2.8 Analytical Techniques: 30-minute Pack

AQA 7405 · Calculator allowed · about 30 minutes

Total Marks

Name: _____ Date: ____ / ____ / _____

Answer ALL questions. Show all your working.

1 A student analyses a sample of 2-chlorobutane, C_4H_9Cl, using a mass spectrometer.

(a) State what is meant by the term 'molecular ion' in mass spectrometry. **(1)**

(b) The mass spectrum of 2-chlorobutane shows the molecular ion split into two peaks, at m/z = 92 and m/z = 94, with relative peak heights in the ratio 3:1. Explain the origin of these two peaks and explain why they occur in this ratio. **(3)**

(c) Calculate the relative molecular mass, Mr, of 2-chlorobutane. Use Ar: C = 12.0, H = 1.0, Cl = 35.5. Show your working. **(2)**

(d) A fragment ion peak is seen at m/z = 57. This fragment forms by loss of a chlorine radical, Cl., from the molecular ion at m/z = 92. Deduce the molecular formula of this fragment and suggest a structure for it. **(3)**

(Total for Question 1 is 9 marks)

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2 1,2-dibromoethane, $BrCH_2CH_2Br$, is analysed by mass spectrometry. Bromine has two naturally occurring isotopes, 79Br (abundance approximately 50.7%) and 81Br (abundance approximately 49.3%). Use Ar values C = 12.0, H = 1.0, Br = 79.9 unless told otherwise, and use 79Br = 79 and 81Br = 81 exactly for nominal mass (m/z) calculations.

(a) Calculate the Mr of 1,2-dibromoethane using the Ar values given, to 1 decimal place. **(2)**

(b) The molecular ion region of the mass spectrum shows three peaks. Using the two bromine isotopes and their abundances, deduce the three nominal m/z values in this region and calculate the ratio of their peak heights, giving the ratio to 2 significant figures. **(4)**

(c) A fragment ion peak appears at m/z = 107. This fragment forms by loss of a bromine atom (as a radical, Br dot) from the lowest-mass molecular ion peak at m/z = 186. Deduce the molecular formula of this fragment ion and suggest a plausible structure for it. **(3)**

(Total for Question 2 is 9 marks)

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3 An unknown organic compound, Z, has molecular formula C_4H_8O (Mr = 72). Data obtained: Mass spectrum: molecular ion peak at m/z = 72; fragment peaks at m/z = 57 and m/z = 29. Infrared spectrum: strong absorption at 1715 cm-1; no absorption between 2500 and 3550 cm-1. 1H NMR spectrum: doublet at 1.15 ppm (6H); multiplet at 2.55 ppm (1H); doublet at 9.60 ppm (1H). Using all the data provided, deduce the structural formula of Z. Your answer should use evidence from the mass spectrum, the infrared spectrum and the 1H NMR spectrum to justify the functional group present, the carbon skeleton, and the final structure.

(Total for Question 3 is 6 marks)

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Mark scheme · 2.8 Analytical Techniques: 30-minute Pack

Question 1

(a) the ion (peak) formed when a molecule loses an electron without fragmenting, giving a peak that represents the relative molecular mass (Mr) of the compound oe **B1**

(a) Answer: The ion formed when a molecule loses one electron without breaking apart; its m/z value gives the Mr of the compound.

(b) chlorine exists naturally as two isotopes, 35Cl and 37Cl oe **B1**

(b) the peak at m/z = 92 is the molecular ion containing 35Cl and the peak at m/z = 94 is the molecular ion containing 37Cl **B1**

(b) the natural abundance of 35Cl to 37Cl is approximately 3:1 (accept approx. 75%:25%), so the peak heights reflect this abundance ratio **B1**

(b) Answer: Two peaks arise from the two chlorine isotopes (35Cl, 37Cl); their natural abundance ratio is about 3:1, matching the peak height ratio.

(c) correct substitution: 4(12.0) + 9(1.0) + 35.5 **M1**

(c) 92.5 (cao) **A1**

(c) Answer: Mr = 92.5

(d) fragment formula is C_4H_9+ **M1**

(d) mass check: 4(12) + 9(1) = 57, consistent with m/z = 57 (cao) **A1**

(d) suggests a valid carbocation structure, e.g. CH3CH2CH2CH2+ or CH_3CH_2+$CHCH_3$ (any structure with formula C_4H_9+ accepted) **B1**

(d) Answer: C_4H_9+, e.g. the butyl cation CH3CH2CH2CH2+ (or the isomeric sec-butyl cation).

Question 2

(a) correct substitution: 2(12.0) + 4(1.0) + 2(79.9) **M1**

(a) 187.8 (cao) **A1**

(a) Answer: Mr = 187.8

(b) identify the three nominal m/z values as 186 (both 79Br), 188 (one 79Br, one 81Br) and 190 (both 81Br) **M1**

(b) probability of both 79Br = 0.507^2 = 0.257 and both 81Br = 0.493^2 = 0.243 **M1**

(b) probability of one of each = 2 x 0.507 x 0.493 = 0.500 **M1**

(b) ratio m/z 186 : 188 : 190 = approximately 1.1 : 2.1 : 1.0 (accept any value awrt this, or the simplified ratio 1:2:1) cao **A1**

(b) Answer: m/z 186 : 188 : 190 is approximately 1.1 : 2.1 : 1.0 (approximately 1:2:1)

(c) fragment formula is C_2H_4Br+ (i.e. CH_2CH_2Br+) **M1**

(c) mass check: 2(12) + 4(1) + 79 = 107, consistent with m/z = 107 (cao) **A1**

(c) suggests a valid structure, e.g. the bromoethyl cation +CH_2CH_2Br (any structure with formula C_2H_4Br+ accepted) **B1**

(c) Answer: C_2H_4Br+, e.g. the bromoethyl cation +CH_2CH_2Br

Question 3

Level 3 A full, logically structured answer that correctly identifies Z as 2-methylpropanal, $(CH_3)_2CHCHO$, using evidence from all three techniques (MS, IR and NMR) to justify both the functional group and the carbon skeleton, with clear reasoning linking specific data (m/z values, wavenumber, chemical shifts, integration, splitting) to structural features. **5-6**

Level 2 Correctly identifies most structural features (e.g. the aldehyde group and/or the branched carbon skeleton) using evidence from at least two techniques, with generally sound reasoning, but the final structure may be incomplete, not fully justified, or contain minor errors or omissions in linking evidence to structure. **3-4**

Level 1 Some relevant points made, e.g. correctly identifies the functional group present or interprets isolated pieces of data, but with little or no attempt to combine evidence from different techniques; the final structure is incorrect or absent. **1-2**

Level 0 No relevant content. **0**

Indicative content:

- IR: absorption at 1715 cm-1 indicates a C=O bond; absence of a broad O-H absorption (2500-3550 cm-1) rules out a carboxylic acid, so an aldehyde or ketone is indicated.
- MS: the fragment at m/z = 29 corresponds to CHO+ (formyl/acylium cation), which is characteristic of an aldehyde, confirming the C=O is terminal (an aldehyde) rather than a ketone.
- MS: the molecular ion at m/z = 72 confirms Mr = 72, consistent with molecular formula C_4H_8O.
- MS: the fragment at m/z = 57 corresponds to loss of CH_3 (mass 15) from the molecular ion (72 - 15 = 57), i.e. loss of a methyl group.
- NMR: the doublet at 1.15 ppm, integration 6H, indicates two equivalent CH_3 groups, each adjacent to only one proton (n+1 rule, n=1 gives a doublet); the 6H integration confirms two equivalent methyl groups, consistent with an isopropyl-type $(CH_3)_2CH$- unit.
- NMR: the multiplet at 2.55 ppm (1H) is the CH proton, coupled to both methyl groups and to the aldehyde proton, consistent with a CH bonded to two CH_3 groups and to a CHO group.
- NMR: the doublet at 9.60 ppm (1H) is the aldehyde CHO proton (characteristic shift 9.5-10 ppm for aldehydes), split into a doublet by the single adjacent CH proton.
- Combining all the evidence gives the structure 2-methylpropanal (isobutyraldehyde), $(CH_3)_2CHCHO$, with a correct displayed or skeletal formula consistent with every data point given.

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