

## Chapter 16: Halogenoalkanes

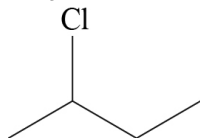
## Homework marking scheme

- 1 a** add aqueous silver nitrate solution [1]  
 observe a pale cream precipitate [1]  
 which is partially soluble in ammonia solution, suggests bromide ions [1]  
 $\text{Ag}^+(\text{aq}) + \text{Br}^-(\text{aq}) \rightarrow \text{AgBr}(\text{s})$  [1]
- b** number of moles  
 use  $PV = nRT$ , rearranged to give  $n = \frac{PV}{RT}$  [1]  

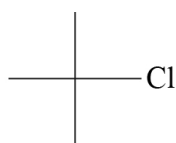
$$n = \frac{1.01 \times 10^5 \times 61 \times 10^{-6}}{8.314 \times 373}$$
 [1]  
 $= 1.99 \times 10^{-3} \text{ mol}$  [1]  
 molar mass  
 $= \frac{0.218}{1.99 \times 10^{-3}} = 109.6 \text{ g mol}^{-1}$  [1]  
 The relative molecular mass of  $\text{CH}_3\text{CH}_2\text{Br}$  is 109, which is close to the value above. [1]  
 Note the need to convert the temperature to an absolute temperature.
- c i**  $\text{CH}_3\text{CH}_2\text{Br} + \text{KCN} \rightarrow \text{CH}_3\text{CH}_2\text{CN} + \text{KBr}$  [1]  
**ii** The substitution of the Br by CN lengthens the carbon chain. [1]  
**iii**
- 
- curly arrow from lone pair or negative charge on cyanide ion [1]  
 dipoles on the C–Br bond [1]  
 curly arrow from the C–Br bond onto the bromine [1]
- d** aqueous NaOH and reflux: [2]  
 $\text{CH}_3\text{CH}_2\text{Br} + \text{NaOH}(\text{aq}) \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{NaBr}$  [1]  
 ethanolic NaOH; heat [2]  
 $\text{CH}_3\text{CH}_2\text{Br} + \text{NaOH} \rightarrow \text{CH}_2\text{CH}_2 + \text{NaBr} + \text{H}_2\text{O}$  [1]
- e i**  $\text{Cl}_2 + 2\text{Br}^- \rightarrow 2\text{Cl}^- + \text{Br}_2$  [1]  
**ii** The oxidation number of the chlorine has decreased from 0 to  $-1$ , therefore reduced. [1]  
 The oxidation number of the bromine increases from  $-1$  to 0, therefore oxidised. [1]  
**iii** Bromine is non-polar. [1]  
 The intermolecular forces between bromine molecules are weak van der Waal's forces. [1]  
 The intermolecular bonds between polar water molecules [1]  
 are much stronger hydrogen bonds. [1]

- 2 a In nucleophilic substitution, the nucleophile attacks the electron-deficient carbon. [1]  
 The greater the electronegativity of the halogen, the more electron-deficient the carbon. [1]  
 The easier it is for the nucleophile to attack the carbon. [1]
- b  $I > Br > Cl$  [1]  
 The lower the bond enthalpy of the C–halogen bond, the easier it is to break it and hence the faster the reaction. [1]
- c Use similar halogenoalkanes, e.g. 1-chlorobutane, 1-bromobutane and 1-iodobutane. [1]  
 Use aqueous silver nitrate mixed with ethanol (to dissolve both the silver nitrate and the halogenoalkane). [2]  
 Add equal (molar) amounts of halogenoalkane. [1]  
 Warm the mixture. [1]  
 Time how long it takes for a precipitate to form. [1]
- d They are unreactive [1]  
 and volatile. [1]
- e They lead to the destruction of the ozone layer. [1]

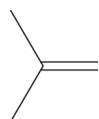
- 3 a  $CH_3CHClCH_2CH_3$  [1]



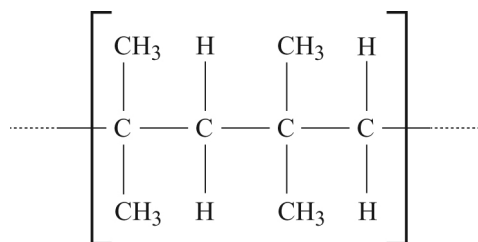
$(CH_3)_2CClCH_3$  (note that  $(CH_3)_3CCl$  is acceptable) [1]



- b i 2-methylpropene [1]



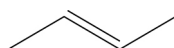
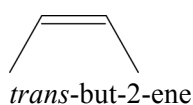
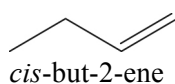
ii



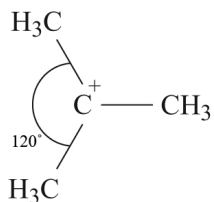
the two methyl groups must be on the same carbon [1]

four-carbon section with lines (preferably dashed) on either side. [1]

- c but-1-ene [1]



d i



correct methyl groups and central +ve charge [1]

correct shape named as trigonal planar [1]

correct bond angle ( $120^\circ$ ). [1]

- ii The three electron-donating methyl groups reduce the +ve charge density on the central carbon, making it more stable. [1]
- iii  $(\text{CH}_3)_2\text{CClCH}_3 \rightarrow (\text{CH}_3)_2\text{C}^+(\text{CH}_3) + \text{Cl}^-$  [1]  
 $(\text{CH}_3)_2\text{C}^+(\text{CH}_3) + \text{OH}^- \rightarrow (\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_3$  [1]
- iv Heterolytic fission is the first step.  
 The C–Cl bond breaks unevenly, and both of the electrons from the bond go to the Cl [1]  
 to give two oppositely charged ions – a carbocation and a chloride ion. [1]