MEGA LECTURE · A LEVEL CHEMISTRY

Chapter 17: Haloalkanes

OCR A Level Chemistry A (H432) — Structured Practice Worksheet

SPECIFICATION	TOTAL MARKS	SUGGESTED TIME
3.2.3 Haloalkanes: polarity, nucleophilic substitution, elimination, ozone depletion	84	1 hour 42 minutes

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Instructions to candidates

- Answer **all** questions in the spaces provided. Show all working in calculations.
- Marks are shown in brackets [ ] at the end of each part.

Question 1 — Naming and polarity of the C−X bond

3.2.3

a. Give the systematic name of each of the following haloalkanes. **[3]**

Structure	Name
$CH_3CH_2CH_2Br$	
$CH_3CHClCH_2CH_3$	
CH_2BrCH_2Br	

b. Explain, in terms of electronegativity, why the carbon−halogen bond in a haloalkane is polar. **[2]**

c. State and explain the trend in the polarity of the carbon−halogen bond from C−F to C−I. **[3]**

Question 1 total: 8 marks

Question 2 — Bond enthalpy and reactivity

3.2.3

Mean bond enthalpies: C−F = 484 kJ mol^{-1}; C−Cl = 338 kJ mol^{-1}; C−Br = 276 kJ mol^{-1}; C−I = 238 kJ mol^{-1}.

a. Describe the trend in carbon−halogen bond enthalpy shown by this data, and state what this suggests about the relative ease of breaking each bond. **[3]**

b.

Explain why iodoalkanes react faster than chloroalkanes in nucleophilic substitution reactions, even though the C−I bond is less polar than the C−Cl bond. **[3]**

c. State which factor, bond polarity or bond enthalpy, is more important in determining the rate of nucleophilic substitution of haloalkanes, and briefly justify your answer. **[2]**

Question 2 total: 8 marks

Question 3 — Nucleophilic substitution with hydroxide ions 3.2.3

Bromoethane is heated with aqueous sodium hydroxide.

a. Write a balanced equation, including state symbols, for this reaction. **[2]**

b. Draw the mechanism for the nucleophilic substitution of bromoethane by hydroxide ions, showing the lone pair on the nucleophile, the dipole on the C−Br bond, both curly arrows, and the leaving group. **[4]**

Mechanism — show the OH− lone pair, dipole, curly arrows and leaving group

c. State the type of mechanism shown in part (b). **[2]**

d. State the conditions used for this hydrolysis reaction. **[2]**

Question 3 total: 10 marks

Question 4 — Nucleophilic substitution with CN^- and NH_3 3.2.3

a. Write an equation for the reaction of bromoethane with potassium cyanide (in ethanol), and state the importance of this reaction in synthesis. **[2]**

b. Write an equation for the reaction of bromoethane with excess ethanolic ammonia, and explain why an excess of ammonia is used. **[3]**

c. Identify the nucleophile in each of the reactions in parts (a) and (b), and explain what structural feature makes each species able to act as a nucleophile. **[3]**

d. State one synthetic use of the nitrile product formed in part (a). **[2]**

Question 4 total: 10 marks

Question 5 — Comparing rates of hydrolysis 3.2.3

A student compares the rates of hydrolysis of 1-chlorobutane, 1-bromobutane and 1-iodobutane using ethanolic silver nitrate solution.

a. Describe how this experiment could be carried out to compare the rates of hydrolysis of the three haloalkanes. **[2]**

b. State what is observed and measured during this experiment. **[2]**

c. State the order of reactivity of the three haloalkanes, from fastest to slowest. **[2]**

d. Explain this order of reactivity in terms of carbon−halogen bond enthalpy, rather than bond polarity. **[3]**

e. Write an ionic equation for the formation of a silver halide precipitate, and state the colour of each of the three silver halide precipitates formed. **[3]**

Question 5 total: 12 marks

Question 6 — Elimination reactions 3.2.3

2-Bromobutane is heated with potassium hydroxide dissolved in ethanol.

a. Write a balanced equation for this elimination reaction. **[2]**

b. State the conditions required for this reaction to occur by elimination. **[2]**

c. State how the conditions would need to be changed for 2-bromobutane to instead undergo substitution to form butan-2-ol. **[2]**

d. Explain the role of the hydroxide ion in this elimination reaction. **[2]**

e. State why a mixture of alkene products can form in this reaction, naming both possible products. **[2]**

Question 6 total: 10 marks

Question 7 — CFCs and the ozone layer 3.2.3

Chlorofluorocarbons (CFCs), such as $CFCl_3$, were once widely used as aerosol propellants and refrigerants.

a. State what is meant by a CFC, giving the meaning of the term and a general example formula. **[2]**

b. Explain why the C−Cl bond in CFC molecules is broken by ultraviolet radiation high in the stratosphere. **[2]**

c. Write two equations to show how chlorine radicals catalyse the decomposition of ozone in the stratosphere. **[3]**

d. Explain why the chlorine species involved is described as acting as a catalyst in this process. **[2]**

e. Explain why a single chlorine radical can lead to the destruction of many thousands of ozone molecules. **[3]**

Question 7 total: 12 marks

Question 8 — Uses of haloalkanes and the Montreal Protocol 3.2.3

a. State two former uses of CFCs. **[2]**

b. Explain why CFCs were once considered ideal chemicals for these uses. **[2]**

c. State what the Montreal Protocol achieved with respect to CFCs. **[2]**

d. Give an example of a class of compound that has replaced CFCs, and explain why it is less damaging to the ozone layer. **[2]**

Question 8 total: 8 marks

Question 9 — Extended response

Synoptic

Haloalkanes can undergo either nucleophilic substitution or elimination depending on the reagent and conditions used, and the carbon−chlorine bond in CFC molecules is broken by ultraviolet radiation high in the stratosphere, initiating a catalytic radical chain reaction that destroys ozone. Discuss how bond enthalpy influences (i) the relative rates of hydrolysis of chloro-, bromo- and iodoalkanes and (ii) the ability of CFCs to persist in the lower atmosphere yet decompose in the stratosphere, and explain why chlorine radicals are so damaging to the ozone layer. **[6]**

This question is marked using a level of response.

Question 9 total: 6 marks

PAPER TOTAL: 84 MARKS

MARK SCHEME — Chapter 17: Haloalkanes

Award marks independently unless stated. ECF applies to calculations.

Q1 (a) [3]

- $CH_3CH_2CH_2Br$ = 1-bromopropane. (1)
- $CH_3CHClCH_2CH_3$ = 2-chlorobutane. (1)
- CH_2BrCH_2Br = 1,2-dibromoethane. (1)

Q1 (b) [2]

- The halogen atom is more electronegative than the carbon atom. (1)
- This causes the bonding electron pair to be pulled towards the halogen, giving a permanent dipole (δ+ on C, δ− on the halogen). (1)

Q1 (c) [3]

- Bond polarity decreases from C−F to C−I (C−F is the most polar, C−I the least polar). (1)
- Electronegativity decreases down group 7, from fluorine to iodine. (1)
- The smaller the electronegativity difference between carbon and the halogen, the smaller the bond dipole/ polarity. (1)

Q2 (a) [3]

- Bond enthalpy decreases from C−F to C−I (C−F strongest, C−I weakest). (1)
- This is because atomic/covalent radius increases down the group, so the bonding pair of electrons is further from (both) nuclei. (1)
- Weaker bonds (lower bond enthalpy) are broken more easily than stronger bonds. (1)

Q2 (b) [3]

- Although the C−I bond is less polar than the C−Cl bond, the C−I bond has a much lower bond enthalpy (is weaker). (1)
- The rate-determining step of nucleophilic substitution involves breaking the carbon−halogen bond. (1)
- Because the C−I bond is weaker and breaks more easily than the C−Cl bond, iodoalkanes react faster despite being less polar. (1)

Q2 (c) [2]

- Bond enthalpy is more important than bond polarity in determining the rate. (1)
- This is because the rate depends on how easily the C−X bond breaks (its strength), not simply on how polarised it is. (1)

Q3 (a) [2]

- $C_2H_5Br(l) + NaOH(aq) \rightarrow C_2H_5OH(aq/l) + NaBr(aq)$ (1 balancing, 1 state symbols). (2)

Q3 (b) [4]

- Lone pair shown on the oxygen atom of OH^-, with the negative charge shown. (1)
- δ+ shown on the carbon atom bonded to bromine and δ− shown on the bromine (correct dipole). (1)
- Curly arrow from the OH^- lone pair to the δ+ carbon atom. (1)
- Curly arrow from the C−Br bond to the bromine atom, showing Br^- leaving as the leaving group, with the product C_2H_5OH shown. (1)

Q3 (c) [2]

- Nucleophilic substitution. (2)

Q3 (d) [2]

- Aqueous sodium (or potassium) hydroxide. (1)
- Heated under reflux. (1)

Q4 (a) [2]

- $C_2H_5Br + KCN \rightarrow C_2H_5CN + KBr$. (1)
- This reaction extends/lengthens the carbon chain by one carbon atom, which is useful in organic synthesis. (1)

Q4 (b) [3]

- $C_2H_5Br + 2NH_3 \rightarrow C_2H_5NH_2 + NH_4Br$. (1)
- Excess ammonia is used to minimise further substitution of the primary amine product. (1)
- Without excess ammonia, the amine formed could itself act as a nucleophile and react with more haloalkane, giving a mixture of secondary/tertiary amine products. (1)

Q4 (c) [3]

- In (a) the nucleophile is the cyanide ion, CN^-; in (b) the nucleophile is ammonia, NH_3. (1)
- Both species possess a lone pair of electrons (on carbon in CN^-, on nitrogen in NH_3). (1)
- This lone pair can be donated to (attack) the δ+ carbon atom of the haloalkane, forming a new covalent bond. (1)

Q4 (d) [2]

- Nitriles can be reduced to primary amines, or hydrolysed to carboxylic acids, so this reaction is used to make longer-chain amines/carboxylic acids from a shorter haloalkane. (2)

Q5 (a) [2]

- Add equal volumes/concentrations of each haloalkane to separate test tubes each containing ethanolic silver nitrate solution (ethanol used as a common solvent for the haloalkane and the ionic $AgNO_3$). (1)
- Place all three tubes in a water bath at the same temperature and time how long each takes to form a precipitate. (1)

Q5 (b) [2]

- A precipitate (cloudiness/turbidity) of the silver halide forms in each tube. (1)
- The time taken for the precipitate to appear (or for a given amount of turbidity to form) is measured/compared. (1)

Q5 (c) [2]

- Iodobutane reacts fastest, then bromobutane, with chlorobutane reacting slowest. (2)

Q5 (d) [3]

- The rate of hydrolysis depends on how easily the carbon−halogen bond breaks, i.e. on bond enthalpy, not on bond polarity. (1)
- The C−I bond has the lowest bond enthalpy (weakest bond) and the C−Cl bond has the highest bond enthalpy (strongest bond) of the three. (1)
- The weaker C−I bond breaks most readily, so 1-iodobutane hydrolyses fastest; the stronger C−Cl bond breaks least readily, so 1-chlorobutane hydrolyses slowest. (1)

Q5 (e) [3]

- $Ag^+(aq) + X^-(aq) \rightarrow AgX(s)$. (1)
- AgCl = white precipitate; AgBr = cream precipitate. (1)
- AgI = yellow precipitate. (1)

Q6 (a) [2]

- $CH_3CHBrCH_2CH_3 + KOH \rightarrow CH_3CH{=}CHCH_3 + KBr + H_2O$ (1 balancing, 1 correct products). (2)

Q6 (b) [2]

- Potassium (or sodium) hydroxide dissolved in ethanol (ethanolic, not aqueous). (1)
- Heated under reflux (concentrated solution). (1)

Q6 (c) [2]

- Use aqueous potassium/sodium hydroxide instead of ethanolic. (1)
- Warmed/heated under reflux (favouring substitution rather than elimination). (1)

Q6 (d) [2]

- The hydroxide ion acts as a base (not a nucleophile) in this reaction. (1)
- It removes/abstracts a hydrogen atom from a carbon atom adjacent to the carbon bonded to bromine, with the electrons forming the C=C double bond and Br^- leaving. (1)

Q6 (e) [2]

- A hydrogen atom can be removed from either of the two different carbon atoms adjacent to the C−Br carbon. (1)
- This gives a mixture of but-1-ene and but-2-ene. (1)

Q7 (a) [2]

- A CFC (chlorofluorocarbon) is an alkane in which some/all hydrogen atoms have been replaced by chlorine and fluorine atoms. (1)
- Example general formula, e.g. $CFCl_3$ or CF_2Cl_2. (1)

Q7 (b) [2]

- High-energy UV radiation is present in the stratosphere (filtered out before reaching the lower atmosphere/troposphere). (1)
- This UV radiation has enough energy to break the (relatively weak) C−Cl bond by homolytic fission, producing chlorine radicals. (1)

Q7 (c) [3]

- $Cl\bullet + O_3 \rightarrow ClO\bullet + O_2$. (2)
- $ClO\bullet + O_3 \rightarrow Cl\bullet + 2O_2$ (or $ClO\bullet + O \rightarrow Cl\bullet + O_2$). (1)

Award full marks for two correctly balanced equations showing a propagation cycle that regenerates a chlorine radical; accept either valid second step shown here.

Q7 (d) [2]

- The chlorine radical is used up in the first step but regenerated (reformed) in the second step of the cycle. (1)
- As it is not permanently consumed overall, and can go on to react again and again, it behaves as a catalyst. (1)

Q7 (e) [3]

- Because the chlorine radical is regenerated at the end of each cycle, it is not destroyed by reacting with ozone. (1)
- The same chlorine radical can therefore repeat the catalytic cycle many times over. (1)
- Each repeat of the cycle destroys further ozone molecules, so one chlorine radical can destroy many thousands of ozone molecules before it is finally removed (e.g. by a termination reaction). (1)

Q8 (a) [2]

- Any two from: aerosol propellants; refrigerants (coolants); solvents; foam-blowing agents. (2)

Q8 (b) [2]

- CFCs are chemically unreactive/inert (stable) under normal conditions. (1)
- They are also non-flammable, non-toxic and volatile, making them safe and convenient for these applications. (1)

Q8 (c) [2]

- The Montreal Protocol (1987) was an international agreement between countries. (1)
- It set targets/timescales to phase out the production and use of CFCs (and other ozone-depleting substances) in order to protect the ozone layer. (1)

Q8 (d) [2]

- HFCs (hydrofluorocarbons) have replaced CFCs in many uses. (1)
- HFCs contain no chlorine (no C−Cl bond), so they cannot generate chlorine radicals and do not catalyse ozone depletion. (1)

Accept that some replacement compounds may still contribute to the greenhouse effect even though they do not deplete ozone.

Q9 [6] — Level of response

- **Level 3 (5–6):** Gives a fully correct, well-linked explanation of the role of bond enthalpy in both hydrolysis rate trends and CFC stability/decomposition, and clearly explains the catalytic radical chain mechanism and why it is so destructive.
- **Level 2 (3–4):** Covers most of the required ideas but with some gaps, or explains one aspect (rate trend, or CFC behaviour/mechanism) more fully than the other.
- **Level 1 (1–2):** Makes some relevant, valid statements about bond enthalpy and/or the ozone-depletion mechanism, but the answer is limited or lacks clear scientific linkage.

Indicative content: *C−I bonds are weaker (lower bond enthalpy) than C−Br and C−Cl bonds, so iodoalkanes hydrolyse fastest and chloroalkanes slowest, since the rate-determining step involves breaking this bond. The C−Cl bond in CFCs is strong enough to survive in the lower atmosphere (and CFCs are otherwise unreactive/insoluble), but in the stratosphere they are exposed to high-energy UV radiation with enough energy to break even this relatively strong bond, generating chlorine radicals by homolytic fission. These radicals are highly reactive and destroy ozone in a two-step propagation cycle (Cl• + O_3 → ClO• + O_2; ClO• + O_3/O → Cl• + products) that regenerates the chlorine radical each cycle, so a single radical can act catalytically and destroy many thousands of ozone molecules before being removed by a termination step.*

END OF MARK SCHEME · 84 marks