InkChemistry

ANSWER BOOK

Amines: preparation, basicity and nucleophilic reactions

Aromatic chemistry and amines · Unit C21

AQA 3.3.11.1, 3.3.11.2, 3.3.11.3 · OCR A 6.2.1 (a), 6.2.1 (b)

19 questions · 62 marks

NAVY EDITION

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SECTION A · Short, 1 to 2 marks

A1 APB-Q12

B1 the positively charged head is attracted to the negatively charged surface of wet fabric fibres. **B1** the hydrocarbon tails point outwards, making the fabric feel smooth and preventing static charge building up. [2]

A2 APB-Q18

B1 in ethanamide the lone pair on nitrogen is delocalised over the N–C=O group, drawn towards the electronegative oxygen. **B1** so it is far less available to accept a proton than the lone pair in ethylamine, which the ethyl group makes more available. [2]

A3 APB-Q22

B1 a pale blue precipitate of copper(II) hydroxide forms at first, as butylamine acts as a base. **B1** in excess the precipitate dissolves to give a deep blue solution of a copper–butylamine complex ion. [2]

SECTION B · Standard, 3 to 5 marks

B1 APB-Q6

B1 a curly arrow from the lone pair on the nitrogen of NH_3 to the carbon bonded to bromine. **B1** a curly arrow from the C–Br bond to the bromine atom. **B1** the structure of the intermediate ion, $CH_3CH_2NH_3^+$, with the positive charge on nitrogen. **B1** a curly arrow from the lone pair on a second NH_3 molecule to an H atom bonded to the N^+. **B1** a curly arrow from that N–H bond to the nitrogen, giving ethylamine and NH_4^+. [5]

B2 APB-Q2

B1 $CH_3CH_2CH_2NH_2$ is propylamine; allow propan-1-amine. **B1** $(CH_3)_4N^+Cl^-$ is tetramethylammonium chloride. **B1** the nitrogen has used its lone pair to form a fourth bond to carbon. **B1** with no lone pair it cannot accept a proton or donate a pair of electrons to a carbon atom. [4]

B3 APB-Q11

B1 the ammonia route is one step, while the nitrile route has two: KCN in ethanol and water, then reduction with $LiAlH_4$ or H_2 and nickel. **B1** the ammonia route gives a mixture of primary, secondary and tertiary amines and a quaternary salt, lowering the yield. **B1** the nitrile route gives only the primary amine, because no halogenoalkane remains when the amine forms. **B1** the nitrile route uses potassium cyanide, which is toxic, and adds a carbon, so it starts from a halogenoalkane with one carbon fewer. [4]

B4 APB-Q14

B1 the reaction is vigorous at room temperature, with white fumes or a white solid as the HCl meets excess amine. **B1** it is a nucleophilic addition–elimination; reject 'nucleophilic substitution'. **B1** the organic product is N-methylethanamide, $CH_3CONHCH_3$. **B1** the HCl formed reacts with a second methylamine molecule: $CH_3COCl + 2CH_3NH_2 \rightarrow CH_3CONHCH_3 + CH_3NH_3^+Cl^-$. [4]

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B5 APB-Q1 **B1** $(CH_3)_2CHNH_2$ is a primary amine, with one carbon group on the nitrogen. **B1** $(CH_3CH_2)_2NH$ is a secondary amine, with two carbon groups on the nitrogen. **B1** $(CH_3)_3N$ is a tertiary amine, with three carbon groups on the nitrogen. [3]

B6 APB-Q3 **B1** the nitrogen atom in methylamine has a lone pair of electrons that accepts a proton, so it is a Brønsted–Lowry base. **B1** $CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$; the equilibrium sign is required. **B1** the proton comes from water, so hydroxide ions are left in solution and the solution is alkaline. [3]

B7 APB-Q5 **B1** the ethylamine formed has a lone pair on its nitrogen, so it is also a nucleophile, and a better one than ammonia. **B1** it attacks further bromoethane to give diethylamine, which in turn gives triethylamine. **B1** triethylamine reacts to give the quaternary salt, tetraethylammonium bromide, so all four products are present. [3]

B8 APB-Q7 **B1** tin and concentrated hydrochloric acid, heated under reflux, as the reducing agent; allow iron for tin. **B1** sodium hydroxide solution is then added. **B1** the sodium hydroxide removes a proton from the phenylammonium ion, releasing free phenylamine. [3]

B9 APB-Q8 **B1** $CH_3CH_2CN + 4[H] \rightarrow CH_3CH_2CH_2NH_2$. **B1** in the laboratory, lithium tetrahydridoaluminate(III), $LiAlH_4$, in dry ether. **B1** in industry, hydrogen with a nickel catalyst, because $LiAlH_4$ is too expensive at scale. [3]

B10 APB-Q10 **M1** total Mr of reactants = 108.9 + 2 × 17.0 = 142.9. **M1** atom economy = 45.0 ÷ 142.9 × 100. **A1** atom economy = 31.5%, to three significant figures. [3]

B11 APB-Q13 **B1** the salt is ionic, so it dissolves more readily in water and in the body. **B1** the salt is a stable solid without the smell of the amine, which may be an oily liquid. **B1** hydroxide ions take the proton from the RNH_3^+ ion, releasing the free amine. [3]

B12 APB-Q16 **B1** phenylmethylamine is the stronger base. **B1** its nitrogen is separated from the ring by a CH_2 group, so its lone pair cannot overlap with the delocalised ring. **B1** the CH_2 group releases electron density onto the nitrogen, so its lone pair is more available to accept a proton. [3]

B13 APB-Q20 **B1** sodium nitrite and hydrochloric acid, which together make nitrous acid, HNO_2. **B1** the mixture is kept below 10 °C, in ice. **B1** above about 10 °C the diazonium ion decomposes, giving off nitrogen and forming phenol. [3]

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B14 APB-Q21

B1 cold benzenediazonium chloride solution is added to phenol dissolved in sodium hydroxide solution. **B1** the diazonium ion substitutes at carbon 4 of the phenol ring, giving a yellow-orange precipitate in which an –N=N– group joins the two rings. **B1** the azo group links the delocalised systems of both rings, and the extended delocalised system absorbs visible light. [3]

B15 APB-Q23

B1 the reduction needs the acid, and the excess acid protonates the phenylamine as it forms, so the product of the first step is the water-soluble salt $C_6H_5NH_3^+Cl^-$ rather than the free amine. **B1** sodium hydroxide must come after the reduction, because it would neutralise the acid the reduction needs; added afterwards it removes the proton, $C_6H_5NH_3^+ + OH^- \rightarrow C_6H_5NH_2 + H_2O$, releasing the free base. **B1** phenylamine is only slightly soluble in water, so once freed it forms a separate oily layer that can be removed, which the ionic salt, dissolved in the water, could not be. [3]

SECTION C · Long, 6 marks or more

C1 APB-Q4

Indicative content [6]

B1 the order is phenylamine weakest, then ammonia, then ethylamine strongest, all compared at the same concentration. **B1** base strength depends on how available the lone pair on the nitrogen is to accept a proton from water or an acid. **B1** in ethylamine the ethyl group releases electron density onto the nitrogen, the positive inductive effect; reject 'larger group'. **B1** so the lone pair on ethylamine's nitrogen is more available than ammonia's, and ethylamine is the stronger base. **B1** in phenylamine the lone pair on nitrogen overlaps with the delocalised π system and is partly delocalised into the benzene ring. **B1** so less electron density remains on the nitrogen, its lone pair is less available to accept a proton, and phenylamine is weaker than ammonia.

Levels

Level 3 (5–6 marks) the order is correct and both comparisons are explained through the availability of the nitrogen lone pair: the positive inductive effect of the ethyl group and the delocalisation of phenylamine's lone pair into the ring; the answer does not rely on size or on 'more alkyl groups'.

Level 2 (3–4 marks) the order is right and one comparison is fully explained through the lone pair; the other is asserted, or put down to the size of the molecule.

Level 1 (1–2 marks) the order is given or the lone pair mentioned; phenylamine is often placed above ammonia because the ring is taken to push electrons towards the nitrogen.

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