

# Chapter 16: Halogenoalkanes

## Homework questions

- 1** Bromoalkanes are important compounds in organic syntheses because they can undergo substitution reactions.
- An organic compound, X, was identified as the halogenoalkane  $\text{CH}_3\text{CH}_2\text{Br}$ , but the labelling on the bottle was unclear. To confirm its identity a student decided to carry out two tests.
- I Hydrolyse the compound and test for bromide ions.
  - II Vaporise a known amount of the compound and measure its volume under known conditions. In this experiment, 0.218 g of the compound occupied  $61 \text{ cm}^3$  at  $100 \text{ }^\circ\text{C}$  and 1 atmosphere pressure ( $1.01 \times 10^5 \text{ N m}^{-2}$ ).
- a Describe the test to confirm the presence of bromide ions. Include an ionic equation in your answer. [4]
  - b Calculate the relative molecular mass of X and confirm that the compound is bromoethane. [5]
  - c Bromoalkanes react with potassium cyanide to form a nitrile.
    - i Give the equation for this reaction. [1]
    - ii Explain why this reaction is useful in organic synthesis. [1]
    - iii Describe the mechanism for this reaction. [3]
  - d Bromoethane undergoes two different reactions with sodium hydroxide, depending on the conditions used.  
Write the equations for both these reactions.  
For each equation, state the conditions and chemicals used. [6]
  - e Bromine can be extracted from seawater by passing chlorine gas through the seawater and then evaporating off the bromine formed.
    - i Give the ionic equation for this extraction of bromine. [1]
    - ii Explain why this is a redox reaction. [2]
    - iii Explain why bromine has a lower boiling point than water. [4]

Total = 27

- 2** Halogenoalkanes undergo nucleophilic substitution with water to give alcohols. The rate of reaction depends on the halogen being substituted. The table below gives data on the halogens in some carbon–halogen bonds, as well as the electronegativity of carbon.

Bond	Bond enthalpy / $\text{kJ mol}^{-1}$	Element	Electronegativity
C–Cl	346	chlorine	3.0
C–Br	290	bromine	2.8
C–I	228	iodine	2.5
		carbon	2.1

- a Explain why the electronegativity values lead to the following predicted order of reactivity of the carbon–halogen bond:  
 $\text{Cl} > \text{Br} > \text{I}$  [3]
- b What is the predicted order of reactivity if the bond enthalpies are used to predict the reactivity of the bonds? Explain your answer. [2]
- c Describe an experiment that would verify which of the above alternatives is the correct one.  
You should give relevant equations and details of conditions needed to make it a fair test. [6]
- d Explain why chlorofluorocarbons (CFCs) were once used in aerosols and refrigerants. [2]
- e It is now forbidden to use CFCs in aerosols and refrigerants. Explain why. [1]

Total = 14

- 3 The halogenoalkanes 2-chlorobutane and 2-chloro-2-methylpropane both undergo elimination reactions when heated with ethanolic sodium hydroxide. In this reaction 2-chlorobutane gives three products whilst 2-chloro-2-methylpropane gives only one product.
- a** Give the structural formulae and skeletal formulae of both these halogenoalkanes. [4]
- b i** Give the name and skeletal formula of the alkene formed from the elimination reaction undergone by 2-chloro-2-methylpropane. [2]
- ii** Draw a four-carbon section of the addition polymer formed from this alkene. [2]
- c** Give the names and skeletal formula of the **three** alkenes formed from the elimination reaction of 2-chlorobutane with ethanolic sodium hydroxide. [6]
- d** When 2-chloro-2-methylpropane reacts with aqueous sodium hydroxide, the reaction proceeds via a two-step mechanism. The first step produces a positive carbocation and, in the second step, this carbocation reacts with a hydroxide ion.
- i** Draw the positive carbonium ion, name its shape and state the bond angle. [3]
- ii** Explain why it is a reasonably stable intermediate. [1]
- iii** Give the equations for both steps in the reaction mechanism. [2]
- iv** In which of the two steps does heterolytic fission take place? Explain your answer. [2]
- Total = 22