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ANSWER BOOK

Halogenoalkanes: nucleophilic substitution and rates of hydrolysis

Alkanes and halogenoalkanes · Unit C17

AQA 3.3.3.1 · OCR A 4.2.1 (e); 4.2.2 (a), 4.2.2 (b); 6.2.1; 6.2.4

17 questions · 53 marks

NAVY EDITION

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SECTION A · Short, 1 to 2 marks

A1 HN-Q16 — **B1** the C–F bond is very strong, 467 kJ mol^{-1}, the strongest carbon-halogen bond. **B1** it is not broken under these conditions, so no fluoride ions are released to react with silver ions. [2]

A2 HN-Q17 — **B1** a new C–C bond forms, so the carbon chain grows by one atom. **B1** the nitrile group can then be converted into other groups, such as a carboxylic acid or an amine. [2]

A3 HN-Q21 — **B1** $CH_3CH_2OH + SOCl_2 \rightarrow CH_3CH_2Cl + SO_2 + HCl$. **B1** both by-products are gases that leave the flask, so the product is easily separated. [2]

SECTION B · Standard, 3 to 5 marks

B1 HN-Q4 — **B1** the dipole: δ+ on the carbon bonded to bromine and δ- on the bromine. **B1** a curly arrow from the lone pair on the nitrogen of NH_3 to the δ+ carbon. **B1** a curly arrow from the C–Br bond to the bromine atom. **B1** the intermediate $CH_3CH_2CH_2NH_3^+$ drawn with the positive charge on the nitrogen. **B1** a curly arrow from the lone pair of a second NH_3 to an H on the N^+, and an arrow from that N–H bond to the nitrogen, giving $CH_3CH_2CH_2NH_2$ and NH_4^+. [5]

B2 HN-Q1 — **B1** bromine is more electronegative than carbon, so the C–Br bond is polar, with the carbon δ+ and the bromine δ-. **B1** a nucleophile is an electron pair donor, and its lone pair is attracted to the δ+ carbon and forms a new bond to it. **B1** with aqueous sodium hydroxide the nucleophile is the hydroxide ion, OH^-. **B1** with potassium cyanide it is the cyanide ion, CN^-, through the lone pair on carbon, and with ammonia it is NH_3, through the lone pair on nitrogen. [4]

B3 HN-Q6 — **B1** potassium cyanide dissolved in ethanol and water, heated under reflux; reject aqueous KCN alone. **B1** the cyanide carbon joins the chain, so CH_3CH_2CN has three carbons counting the C of the C≡N: propanenitrile. **B1** an excess of ammonia, dissolved in ethanol. **B1** heated in a sealed tube, under pressure, so the ammonia cannot escape. [4]

B4 HN-Q9 — **B1** equal volumes of each halogenoalkane are mixed with ethanol in separate tubes and warmed to the same temperature in a water bath. **B1** equal volumes of aqueous silver nitrate, at the same temperature, are added and a clock is started. **B1** the time for a precipitate to appear is recorded; a shorter time means a faster hydrolysis. **B1** the iodo compound gives a yellow precipitate first, the bromo a cream one later and the chloro a white one last. [4]

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B5 HN-Q3

B1 the dipole: δ+ on the carbon bonded to bromine and δ- on the bromine. **B1** a curly arrow from a lone pair on the oxygen of OH^- to the δ+ carbon; allow the arrow from the minus sign, reject an arrow from the H. **B1** a curly arrow from the C–Br bond to the bromine atom, giving CH_3CH_2OH and Br^-. [3]

B6 HN-Q5

B1 a curly arrow from the lone pair on the carbon of the cyanide ion to the δ+ carbon bonded to chlorine. **B1** the dipole on the C–Cl bond, and a curly arrow from the C–Cl bond to the chlorine atom. **B1** the product is $CH_3CH_2CH_2CH_2CN$, pentanenitrile; reject butanenitrile, which omits the carbon of the C≡N. [3]

B7 HN-Q8

B1 the rate is determined by the C–X bond enthalpy, because the bond must break for substitution to occur. **B1** the C–I bond (228 kJ mol^{-1}) is weaker than the C–Cl bond (346 kJ mol^{-1}). **B1** less energy is needed to break C–I, so the activation energy is lower and the reaction is faster. [3]

B8 HN-Q10

B1 halogenoalkanes do not mix with the aqueous silver nitrate solution. **B1** ethanol is a solvent for both, so they form one solution and the water can react with the halogenoalkane. **B1** hydroxide ions would react with silver ions to precipitate silver oxide, hiding the halide precipitate. [3]

B9 HN-Q13

B1 $CH_3CH(CN)CH_3$, the cyanide group replacing bromine on the middle carbon. **B1** 2-methylpropanenitrile, since the longest chain including the nitrile carbon has three carbons with a methyl branch. **B1** four carbon atoms in all, one more than 2-bromopropane, because the new bond is C–C. [3]

B10 HN-Q14

B1 ethylamine has a lone pair on nitrogen, so it is also a nucleophile. **B1** it can react with more bromoethane to give diethylamine, and further substitution can follow. **B1** with ammonia in excess, bromoethane is more likely to meet ammonia than ethylamine, so the primary amine is the main product. [3]

B11 HN-Q15

B1 in both, a lone pair on the nucleophile attacks the δ+ carbon and the C–Br bond breaks, releasing Br^-. **B1** hydroxide is negatively charged and gives the alcohol in one step; ammonia is neutral and first gives a positively charged ammonium intermediate that must lose H^+. **B1** hydroxide is used in warm aqueous solution; ammonia in excess, in ethanol, in a sealed tube. [3]

B12 HN-Q18

B1 a tertiary halogenoalkane reacts by SN1: the C–X bond breaks first to give a carbocation. **B1** the carbocation is planar, so the nucleophile attacks either face with equal probability. **B1** equal amounts of the two enantiomers form, a racemic mixture, whose rotations cancel. [3]

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B13
HN-Q19

B1 both are C_4H_9Br and break a C–Br bond, so the halogen and the bond enthalpy are the same and only the type of carbon differs. **B1** the tertiary compound reacts by a different route: the C–Br bond breaks first to give a tertiary carbocation. **B1** the carbocation is stabilised by its three alkyl groups pushing electron density towards it, so it forms readily and bromide ions are released faster. [3]

B14
HN-Q20

B1 step 1: potassium cyanide in ethanol and water, heated under reflux. **B1** the intermediate is propanenitrile, CH_3CH_2CN. **B1** step 2: dilute hydrochloric acid, heated under reflux, hydrolyses the nitrile to CH_3CH_2COOH. [3]

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