative ion / phenoxide ion this stabilises resultant anion negative ion / $–CO_2^-$ group/carboxylate ion • the alkyl group in hexan-1-ol donates electrons this strengthens O–H bond Award 1 mark for each bullet point identified.	**3**

Q10.

(b)(i)	propanoic acid, phenol, propan-1-ol	**1**
(b)(ii)	∝ propan-1-ol: O-H bond strengthened by positive inductive effect of alkyl group **OR** propoxide ion is destabilised by positive inductive effect of alkyl group ∞ phenol: O-H bond weakened by negative inductive effect of ring **OR** phenoxide ion is stabilised by delocalisation of oxygen lone pair into ring ∞ propanoic acid: O-H bond weakened by negative inductive effect of C=O **OR** propanoate ion is stabilised by delocalisation of minus charge by C=O 1 mark for a correct explanation, max 2 marks	**2**
(c)	Tollens' reagent **or** Fehling's reagent	**1**
	methanoic acid gives a silver mirror/solid with Tollen's reagent **OR** red / orange ppt / solid with Fehlings' reagent	**1**

Q11.

(c)(i)		**1**
(c)(ii)	CO_2	**1**
	oxidation / oxidative cleavage	**1**
(c)(iii)	CH_3COCO_2H	**1**