2.11 Chemistry: Aromatic Chemistry, Carbonyls and Amines: 1-hour Pack

AQA 7405 · Calculator allowed · about 60 minutes

Total Marks

Name: _____ Date: ____ / ____ / _____

Answer ALL questions. Show all your working.

1 Poly(ethylene terephthalate), PET, is a polyester formed from benzene-1,4-dicarboxylic acid (terephthalic acid) and ethane-1,2-diol. Nylon-6,6 is a polyamide formed from hexanedioic acid and 1,6-diaminohexane.

(a) Identify the type of polymerisation that forms PET, and state the small molecule released during its formation. **(3)**

(b) Write an equation to show the formation of one amide (peptide-type) linkage between one molecule of hexanedioic acid and one molecule of 1,6-diaminohexane, identifying the small molecule by-product. **(3)**

(c) Evaluate the environmental impact of using condensation polymers such as PET and nylon in packaging and clothing, compared with using naturally occurring materials, and discuss strategies that could be used to reduce this impact. **(6)**

(Total for Question 1 is 12 marks)

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2 A four-step synthetic route converts benzene into 1-phenylethylamine, $C_6H_5CH(NH_2)CH_3$, as follows. Step 1: benzene -> phenylethanone ($C_6H_5COCH_3$), using ethanoyl chloride and a catalyst. Step 2: phenylethanone -> 1-phenylethanol, $C_6H_5CH(OH)CH_3$, using $NaBH_4$. Step 3: 1-phenylethanol -> (1-chloroethyl)benzene, $C_6H_5CHClCH_3$, using a suitable chlorinating reagent. Step 4: (1-chloroethyl)benzene -> 1-phenylethylamine, using excess ethanolic ammonia.

(a) Name the catalyst used in Step 1, state the type of mechanism, and describe the catalyst's role in generating the electrophile. **(3)**

(b) State the type of reaction occurring in Step 2, and identify the nucleophile involved in its mechanism. **(2)**

(c) Name a suitable reagent for Step 3, and state one observation that might be made during this reaction. **(2)**

(d) Explain why, in Step 4, the ammonia used must be (i) in excess and (ii) dissolved in ethanol rather than water. **(2)**

(e) Calculate the atom economy of Step 4, given Mr[(1-chloroethyl)benzene] = 140.5, Mr(NH_3) = 17.0, Mr(1-phenylethylamine) = 121, and Mr(HCl) = 36.5, if only 1-phenylethylamine is considered the desired product. **(3)**

(Total for Question 2 is 12 marks)

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3 Benzene reacts with a mixture of concentrated nitric acid and concentrated sulfuric acid to form nitrobenzene.

(a) State the conditions used for this nitration reaction. **(2)**

(b) Write an equation to show how the electrophile is generated from nitric acid in the presence of sulfuric acid. **(2)**

(c) Describe the mechanism for the nitration of benzene by the electrophile NO_2^+, including the structure of the intermediate formed. **(4)**

(d) Nitration of methylbenzene occurs faster than nitration of benzene, and gives mainly a mixture of 2-nitromethylbenzene and 4-nitromethylbenzene (with very little of the 3-isomer). Explain, in terms of the effect of the methyl group on the ring, (i) why methylbenzene reacts faster than benzene and (ii) why substitution occurs mainly at the 2- and 4-positions. **(4)**

(Total for Question 3 is 12 marks)

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4 Ethanoic acid reacts with phosphorus(V) chloride, PCl_5, to form ethanoyl chloride, CH_3COCl.

(a) Write a balanced equation for this reaction and state what would be observed. **(3)**

(b) Ethanoyl chloride reacts with water far more readily (violently) than an ester such as ethyl ethanoate does. Explain, in terms of the bonding and leaving group involved, why acyl chlorides are much more reactive towards nucleophiles such as water than esters. **(3)**

(c) A 2.50 g sample of ethyl butanoate, $C_6H_{12}O_2$ (Mr = 116), is completely hydrolysed by refluxing with an excess of water in the presence of a dilute acid catalyst. Calculate the maximum mass of butanoic acid, $C_4H_8O_2$ (Mr = 88), that could be formed. **(3)**

(d) State the other organic product formed in this hydrolysis. **(1)**

(Total for Question 4 is 10 marks)

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Mark scheme · 2.11 Chemistry: Aromatic Chemistry, Carbonyls and Amines: 1-hour Pack

Question 1

(a) condensation polymerisation **B1**

(a) water, H_2O, is released (at each ester linkage formed) **B1**

(a) the polymer chain contains repeating ester linkages (-C(=O)-O-) formed between the -COOH groups of the diacid and the -OH groups of the diol **B1**

(a) Answer: Condensation polymerisation; water is released at each ester linkage formed between the diacid and the diol.

(b) $HOOC-(CH_2)_4-COOH + H_2N-(CH_2)_6-NH_2 \rightarrow HOOC-(CH_2)_4-CONH-(CH_2)_6-NH_2 + H_2O$ **M1**

(b) structure correctly shows one new amide (-CONH-) linkage formed, with one -COOH and one $-NH_2$ group remaining unreacted at the ends **A1**

(b) water, H_2O, identified as the by-product **B1**

(b) Answer: $HOOC-(CH_2)_4-COOH + H_2N-(CH_2)_6-NH_2 \rightarrow HOOC-(CH_2)_4-CONH-(CH_2)_6-NH_2 + H_2O$

(c) **L3** A well-developed, balanced evaluation is given, covering both environmental drawbacks and possible benefits/counterpoints, together with at least two distinct, relevant strategies to reduce impact, supported by chemical reasoning (e.g. reference to bond types/structure). The answer is coherent and logically structured throughout. **5-6**

(c) **L2** A reasonably clear discussion is given, covering some environmental drawbacks and at least one relevant strategy to reduce impact, with some supporting reasoning. The answer shows some structure but may lack balance or full development. **3-4**

(c) **L1** Basic, isolated relevant points are made (e.g. a simple statement that polymers do not biodegrade, or one disposal method named), with little or no supporting reasoning or structure. **1-2**

(c) **L0** No relevant content, or the response does not address the question. **0**

(c) Indicative content:

- Condensation polymers such as PET and nylon are generally not readily biodegradable, as microorganisms lack enzymes able to break the ester/amide linkages quickly, unlike many naturally occurring polymers such as cellulose or proteins, which are broken down by natural enzymes/organisms, so they persist in landfill or the environment for a very long time
- Most condensation polymers are made from non-renewable, fossil-fuel-derived monomers (crude oil feedstocks), depleting finite resources and contributing to carbon dioxide emissions during their manufacture
- However, condensation polymers such as PET are strong, lightweight and durable, which can reduce material use, food waste (via effective packaging/preservation) and transport emissions compared with heavier or less durable natural-material alternatives, so a straightforward comparison is not always fair
- Strategy: mechanical recycling - used PET/nylon items can be collected, cleaned, melted and reformed into new products, reducing the demand for virgin monomers/crude oil and reducing landfill waste
- Strategy: chemical recycling (hydrolysis) - the ester/amide linkages in used PET or nylon can be hydrolysed back into their original monomers (the diacid and diol/diamine), which can then be re-polymerised, in principle allowing indefinite reuse of the same atoms
- Strategy: development and use of biodegradable polyesters (e.g. those containing more easily hydrolysed linkages, or blends with natural biodegradable polymers) as substitutes in single-use applications
- Strategy: incineration with energy recovery, as an alternative to landfill, though this releases CO_2 and requires careful control of emissions
- A balanced evaluation should weigh the durability/resource benefits of these polymers against their persistence and fossil-fuel origin, and recognise that no single disposal strategy solves the whole problem

(c) Answer: Awarded via levels of response (0-6) against the indicative content: a full-mark answer balances drawbacks (non-biodegradability, fossil-fuel origin) against benefits (durability, reduced waste elsewhere), and gives at least two well-explained reduction strategies (e.g. mechanical recycling, chemical hydrolysis/re-polymerisation, biodegradable alternatives, energy recovery).

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Question 2

(a) aluminium chloride, $AlCl_3$ (a halogen carrier) **B1**

(a) electrophilic substitution (Friedel-Crafts acylation) **B1**

(a) $AlCl_3$ accepts a lone pair of electrons from the chlorine atom of ethanoyl chloride (CH_3COCl), polarising and breaking the C-Cl bond to generate the acylium ion, CH_3CO+, as the electrophile (and $[AlCl_4]^-$) **B1**

(a) Answer: $AlCl_3$ (halogen carrier catalyst); Friedel-Crafts acylation (electrophilic substitution); $AlCl_3$ accepts a lone pair from Cl in CH_3COCl, generating the electrophile CH_3CO+ and $[AlCl_4]^-$.

(b) reduction (nucleophilic addition) **B1**

(b) hydride ion, H- (from $NaBH_4$) **B1**

(b) Answer: Reduction, by nucleophilic addition; the nucleophile is the hydride ion, H-.

(c) phosphorus(V) chloride, PCl_5 (accept $SOCl_2$ or PCl_3) **B1**

(c) steamy white fumes (of HCl) are seen (if using PCl_5 or $SOCl_2$) **B1**

(c) Answer: PCl_5 (or $SOCl_2$); steamy white fumes of HCl are observed.

(d) (i) excess ammonia favours reaction of the haloalkane with NH_3 rather than with the primary amine product formed, minimising further substitution to secondary/tertiary amines or a quaternary ammonium salt **B1**

(d) (ii) an aqueous solvent would allow water (a nucleophile) to compete with ammonia in a hydrolysis side reaction with the haloalkane (substitution by OH^-, giving the alcohol back); ethanol dissolves both the organic haloalkane and ammonia without this competing reaction **B1**

(d) Answer: (i) Excess NH_3 minimises further nucleophilic substitution to secondary/tertiary amines or a quaternary salt. (ii) Ethanol (rather than water) avoids competing hydrolysis of the haloalkane by water and dissolves both reactants.

(e) sum of Mr of reactants = 140.5 + 17.0 = 157.5 **M1**

(e) atom economy = (Mr desired product / sum Mr reactants) x 100 = (121 / 157.5) x 100 **M1**

(e) = 76.8% (awrt 76.8-76.9%) **A1**

(e) Answer: Atom economy = 76.8%

Question 3

(a) concentrated nitric acid and concentrated sulfuric acid (as a catalyst) used together **B1**

(a) temperature kept at or below about 50°C (reflux); higher temperatures/prolonged heating cause further substitution to give dinitrobenzene products oe **B1**

(a) Answer: Conc. HNO_3 + conc. H_2SO_4 (catalyst), maintained at around 50°C.

(b) $HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$ (state symbols not required) **M1**

(b) correctly balanced with NO_2^+ identified as the electrophile (nitronium ion) **A1**

(b) Answer: $HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$

(c) NO_2^+ is attracted to/attacks the delocalised π electron ring (electrophilic attack) **B1**

(c) a pair of electrons from the ring forms a new C-N bond to the nitrogen of NO_2^+ **B1**

(c) this generates a positively charged intermediate (arenium/Wheland ion) in which the delocalised ring system now extends over only five carbon atoms (the ring is no longer fully aromatic; positive charge delocalised over the remaining five carbons) **B1**

(c) a proton, H^+, is lost from the carbon bearing both the H and the NO_2 group, which restores the full delocalised aromatic ring, regenerating a catalytic H^+ that reforms H_2SO_4 with HSO_4^- **B1**

(c) Answer: NO_2^+ attacks the ring; a C-N bond forms, breaking full delocalisation and giving a positively charged arenium intermediate (delocalised over 5 C); loss of H^+ restores the aromatic ring, regenerating the H_2SO_4 catalyst.

(d) the methyl group is electron-donating (positive inductive/hyperconjugative effect), which increases the electron density of the delocalised ring π system **B1**

(d) this makes the ring more strongly attract (more strongly polarise) the electrophile NO_2^+, so the reaction is faster than with benzene **B1**

(d) the increase in electron density is greatest at the carbon atoms ortho (2-) and para (4-) to the methyl group oe **B1**

(d) so the arenium (Wheland) intermediates formed by attack at the 2- and 4- positions are more stabilised/lower in energy than attack at the 3-position, so 2- and 4- substitution predominate **B1**

(d) Answer: The methyl group donates electron density into the ring (activating it, so reaction is faster than benzene) and increases electron density most at the 2- and 4- positions, favouring attack (and forming more stable intermediates) there rather than at the 3-position.

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Question 4

(a) $CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$ **M1**

(a) correctly balanced (all species; state symbols not required) **A1**

(a) steamy white fumes (of HCl gas) are observed **B1**

(a) Answer: $CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$; steamy white fumes of HCl are seen.

(b) in both compounds, water (a nucleophile) attacks the delta-positive carbonyl carbon (nucleophilic addition-elimination) **B1**

(b) chlorine is more electronegative than oxygen, so it withdraws electron density more strongly from the carbonyl carbon in the acyl chloride, making that carbon more delta-positive/more strongly attacked by the nucleophile than in an ester **B1**

(b) chloride ion, Cl^-, is also a much better/more stable leaving group than the alkoxide/RO- group that would have to leave in the corresponding step for an ester, so elimination occurs much more readily for the acyl chloride **B1**

(b) Answer: The more electronegative Cl makes the carbonyl carbon of an acyl chloride more strongly delta+ than in an ester, and Cl^- is a far better leaving group than RO-, so acyl chlorides react with nucleophiles like water much faster than esters do.

(c) moles of ethyl butanoate = 2.50 / 116 = 0.02155 mol **M1**

(c) since the ratio of ester : acid is 1:1, mass of butanoic acid = 0.02155 x 88 **M1**

(c) = 1.90 g (3 sf) **A1**

(c) Answer: Maximum mass of butanoic acid = 1.90 g

(d) ethanol **B1**

(d) Answer: Ethanol

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