

2

1

2-bromo-2-methylpentane is heated with potassium hydroxide dissolved in ethanol. Two structural isomers are formed.

(a) State the meaning of the term **structural isomers**.

------

Page 1 of 88

(1)

(b) Name and draw the mechanism for the formation of **one** of the isomers.

Name of mechanism .....

Mechanism

(5) (Total 6 marks)

**3** Consider the following scheme of reactions.



(a) Give the IUPAC name for compound  $\mathbf{P}$  and that for compound  $\mathbf{Q}$ .

Ρ	
Q	

(b)	The conversion of <b>P</b> into <b>Q</b> in Reaction <b>1</b> uses HCI	
	Name and outline a mechanism for this reaction.	
		(5)
		(5)
(c)	The conversion of ${\bf Q}$ into ${\bf R}$ in Reaction 2 uses NH <sub>3</sub>	
	Name and outline a mechanism for this reaction.	
		(5)
(d)	State the type of reaction shown by Reaction <b>3</b> .	
	Identify a reagent for this reaction.	
	Give <b>one</b> condition necessary for a high yield of product when <b>Q</b> is converted into <b>P</b> .	

(3)

(e) Hydrogen bromide (HBr) could be used in the overall conversion of **P** into **R**, instead of using HCI

Hydrogen bromide is made by the reaction of NaBr with concentrated phosphoric acid. Concentrated sulfuric acid is **not** used to make HBr from NaBr

Write an equation for the reaction of NaBr with  $H_3PO_4$  to produce HBr and  $Na_3PO_4$  only.

Identify **two** toxic gases that are formed, together with HBr, when NaBr reacts with concentrated  $H_2SO_4$ 

State the role of  $H_2SO_4$  in the formation of these two toxic gases.

(4) (Total 19 marks)

4

Haloalkanes are used in the synthesis of other organic compounds.

- (a) Hot concentrated ethanolic potassium hydroxide reacts with 2-bromo-3-methylbutane to form two alkenes that are structural isomers of each other. The major product is 2-methylbut-2-ene.
  - (i) Name and outline a mechanism for the conversion of 2-bromo-3-methylbutane into 2-methylbut-2-ene according to the equation.

(CH <sub>3</sub> ) <sub>2</sub> CHCHBrCH <sub>3</sub>	+	KOH	$\rightarrow$	$(CH_3)_2C=CHCH_3$	+	KBr	+	$H_2O$
---	---	-----	---------------	--------------------	---	-----	---	--------

Name of mechanism .....

Mechanism

(ii) Draw the **displayed formula** for the other isomer that is formed.

			(1)
	(iii)	State the type of structural isomerism shown by these two alkenes.	
			(1)
(b)	A sn form 3-me	nall amount of another organic compound, <b>X</b> , can be detected in the reaction mixture ed when hot concentrated ethanolic potassium hydroxide reacts with 2-bromo- ethylbutane.	
	Corr	pound <b>X</b> has the molecular formula $C_5H_{12}O$ and is a secondary alcohol.	
	(i)	Draw the <b>displayed formula</b> for <b>X</b> .	(1)
	(ii)	Suggest <b>one</b> change to the reaction conditions that would increase the yield of <b>X</b> .	
	(iii)	State the type of mechanism for the conversion of 2-bromo-3-methylbutane into ${f X}$ .	(1)
			(1)

(iv) Identify one feature of this infrared spectrum of a pure sample of X that may be used to confirm that X is an alcohol.
 You may find it helpful to refer to Table 1 on the Data Sheet.



Consider the following reactions.

5



Name of mechanism .....

Mechanism

(5)

(b)	Name and outline a mechanism for Reaction 2.
	Name of mechanism
	Mechanism

- (c) State the type of reaction in Reaction 3. Give the name of substance X.
- (d) The haloalkane produced in Reaction **1** can be converted back into propene in an elimination reaction using ethanolic potassium hydroxide.

 $CH_{3}CHBrCH_{3} \xrightarrow{KOH} H_{2}C=CHCH_{3}$ 

Outline a mechanism for this conversion.

(3) (Total 15 marks)

(2)

6

Alkenes are useful intermediates in the synthesis of organic compounds.

(a) (i) Complete the elimination mechanism by drawing appropriate curly arrows.

нō:



3-bromohexane

hex-3-ene

(3)

	E isomer of hex-3-ene	Z isomer of hex-3-ene
(iii)	State the meaning of the term stered	pisomers.
	(Extra space)	

Draw structures for the E and Z stereoisomers of hex-3-ene.

(ii)

(b) The equation for the first reaction in the conversion of hex-3-ene into hexan-3-ol is shown below.

 $CH_3CH_2CH=CHCH_2CH_3 + H_2SO_4 \longrightarrow CH_3CH_2CH_2CH(OSO_2OH)CH_2CH_3$ 

Outline a mechanism for this reaction.

(4) (Total 11 marks)

(2)

7

Organic reaction mechanisms help chemists to understand how the reactions of organic compounds occur.

The following conversions illustrate a number of different types of reaction mechanism.

- (a) When 2-bromopentane reacts with ethanolic KOH, two structurally isomeric alkenes are formed.
  - (i) Name and outline a mechanism for the conversion of 2-bromopentane into pent-2-ene as shown below.

 $\begin{array}{cccc} \mbox{ethanolic KOH} \\ \mbox{CH}_3\mbox{CH}_2$ 

(ii) Draw the structure of the other structurally isomeric alkene produced when 2-bromopentane reacts with ethanolic KOH.

(4)

(1)

(b) Name and outline a mechanism for the following conversion.



(c) Name and outline a mechanism for the following conversion.

 $\label{eq:ch_3CH_2CH_2Br} \begin{array}{c} \mathsf{NH_3} \\ \longrightarrow \\ \mathsf{CH_3CH_2CH_2Br} \end{array} \xrightarrow{} \begin{array}{c} \mathsf{NH_3} \\ \leftarrow \mathsf{CH_3CH_2CH_2NH_2} \end{array}$ 

(5) (Total 15 marks)

(5)

Page 11 of 88

Haloalkanes contain a polar covalent bond. The carbon atom of the polar covalent bond can be attacked by nucleophiles. Nucleophilic attack enables haloalkanes to undergo substitution reactions. A nucleophilic substitution reaction occurs when a haloalkane undergoes hydrolysis; the rate of hydrolysis of the haloalkane is influenced by the

carbon-halogen bond enthalpy.

- (a) Explain the meaning of each of the following terms in the information given above.
  - nucleophile (i) ..... ..... ..... (1) (ii) substitution, as applied to nucleophilic substitution in a haloalkane ..... ..... ..... (1) hydrolysis (iii) ..... ..... (1) bond enthalpy, as applied to a carbon-halogen bond. (iv) ..... ..... (1)

(b) Outline a mechanism for the nucleophilic substitution reaction in which 2-bromopropane (CH<sub>3</sub>CHBrCH<sub>3</sub>) reacts with potassium hydroxide to form propan-2-ol.

- (c) Haloalkanes also undergo elimination reactions to produce alkenes.
  - (i) Outline a mechanism for the elimination reaction in which 2-bromopropane reacts with potassium hydroxide to form propene.

(3)

(ii) A student obtained the following infrared spectrum for the product from this elimination reaction.



Use information from the infrared spectrum to state and explain how the student deduced that the product was an alkene.

You may find it helpful to refer to **Table 1** on the Data Sheet.



(2) (Total 11 marks)

## (a) Consider the following reaction.

9

(i) Name and outline a mechanism for this reaction.

Name of mechanism .....

Mechanism

(ii) Name the haloalkane in this reaction.
(iii) Identify the characteristic of the haloalkane molecule that enables it to undergo this type of reaction.
(1)

Page 15 of 88

(b) An alternative reaction can occur between this haloalkane and potassium hydroxide as shown by the following equation.

Name and outline a mechanism for this reaction.

Name of mechanism .....

Mechanism

(4) (C) Give one condition needed to favour the reaction shown in part (b) rather than that shown in part (a). ..... (1) (d) Alkenes can be polymerised to produce poly(alkenes). (i) State the type of polymerisation that alkenes undergo. ..... (1) (ii) Name the alkene that gives a polymer with the repeating unit shown below.  $\begin{array}{c} H & CH_3 \\ | & | \\ -C - C - \\ | & | \\ CH_3 H \end{array}$ Name of alkene ..... (1) (Total 12 marks)

Nucleophiles react with bromoethane in substitution reactions. This type of reaction is illustrated in the following scheme.

10

CH prop	3CH2CN anenitrile	Reaction 1 KCN Rea	CH <sub>3</sub> CH <sub>2</sub> Br action 2 NH <sub>3</sub> CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub> ethylamine	Reaction 3 KOH	CH <sub>3</sub> CH <sub>2</sub> OH ethanol	
(a)	State what i	s meant by the	term nucleophile.			
(b)	Outline a mail (Reaction 1)	echanism for th ).	e reaction of pota	ssium cyanide w	ith bromoethane	(1)
						(2)
(c)	Explain why ethylamine.	an excess of a	mmonia is neede	d in Reaction <b>2</b> t	o produce a high yield of	

.....

(1)

(d) When potassium hydroxide reacts with bromoethane, ethene can also be formed. Name and outline a mechanism for this reaction.

Name of mechanism .....

Mechanism

(4) (Total 8 marks)

11

Organic reaction mechanisms help to develop an understanding of how and why reactions occur.

(a) Propene reacts with hydrogen bromide by an electrophilic addition mechanism forming 2-bromopropane as the major product.

The equation for this reaction is shown below.

$$\begin{array}{c} H_{3}C \\ H \end{array} \xrightarrow{} C = C \xrightarrow{H} \\ H \end{array} + HBr \rightarrow H_{3}C \xrightarrow{Br} H \\ I \\ H \\ H \\ H \end{array}$$

(i) Outline the mechanism for this reaction, showing the structure of the intermediate carbocation formed.

(ii) Give the structure of the alternative carbocation which could be formed in the reaction between propene and hydrogen bromide.

(5)

- (b) A substitution reaction occurs when 2-bromopropane reacts with aqueous sodium hydroxide.
  - (i) Draw the structure of the organic product of this reaction and give its name.

Structure

Name .....

(ii) Name and outline the mechanism for this reaction.

Name of mechanism .....

Mechanism

(5)

(c)	Under different conditions,	2-bromopropane reacts v	with sodium hy	/droxide to	produce
	propene.				

(i) Name the mechanism for this reaction

.....

(ii) State the role of sodium hydroxide in this reaction

.....

(2) (Total 12 marks)

12

How many different alkenes are formed when 2-bromo-3-methylbutane reacts with ethanolic potassium hydroxide?

- **A** 2
- **B** 3
- **C** 4
- **D** 5

(Total 1 mark)

Name of mechanism         Mechanism         (b) Two stereoisomers of but-2-ene are formed when 2-bromobutane reacts with ethanolic potassium hydroxide.         (i) Explain what is meant by the term stereoisomers.         (ii) Explain what is meant by the term stereoisomers.         (iii) Draw the structures and give the names of the <b>two</b> stereoisomers of but-2-ene.         Stereoisomer 1       Stereoisomer 2         Name         (iii) Name this type of stereoisomerism.         (iiii) Name this type of stereoisomerism.         (iii) Stereoisomer 2         State the role of the hydroxide ions in this reaction.         State the role of the hydroxide ions in this reaction.	(a)	Nan etha	ne and outline a mechanism for the reaction of 2-bromo-2-methylpropane with nolic potassium hydroxide to form the alkene 2-methylpropene, $(CH_3)_2C=CH_2$	
Mechanism         (b) Two stereoisomers of but-2-ene are formed when 2-bromobutane reacts with ethanolic potassium hydroxide.         (i) Explain what is meant by the term stereoisomers.		Narr	ne of mechanism	
<ul> <li>(b) Two stereoisomers of but-2-ene are formed when 2-bromobutane reacts with ethanolic potassium hydroxide.</li> <li>(i) Explain what is meant by the term <i>stereoisomers</i>.</li> <li></li></ul>		Mec	hanism	
potassium hydroxide. (i) Explain what is meant by the term <i>stereoisomers</i> . 	(b)	Two	stereoisomers of but-2-ene are formed when 2-bromobutane reacts with ethanolic	
(ii) Draw the structures and give the names of the <b>two</b> stereoisomers of but-2-ene. Stereoisomer 1 Stereoisomer 2 Name		pota (i)	ssium hydroxide. Explain what is meant by the term <i>stereoisomers</i> .	
(ii) Draw the structures and give the names of the <b>two</b> stereoisomers of but-2-ene. Stereoisomer 1 Stereoisomer 2 Name			· · · · · · · · · · · · · · · · · · ·	
(ii) Draw the structures and give the names of the <b>two</b> stereoisomers of but-2-ene. Stereoisomer 1 Stereoisomer 2 Name				
Stereoisomer 1       Stereoisomer 2         Name       Name         (iii)       Name this type of stereoisomerism.         (iii)       Name this type of stereoisomerism.         (c)       When 2-bromo-2-methylpropane reacts with aqueous potassium hydroxide, 2-methylpropan-2-ol is formed as shown by the following equation.         (c)       When 2-bromo-2-methylpropane reacts with aqueous potassium hydroxide, 2-methylpropan-2-ol is formed as shown by the following equation.         (c) $H_3C - C + G_{H_3} + KOH + H_3C + C + G_{H_3} + KBr$ $H_3C - C + G_{H_3} + KOH + H_3C + C + G_{H_3} + KBr$ State the role of the hydroxide ions in this reaction.		(ii)	Draw the structures and give the names of the <b>two</b> stereoisomers of but-2-ene.	
Name			Stereoisomer 1 Stereoisomer 2	
(iii) Name this type of stereoisomerism. (c) When 2-bromo-2-methylpropane reacts with aqueous potassium hydroxide, 2-methylpropan-2-ol is formed as shown by the following equation. $H_{3}C \xrightarrow{CH_{3}}_{H_{3}C} \xrightarrow{CH_{3}}_{H_{3}C} \xrightarrow{CH_{3}}_{H_{3}C} \xrightarrow{CH_{3}}_{H_{3}C} + KBr$ State the role of the hydroxide ions in this reaction.			Name	
(c) When 2-bromo-2-methylpropane reacts with aqueous potassium hydroxide, 2-methylpropan-2-ol is formed as shown by the following equation. $\begin{array}{c} & & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ $		(iii)	Name this type of stereoisomerism.	
$\begin{array}{c} CH_{3} \\ H_{3}C \longrightarrow CH_{3$	(c)	Whe 2-me	n 2-bromo-2-methylpropane reacts with aqueous potassium hydroxide, ethylpropan-2-ol is formed as shown by the following equation.	(
State the role of the hydroxide ions in this reaction.		H₃C	$\begin{array}{ccccc} CH_3 & CH_3 \\   &   \\ C & C & CH_3 + KOH \longrightarrow H_3C & CH_3 + KBr \\   &   \\ Br & OH \end{array}$	
		State	e the role of the hydroxide ions in this reaction.	
				1.

(d) Write an equation for the reaction that occurs when  $CH_3CH_2CH_2CH_2Br$  reacts with an excess of ammonia. Name the organic product of this reaction.

Equation .....

me of product
---------------

(3) (Total 13 marks)

(4)

(1)

- (c) Another alkene, which is a structural isomer of but-2-ene, is also formed during this reaction.
  - (i) State what is meant by the term *structural isomers*.

.....

(ii) Draw the structure of this other alkene.

(2) (Total 7 marks)

**15** How many different alkenes are formed when 2-bromo-2-methylbutane reacts with ethanolic potassium hydroxide?

- **A** 2
- **B** 3
- **C** 4
- **D** 5

(Total 1 mark)



(a) Complete the mechanism below by drawing appropriate curly arrows.



(3)

(b) Draw and name the geometrical E-Z isomers of pent-2-ene.

		Isomer 1	Isomer 2	
	Narr	1e	Name	(2)
(c)	Pent <sup>.</sup> prod	<ul> <li>1-ene reacts with hydrogen bromide to uct.</li> </ul>	produce 2-bromopentane as	the major
	(i)	Outline the mechanism for this reactio	).	
	(ii)	Identify the minor product formed in th	s reaction.	
	(iii)	Explain why 2-bromopentane is the m	ajor product of this reaction.	
				 (7) (Total 12 marks)

For this question refer to the reaction scheme below.



Which one of the following reagents would **not** bring about the reaction indicated?

A Step 1 : alcoholic KOH

17

- B Step 2 : aqueous Br<sub>2</sub>
- C Step 3 : aqueous NaOH
- **C** Step 4 : concentrated H<sub>2</sub>SO<sub>4</sub>

(Total 1 mark)

**18** Ethene is an important starting point for the manufacture of plastics and pharmaceutical chemicals. Most of the ethene used by industry is produced by the thermal cracking of ethane obtained from North Sea gas (**Reaction 1**). It is also possible to make ethene either from chloroethane (**Reaction 2**) or from ethanol (**Reaction 3**).



(a) Give essential conditions and reagents for each of **Reactions 2** and **3**.

(4)

(b) Name and outline a mechanism for **Reaction 2**. Suggest a reason why chloroethane is **not** chosen by industry as a starting material to make ethene commercially.

(5)

(c) Name and outline a mechanism for **Reaction 3**. Suggest why this route to ethene may become used more commonly in the future as supplies of North Sea gas begin to run out.

(6) (Total 15 marks)

- (a) Compounds with double bonds between carbon atoms can exhibit geometrical isomerism.
  - (i) Draw structures for the two geometrical isomers of 1,2-dichloroethene.

Isomer 1 Isomer 2

(ii) What feature of the double bond prevents isomer 1 from changing into isomer 2?

- (3)
- (b) When 2-chloropropane reacts with sodium hydroxide, two different reactions occur. Each reaction produces a different organic product.

**Reaction 1**  $CH_3 - C - CH_3 + NaOH \rightarrow CH_3 - CH - CH_3 + NaCl$   $\downarrow$  Cl OH **Reaction 2**  $CH_3 - C - CH_3 + NaOH \rightarrow CH_3 - CH = CH_2 + NaCl + H_2O$   $\downarrow$ Cl

(i) Outline a mechanism for **Reaction 1** and state the role of the hydroxide ion in this reaction.

Mechanism

19

Role of the hydroxide ion .....

(ii) Outline a mechanism for **Reaction 2** and state the role of the hydroxide ion in this reaction.

Mechanism

Role of the hydroxide ion .....

(7) (Total 10 marks)

(a) Propene reacts with hydrogen bromide by an electrophilic addition mechanism forming
 2-bromopropane as the major product.

The equation for this reaction is shown below.



(i) Outline the mechanism for this reaction, showing the structure of the intermediate carbocation formed.

(ii) Give the structure of the alternative carbocation which could be formed in the reaction between propene and hydrogen bromide.

- (b) A substitution reaction occurs when 2-bromopropane reacts with aqueous sodium hydroxide.
  - (i) Draw the structure of the organic product of this reaction and give its name.

Structure

Name .....

(5)

(II) Name and outline the mechanism for this reaction.
--

Name of mechanism .....

Mechanism

(5)

(c)	Under different conditions, 2-bromopropane reacts with sodium hydroxide to produce propene.	
	(i)	Name the mechanism for this reaction.
	(ii)	State the role of sodium hydroxide in this reaction.
		(2) (Total 12 marks)

The conversion of compound **A** into compound **B** can be achieved in two steps as shown below.



The intermediate compound, **X**, has an absorption at 1650  $\text{cm}^{-1}$  in its infra-red spectrum.

(a) Identify compound X. Explain your answer.

21

(b) For each step in this conversion, give the reagents and essential conditions required and outline a mechanism.

(11)

(c) Show how the number of peaks in their proton n.m.r. spectra would enable you to distinguish between compounds **A** and **B**.

(2) (Total 15 marks)



(4)

(b) Name alcohol E and draw its structural formula. By reference to the structure of the halogenoalkane, explain why the initial step in the mechanism of the reaction producing the alcohol occurs.

(5)

(c) When 2-bromobutane reacts with ethanolic potassium hydroxide, two structurally isomeric alkenes are produced, one of which shows stereoisomerism.

Outline the mechanism for the formation of one of the structurally isomeric alkenes. Explain why two structurally isomeric alkenes are formed and draw the structure of the second structural isomer. Draw the structural formulae of the two stereoisomers.

> (8) (Total 17 marks)

(a) The equation below shows the reaction of 2-bromopropane with an excess of ammonia.

 $CH_{3}CHBrCH_{3} \ + \ 2NH_{3} \ \rightarrow \ CH_{3}CH(NH_{2})CH_{3} \ + \ NH_{4}Br$ 

Name and outline the mechanism involved.

Name of mechanism .....

Mechanism

(5)

(b) When 2-bromopropane is heated with ethanolic potassium hydroxide, an elimination reaction occurs. State the role of potassium hydroxide and outline a mechanism for this reaction.

Role of potassium hydroxide .....

Mechanism

(5) (Total 10 marks)

- **25** Refrigerants are substances used to cool refrigerators and freezers. Until recently, many of the compounds used as refrigerants were chlorofluorocarbons (CFCs), but these are now known to form chlorine radicals. CFCs have been phased out in many countries by international agreement.
  - (a) Write **two** equations to show how chlorine radicals react with ozone molecules in the upper atmosphere.

1	
2	

(b) Chloropentafluoroethane is a CFC that has been used as a refrigerant.

Draw its displayed formula.

(1)

(c) 1,1,1-trifluoroethane ( $CF_3CH_3$ ) is one of the molecules that has been used as a refrigerant in place of CFCs.

Explain why 1,1,1-trifluoroethane does not lead to the depletion of the ozone in the upper atmosphere.

\_\_\_\_\_

(1)

(d) One of the steps in the synthesis of 1,1,1-trifluoroethane  $(CF_3CH_3)$  is the reaction of 1,1-difluoroethane  $(CHF_2CH_3)$  with fluorine in a free-radical substitution reaction.

Write **two** equations to represent the propagation steps in this conversion of  $CHF_2CH_3$  into  $CF_3CH_3$ 

Propagation step 1

.....

Propagation step 2

.....

(e) A refrigerator contains 1.41 kg of 1,1,1-trifluoroethane ( $CF_3CH_3$ ).

Calculate the number of molecules of 1,1,1-trifluoroethane in the refrigerator. Give your answer to an appropriate number of significant figures. (The Avogadro constant L =  $6.022 \times 10^{23} \text{ mol}^{-1}$ )

.....

(f) There are growing concerns about the use of 1,1,1-trifluoroethane as a refrigerant as it is a greenhouse gas that absorbs some of Earth's infrared radiation.

Give **one** reason why bonds in molecules such as carbon dioxide and 1,1,1-trifluoroethane absorb infrared radiation.

.....

.....

(1) (Total 9 marks)

(2)

- **26** CCl<sub>4</sub> is an effective fire extinguisher but it is no longer used because of its toxicity and its role in the depletion of the ozone layer. In the upper atmosphere, a bond in CCl<sub>4</sub> breaks and reactive species are formed.
  - (a) Identify the condition that causes a bond in  $CCI_4$  to break in the upper atmosphere. Deduce an equation for the formation of the reactive species.

Condition .....

Equation

.....

(b) One of the reactive species formed from CCl<sub>4</sub> acts as a catalyst in the decomposition of ozone.

Write **two** equations to show how this species acts as a catalyst.

Equation 1

.....

Equation 2

.....

(c) A small amount of the freon CF<sub>3</sub>Cl with a mass of 1.78 × 10<sup>-4</sup> kg escaped from a refrigerator, into a room of volume 100 m<sup>3</sup>. Assuming that the freon is evenly distributed throughout the air in the room, calculate the number of freon molecules in a volume of 500 cm<sup>3</sup>.

Give your answer to the appropriate number of significant figures.

The Avogadro constant =  $6.02 \times 10^{23} \text{ mol}^{-1}$ .

Number of molecules = .....

(3) (Total 7 marks)

There are many uses of halogenated organic compounds despite environmental concerns.

Bromotrifluoromethane is used in fire extinguishers in aircraft.
 Bromotrifluoromethane is formed when trifluoromethane reacts with bromine.

 $\mathsf{CHF}_3 \ + \ \mathsf{Br}_2 \ \longrightarrow \ \mathsf{CBrF}_3 \ + \ \mathsf{HBr}$ 

The reaction is a free-radical substitution reaction similar to the reaction of methane with chlorine.

(i) Write an equation for each of the following steps in the mechanism for the reaction of CHF<sub>3</sub> with Br<sub>2</sub>

Initiation step

27

.....

First propagation step

.....

Second propagation step

.....

A termination step

.....

(4)

(ii) State **one** condition necessary for the initiation of this reaction.

.....

(1)

- (b) Bromine-containing and chlorine-containing organic compounds may have a role in the decomposition of ozone in the upper atmosphere.
  - (i) Draw an appropriate **displayed formula** in the space provided to complete the following equation to show how CBrF<sub>3</sub> may produce bromine atoms in the upper atmosphere.

 $CBrF_3 \longrightarrow + Br'$ 

(ii) In the upper atmosphere, it is more likely for CBrF<sub>3</sub> to produce bromine atoms than it is for CCIF<sub>3</sub> to produce chlorine atoms.

Suggest one reason for this.

\_\_\_\_\_

(1)

(1)

 Bromine atoms have a similar role to chlorine atoms in the decomposition of ozone. The overall equation for the decomposition of ozone is

 $2O_3 \longrightarrow 3O_2$ 

Write **two** equations to show how bromine atoms (Br•) act as a catalyst in the decomposition of ozone.

Explain how these two decomposition equations show that bromine atoms behave as a catalyst.

Equation 1

.....

Equation 2

Explanation .....

.....

(3) (Total 10 marks) Trifluoromethane (CHF<sub>3</sub>) can be used to make the refrigerant chlorotrifluoromethane(CCIF<sub>3</sub>).

(a) Chlorotrifluoromethane is formed when trifluoromethane reacts with chlorine.

28

(b)

 $CHF_3 + CI_2 \longrightarrow CCIF_3 + HCI$ 

The reaction is a free-radical substitution reaction similar to the reaction of methane with chlorine.

(i) Write an equation for each of the following steps in the mechanism for the reaction of  $CHF_3$  with  $CI_2$ 

Initiation step First propagation step ..... Second propagation step ..... Termination step to form hexafluoroethane ..... (4) Give one essential condition for this reaction. (ii) ..... (1) In some refrigeration systems, CHF<sub>3</sub> has replaced CCIF<sub>3</sub> because of concerns about ozone depletion. Identify the species formed from CCIF<sub>3</sub> that is responsible for the catalytic (i) decomposition of ozone in the upper atmosphere. ..... (1) Write an overall equation to represent the decomposition of ozone into oxygen. (ii) ..... (1) (Total 7 marks)


(b)

Chlorine can be used to make chlorinated alkanes such as dichloromethane.

(a) Write an equation for each of the following steps in the mechanism for the reaction of chloromethane ( $CH_3CI$ ) with chlorine to form dichloromethane ( $CH_2CI_2$ ).

Initiation step

Second propagation step $(4)$ When chlorinated alkanes enter the upper atmosphere, carbon-chlorine bonds are broken. This process produces a reactive intermediate that catalyses the decomposition of ozone. The overall equation for this decomposition is $2O_3 \implies 3O_2$ (i) Name the type of reactive intermediate that acts as a catalyst in this reaction. (1) (ii) Write two equations to show how this intermediate is involved as a catalyst in them decomposition of ozone. Equation 1	First propagation step
<ul> <li>The termination step that forms a compound with empirical formula CH<sub>2</sub>Cl.</li> <li>(4)</li> <li>When chlorinated alkanes enter the upper atmosphere, carbon-chlorine bonds are broken. This process produces a reactive intermediate that catalyses the decomposition of ozone. The overall equation for this decomposition is <ul> <li>2O<sub>3</sub> == 3O<sub>2</sub></li> </ul> </li> <li>(i) Name the type of reactive intermediate that acts as a catalyst in this reaction</li></ul>	Second propagation step
<ul> <li>(4)</li> <li>When chlorinated alkanes enter the upper atmosphere, carbon-chlorine bonds are broken. This process produces a reactive intermediate that catalyses the decomposition of ozone. The overall equation for this decomposition is</li> <li>2O<sub>3</sub> = 3O<sub>2</sub></li> <li>(i) Name the type of reactive intermediate that acts as a catalyst in this reaction.</li> <li>(ii) Write two equations to show how this intermediate is involved as a catalyst in them decomposition of ozone.</li> <li>Equation 1</li> </ul>	The termination step that forms a compound with empirical formula $CH_2CI$ .
<ul> <li>2O<sub>3</sub> = 3O<sub>2</sub></li> <li>(i) Name the type of reactive intermediate that acts as a catalyst in this reaction.</li> <li>(ii) Write two equations to show how this intermediate is involved as a catalyst in them decomposition of ozone.</li> <li>Equation 1</li> </ul>	(4) When chlorinated alkanes enter the upper atmosphere, carbon-chlorine bonds are broken. This process produces a reactive intermediate that catalyses the decomposition of ozone. The overall equation for this decomposition is
<ul> <li>(i) Name the type of reactive intermediate that acts as a catalyst in this reaction.</li> <li>(ii) Write two equations to show how this intermediate is involved as a catalyst in them decomposition of ozone.</li> <li>Equation 1</li> </ul>	$2O_3 \implies 3O_2$
<ul> <li>(ii) Write two equations to show how this intermediate is involved as a catalyst in them decomposition of ozone.</li> <li>Equation 1</li> </ul>	(i) Name the type of reactive intermediate that acts as a catalyst in this reaction.
<ul><li>(ii) Write two equations to show how this intermediate is involved as a catalyst in them decomposition of ozone.</li><li>Equation 1</li></ul>	
Equation 1	<ul> <li>(ii) Write two equations to show how this intermediate is involved as a catalyst in them decomposition of ozone.</li> </ul>
	Equation 1
Equation 2 (2) (Total 7 marks)	Equation 2(2) (Total 7 marks)

The refrigerant R410A, used in air conditioners, is a mixture of two fluoroalkanes, 30 pentafluoroethane and difluoromethane. (a) (i) The mechanism for the reaction of fluorine with either an alkane or a fluoroalkane is similar to that for the reaction of chlorine with methane. Name the type of mechanism for the reaction of chlorine with methane. ..... (1) (ii) Write equations for the following steps in the mechanism for the reaction of fluorine with fluoromethane ( $CH_3F$ ) to form difluoromethane ( $CH_2F_2$ ). Initiation step ..... First propagation step ..... Second propagation step

-----

A termination step leading to the formation of 1,2-difluoroethane.

.....

(iii) Write an overall equation for the reaction of fluorine with ethane to form pentafluoroethane  $(CF_3CHF_2)$  by this mechanism.

.....

(1)

(4)

(b) The refrigerant R112A (CCl<sub>3</sub>CF<sub>2</sub>Cl) has been banned because of concerns about ozone depletion.

Give the IUPAC name for CCI<sub>3</sub>CF<sub>2</sub>CI

(1)

	(c)	Nitro	ogen monoxide (NO) catalyses the decomposition of ozone into oxygen.	
		(i)	Write the overall equation for this decomposition.	
				(1)
		(ii)	Use the overall equation to deduce Step <b>3</b> in the following mechanism that shows how nitrogen monoxide catalyses this decomposition.	
			Step 1 $O_3 \longrightarrow O + O_2$	
			Step <b>2</b> NO + $O_3 \longrightarrow NO_2 + O_2$	
			Step <b>3</b>	
			(Total 9 ma	(1) rks)
31	Oxy Chlo the The	vgen a orine a ozone se chlo	nd ozone ( $O_3$ ) both occur as gases in the upper atmosphere. toms catalyse the decomposition of ozone and contribute to the formation of a hole in layer. orine atoms are formed from chlorofluorocarbons (CFCs) such as CF <sub>3</sub> CI	
	(a)	(i)	Give the IUPAC name of $CF_3CI$	
				(1)
		(ii)	Complete the following equation that shows the formation of a chlorine atom from a molecule of $CF_3CI$	
			F 	
			$F - C - Cl \longrightarrow + Cl$	
			Ė	(4)
		(iii)	State what the • represents in Cl•	(1)
				(1)
	(b)	Write into	e two equations that show how chlorine atoms catalyse the decomposition of ozone oxygen.	
		Equa	ation 1	
		Equ	ation 2	·
				(2)

(c) An equilibrium is established between oxygen and ozone molecules as shown below.

	$3O_2(g) \rightleftharpoons 2O_3(g)$	$\Delta H = +284 \text{ kJ mol}^{-1}$	
(i)	State Le Chatelier's principle.		
			(1)
(ii)	Use Le Chatelier's principle to expl increase in the equilibrium yield of	lain how an increase in temperature causes an ozone.	
			(2)
Che pent With refriq	mists supported the legislation to ba ane rather than CFCs as refrigerant reference to its formula, state why gerant.	an the use of CFCs. Modern refrigerators use ts. pentane is a more environmentally acceptable	(-)
			(1)
		(Total	9 marks)

(d)

One of the first substances used as an anaesthetic in medicine was chloroform (trichloromethane, CHCl<sub>3</sub>). By 1950, *halothane* was in common use but by 1990 this had been replaced by more acceptable anaesthetics such as *desflurane*.

CF <sub>3</sub> CHBrCl	CF <sub>3</sub> CHFOCHF <sub>2</sub>
halothane	desflurane

32

One reason for replacing *halothane* was that it is an organic compound that contains chlorine. Chlorine-containing organic compounds are thought to cause damage to the ozone layer in the upper atmosphere.

(a) Name and outline a mechanism for the reaction of chlorine with methane to form chloromethane ( $CH_3CI$ ).

Write an overall equation for the reaction of chlorine with methane to form trichloromethane (CHCl<sub>3</sub>).


(b) Explain how chlorine atoms are formed from chlorine-containing organic compounds in the upper atmosphere.

Explain, with the aid of equations, how chlorine atoms act as a catalyst in the decomposition of ozone into oxygen.

..... ..... ..... ..... ..... ..... ..... ..... ..... ..... ..... Use the formulae of the two anaesthetics, halothane and desflurane, to help to explain why desflurane is considered to be a more environmentally acceptable anaesthetic than halothane. ..... ..... ..... .....

(c)

(2) (Total 13 marks)

(6)

# Mark schemes

н



3

(a)

3,3-dimethylbut-1-ene

accept 3,3-dimethylbutene

Ignore absence of commas, hyphens and gaps Require correct spelling

**Q** 3-chloro-2,2-dimethylbutane

#### OR

Ρ

OR

accept 2-chloro-3,3-dimethylbutane

In Q, "chloro" must come before "dimethyl"

#### (b) M1 Electrophilic addition



M2 must show an arrow from the double bond towards the H atom of HCI M3 must show the breaking of the H–CI bond

M4 is for the structure of the carbocation

**M5** must show an arrow from the lone pair of electrons on the negatively charged chloride ion towards the positively charged carbon atom on <u>their</u> carbocation.

#### NB The arrows here are double-headed

M1 both words required

#### For the mechanism

**M3** Penalise incorrect partial charge on H–Cl bond and penalise formal charges

Ignore partial negative charge on the double bond.

<u>Maximum 3 of 4 marks for a correct mechanism</u> using HBr or the wrong organic reactant or wrong organic product (if shown) or a primary carbocation

Penalise once only in any part of the mechanism for a line and two dots to show a bond

Credit the correct use of "sticks"

For **M5**, credit attack on a partially positively charged carbocation structure, but penalise **M4** 

5

For **M1**, both words required. Accept phonetic spelling



**M2** must show an arrow from the lone pair of electrons **on the nitrogen atom** of an ammonia molecule to the correct C atom

M3 must show the movement of a pair of electrons from the C- Cl bond to the Cl atom. Mark M3 independently provided it is from <u>their original molecule</u> M4 is for the structure of the alkylammonium ion, which could be a condensed formula. A positive charge **must** be shown on, or close to, the N atom. M5 is for an arrow from the N-H bond to the N atom

Award full marks for an  $S_{\text{N}}\text{1}$  mechanism in which M2 is the attack of the ammonia on the intermediate carbocation

# NB These are double-headed arrows

# For the mechanism

Penalise **M2** if  $NH_3$  is negatively charged.

Penalise **M3** for formal charge on C of the C–Cl or incorrect partial charges on C–Cl

Penalise **M3** for an additional arrow from the CI to something else The second mole of ammonia is not essential for **M5**; therefore ignore any species here

Penalise once only for a line and two dots to show a bond

<u>Maximum 3 of 4 marks for the mechanism</u> for wrong organic reactant OR wrong organic product if shown

Accept the correct use of "sticks"

### (d) M1 (base) elimination

# M1 Dehydrohalogenation

# M2 KOH OR NaOH

**M3** Must be consequential on a correct reagent in **M2**, but if incomplete or inaccurate attempt at reagent (e.g. hydroxide ion), **penalise M2 only and mark on** 

# Any **one** from

- high temperature OR hot OR heat / boil under reflux
- <u>concentrated</u>
- alcohol / ethanol (as a solvent) / (ethanolic conditions)

**M3** not "reflux" alone **M3** if a temperature is stated it must be in the range 78°C to 200 °C Ignore "pressure"

# (e) **M1**

 $3NaBr + H_3PO_4 \longrightarrow 3HBr + Na_3PO_4$ 

M1 Credit correct ionic species in the equation

# M2 and M3

SO<sub>2</sub> and Br<sub>2</sub> identified M4

Concentrated sulfuric acid

- is an oxidising agent
- oxidises the bromide (ion) or Br<sup>-</sup> or NaBr or HBr
- is an electron acceptor

In **M2** and **M3** the two gases need to be identified. If equations are used using sulfuric acid and the toxic gases are not identified clearly, allow one mark for the formulas of  $SO_2$  and  $Br_2$ 

- apply the list principle as appropriate but ignore any reference to HBr
- the marks are for identifying the two gases either by name or formula

[19]

4

(i) M1 Elimination

M1 Credit "base elimination" but no other prefix.



Penalise **M2** if covalent KOH Penalise **M4** for formal charge on C or Br of C–Br or incorrect partial charges on C–Br

M2 must show an arrow from the <u>lone pair on the oxygen</u> of a negatively charged hydroxide ion <u>to a correct</u> H atom

Ignore other partial charges

M3 must show an arrow from a correct C–H bond adjacent to the C–Br bond to a correct C-C bond. Only award if an arrow is shown attacking the H atom of a correct adjacent C–H bond in M2

Penalise **once only** in any part of the mechanism for a line and two dots to show a bond

M4 is independent provided it is from their <u>original molecule</u>, **BUT CE=0** <u>for the</u> <u>mechanism (penalise M2, M3 and M4 only)</u> if nucleophilic substitution mechanism is shown

<u>Maximum any 2 of 3 marks for the mechanism</u> for wrong organic reactant or wrong organic product (if shown).

Credit the correct use of "sticks" for the molecule except for the C-H being attacked

Award full marks for an E1 mechanism in which **M4** is on the correct carbocation

Penalise M4, if an additional arrow is drawn from Br eg to K<sup>+</sup>

#### NB These are double-headed arrows

4

(ii) <u>Displayed formula</u> for 3-methylbut-1-ene



All bonds and atoms must be drawn out, but ignore bond angles

) (a)

4

(iii) <u>Position(al)</u> (isomerism or isomer)

Penalise any other words that are written in addition to these.

(b) (i) Displayed formula for 3-methylbutan-2-ol



All bonds and atoms must be drawn out, but ignore bond angles.

- (ii) Any **one** from
  - Lower / decreased temperature OR cold
  - Less concentrated (comparative) OR dilute KOH
  - Water (as a solvent) / (aqueous conditions)
     Ignore "pressure".
- (iii) <u>Nucleophilic substitution</u> Both words needed - credit phonetic spelling.
- (iv) (Strong / broad) absorption / peak in the range <u>3230 to 3550</u> cm<sup>-1</sup> or specified value in this range or marked correctly on spectrum
   Allow the words "dip" OR "spike" OR "trough" OR "low transmittance" as alternatives for absorption.

[10]

1

1

1

1

5

For **M1**, both words required Accept phonetic spelling



#### For the mechanism

M2 Ignore partial negative charge on the double bond

M2 must show an arrow from the double bond towards the H atom of the H–Br molecule

**M3** Penalise partial charges on H–Br bond if wrong way and penalise formal charges

M3 must show the breaking of the H–Br bond

Penalise once only in any part of the mechanism for a line and two dots to show a bond

M5 must show an arrow from the lone pair of electrons on the negatively charged bromide ion towards the correct (positively charged) carbon atom

<u>Maximum any 3 of 4 marks for the mechanism</u> for wrong (organic) reactant OR wrong organic product (if shown) OR primary carbocation Accept the correct use of sticks

#### NB These are double-headed arrows

#### (b) M1 Nucleophilic substitution

For **M1**, both words required Accept phonetic spelling



For the mechanism Penalise M2 if  $NH_3$  is negatively charged

M2 must show an arrow from the lone pair of electrons **on the nitrogen atom** of an ammonia molecule to the correct C atom

Penalise **M3** for formal charge on C of the C–Br or incorrect partial charges on C–Br

Penalise M3 for an additional arrow from the Br to something else

M3 must show the movement of a pair of electrons from the C–Br bond to the Br atom. Mark **M3** independently provided it is from <u>their original molecule</u>

The second mole of ammonia is not essential for **M5**; therefore ignore any species here

M4 is for the structure of the alkylammonium ion, which could be a condensed formula. A positive charge **must** be shown on / or close to, the N atom

Penalise once only for a line and two dots to show a bond

M5 is for an arrow from the N–H bond to the N atom

<u>Maximum any 3 of 4 marks for the mechanism</u> for wrong organic reactant **OR** wrong organic product if shown

Award full marks for an  $S_N$ 1 mechanism in which **M2** is the attack of the ammonia on the intermediate carbocation

Accept the correct use of "sticks"

### NB These are double-headed arrows

M1 (addition) polymerisation OR poly-addition
 Ignore "additional"
 Credit polyprop-1-ene and polypropylene

M2 poly(propene) / polypropene Penalise "condensation polymerisation"



Penalise M1 if covalent KOH

M1 must show an arrow from the lone pair on the oxygen of a negatively charged hydroxide ion to a correct H atom

Penalise **M3** for formal charge on C of C–Br or incorrect partial charges on C–Br.

M2 must show an arrow from a correct C–H bond adjacent to the C–Br bond to the appropriate C–C bond. Only award if an arrow is shown <u>attacking</u> the H atom of a correct C–H bond in **M1** 

Ignore other partial charges Penalise once only in any part of the mechanism for a line and two dots to show a bond

M3 is independent provided it is from their <u>original molecule</u>, but **CE=0 if nucleophilic substitution** 

Maximum any 2 of 3 marks for wrong organic reactant

Award full marks for an E1 mechanism in which M3 is on the correct carbocation.

Accept the correct use of "sticks" for the molecule except for the C–H being attacked

#### NB These are double-headed arrows

6

(a)

(i)



Penalise one mark from <u>their</u> total if half-headed arrows are used Penalise **M3** for formal charge on C of the C-Br or incorrect partial charges on C-Br Ignore other partial charges [15]

**M1** must show an arrow from the lone pair on oxygen of a negatively charged hydroxide ion to the correct H atom

Penalise once only in any part of the mechanism for a line and two dots to show a bond.

**M2** must show an arrow from the correct C–H bond to the correct C–C bond. Only award if an arrow is shown <u>attacking</u> the H atom of the correct C–H bond in **M1** 

M3 is independent but CE=0 if nucleophilic substitution

#### N.B these are double-headed arrows

- (ii) M1 E isomer M2 Z isomer н  $H_5C_2$ H<sub>5</sub>C<sub>2</sub>  $_{2}H_{5}$ Award 1 mark if both correct stereoisomers but in the wrong places Accept no other alkenes. Be reasonably lenient on the bonds to ethyl (or to  $CH_2CH_3$ ) since the question is about E and Z positions but penalise once only if connection is clearly to the  $CH_3$  of  $CH_2CH_3$ Accept linear structures 2 (iii) M1 (Compounds / molecules with) the same structural formula Penalise M1 if "same structure" M2 with atoms/bonds/groups arranged differently in space Ignore references to "same molecular formula" or "same empirical
  - OR

<u>atoms/bonds/groups</u> that have <u>different spatial arrangements / different</u> <u>orientation</u>. *Mark independently* 

formula" or any reference to "displayed formula"

2



**M1**must show an arrow from the double bond towards the H atom of the H – O bond OR HO on a compound with molecular formula for  $H_2SO_4$ 

M1 could be to an H+ ion and M2 an independent O – H bond break on a compound with molecular formula for  $H_2SO_4$ 

M1 Ignore partial negative charge on the double bond.

**M2** must show the breaking of the O - H bond.

**M2** Penalise partial charges on O – H bond if wrong way and penalise formal charges In M2 do not penalise incorrect structures for  $H_2SO_4$ 

M3 is for the structure of the carbocation.

**M4** must show an arrow from the lone pair of electrons on the correct oxygen of the negatively charged ion towards a correct (positively charged) carbon atom.

 $M4 NOT HSO_4^-$ 

For **M4**, credit <u>as shown</u> or  $\overline{\ OSO_3H}$  ONLY with the negative charge anywhere on this ion

OR <u>correctly</u> drawn out with the negative charge placed correctly on oxygen

Penalise once only in any part of the mechanism for a line and two dots to show a bond

#### NB The arrows here are double-headed

<u>Max 3 of any 4 marks</u> for wrong organic reactant or wrong organic product (if shown) Accept the correct use of "sticks"

[11]

4

(a) (i) M1 Elimination

7



 $H_3C - CH_2 - CH = CH - CH_3 + H_2O + Br$ 

**M2** must show an arrow from the <u>lone pair on the oxygen</u> of a negatively charged hydroxide ion <u>to a correct</u> H atom

**M3** must show an arrow from a C-H bond adjacent to the C-Br bond towards the appropriate C-C bond. Only award if a reasonable attempt has been made at the attack on the H atom of the appropriate adjacent C-H

M4 is independent provided it is from their original molecule

Award full marks for an E1 mechanism in which M3 is on the correct carbocation.

#### N.B. These are double-headed arrows

For M1, accept "Base elimination" but <u>no other prefix</u>.
Penalise M2 if covalent KOH
Penalise M4 for formal charge on C of C-Br or incorrect partial charges on C-Br
Ignore other partial charges
Penalise once only in any part of the mechanism for a line and two dots to show a bond.
<u>Max any 2 of 3 marks for the mechanism</u> for wrong reactant (or wrong product if shown).
Accept the correct use of "sticks" for the molecule except for the C-H being attacked

4

### (ii) Structure for pent-1-ene

 $CH_3CH_2CH_2CH=CH_2$ Penalise  $C_3H_7$ Accept correct "sticks"

### (b) M1 Electrophilic addition



M2 must show an arrow from the double bond towards the Br atom of the Br-Br molecule

M3 must show the breaking of the Br-Br bond.

M4 is for the structure of the tertiary carbocation with Br on the correct carbon atom.

**M5** must show an arrow from the lone pair of electrons on the negatively charged bromide ion towards the positively charged carbon atom.

### N.B. These are double-headed arrows

For M1, both words required. For the mechanism M2 Ignore partial negative charge on the double bond. M3 Penalise partial charges on Br-Br bond if wrong way and penalise formal charges Penalise once only in any part of the mechanism for a line and two dots to show a bond <u>Max any 3 of 4 marks for the mechanism</u> for wrong organic reactant or wrong organic product (if shown) or primary carbocation. If HBr is used, max 2 marks for their mechanism Accept the correct use of "sticks"

#### (c) M1 Nucleophilic substitution



**M2** must show an arrow from the lone pair of electrons on the nitrogen atom of an ammonia molecule to the C atom.

**M3** must show the movement of a pair of electrons from the C-Br bond to the Br atom. **M3** is independent provided it is from their <u>original molecule</u>

**M4** is for the structure of the alkylammonium ion, which could be a condensed formula. A positive charge must be shown on/or close to, the N atom.

**M5** is for an arrow from the N-H bond to the N atom.

Award full marks for an  $S_N$ 1 mechanism in which M2 is the attack of the ammonia on the intermediate carbocation.

#### N.B. These are double-headed arrows

For M1, both words required.
Penalise M2 if NH<sub>3</sub> is negatively charged.
Penalise M3 for formal charge on C or incorrect partial charges
The second mole of ammonia is not essential for M5; therefore ignore any species here.
Penalise once only for a line and two dots to show a bond.
Max any 3 of 4 marks <u>for the mechanism</u> for wrong organic reactant (or wrong organic product if shown)
Accept the correct use of "sticks"

5

8

(a)

# (i) <u>Electron pair donor</u>

#### OR

Species which uses a pair of electrons to form a co-ordinate/covalent bond.

Credit "lone pair" as alternative wording Credit "electron pair donator"

### (ii) <u>Replacement of the halogen</u> (atom) (by the nucleophile)

#### OR

The <u>carbon-halogen bond/C-X</u> breaks and a bond forms with the nucleophile or between the carbon and the nucleophile

They must describe the idea of substitution in a haloalkane. Accept the idea that a nucleophile replaces the halogen which becomes a halide ion Penalise reference to "halogen molecule" and penalise the idea that the haloalkane contains a halide

1

1

#### (iii) Splitting molecules using/by water

#### OR

breaking/splitting/dissociating (C<sub>i</sub>VX) bond(s)/using/by water NOT simply the reaction with water or simply the addition of water. Ignore "compound"

(iv) (Heat) <u>energy/enthalpy required/needed/absorbed (at constant</u> pressure) <u>to break/split it/the</u> (carbon-halogen) <u>bond</u>

#### OR

(Heat) <u>energy/enthalpy required/needed/absorbed</u> (at constant pressure) for <u>homolysis</u> of <u>the</u> (C–X/the carbon-halogen) <u>bond</u> *Ignore bond formation Ignore "average*"

(b)



- M1 must show an arrow from the lone pair of electrons on the oxygen atom of the negatively charged hydroxide ion to the central C atom.
- M2 must show the movement of a pair of electrons from the C-Br bond to the Br atom. Mark M2 independently.

Award full marks for an  $S_N$ 1 mechanism in which M1 is the attack of the hydroxide ion on the intermediate carbocation.

Penalise M1 if covalent KOH is used Penalise M2 for formal charge on C or incorrect partial charges Penalise once only for a line and two dots to show a bond. Max 1 mark for the wrong reactant Accept the correct use of "sticks"

(c) (i)



- M1 must show an arrow from the lone pair on oxygen of a negatively charged hydroxide ion to the correct H atom
- M2 must show an arrow from the correct C-H bond to the C-C bond and should only be awarded if an attempt has been made at M1

1

M3 is independent provided it is from the original molecule

Award full marks for an E1 mechanism in which M2 is on the correct carbocation.

Penalise M1 if covalent KOH Penalise M3 for formal charge on C or incorrect partial charges Penalise once only for a line and two dots to show a bond. Max 2 marks for wrong reactant Accept the correct use of "sticks" for the molecule except for the C-H being attacked

3

2

(ii) M1 <u>Stated</u> that the spectrum has an <u>absorption/absorbance/</u> <u>peak in the range 1620 cm<sup>-1</sup> to 1680</u> (cm<sup>-1</sup>) or specified <u>correctly in this range</u> from the spectrum

#### M2 depends on correct range or wavenumber being specified

M2 (Infrared absorption) <u>due to C=C OR carbon-carbon double bond</u>
 *QoL for correct M1 statement which includes both the word absorption (or alternative) and the correct range or wavenumber* Allow "peak" OR "dip" OR "spike" OR "trough"
 OR "low transmittance" as alternatives for absorption.
 For M2 it is not sufficient simply to state that an alkene has C=C

M2 could be on the spectrum

Ignore reference to other absorptions



1

**M1** must show an arrow from the lone pair of electrons on the oxygen atom of the negatively charged hydroxide ion to the central C atom.

**M2** must show the movement of a pair of electrons from the C-Br bond to the Br atom. Mark M2 independently.

Penalise M1 if covalent KOH is used Penalise M2 for formal charge on C or incorrect partial charges Penalise once only for a line and two dots to show a bond. Max 1 mark <u>for the mechanism</u> for the wrong reactant and/or "sticks"

Ignore product

Award full marks for an  $S_N$ 1 mechanism in which M1 is the attack of the hydroxide ion on the intermediate carbocation.

(ii) 2-bromopropane ONLY

1

(iii) Polar C–Br OR polar carbon–bromine bond OR dipole on C–Br
 OR δ+ (δ–)
 C atom of carbon–bromine bond is δ+/electron deficient OR C–Br

(Credit carbon-halogen bond as an alternative to carbon-bromine bond)

It must be clear that the discussion is about the carbon atom of the C–Br bond. NOT just reference to a polar molecule. Ignore X for halogen

1

### (b) Elimination

Credit "base elimination" but NOT "nucleophilic elimination" No other prefix.



3

1

**M1** must show an arrow from the lone pair on oxygen of a negatively charged hydroxide ion to the correct H atom

**M2** must show an arrow from the correct C-H bond to the C-C bond and should only be awarded if an attempt has been made at M1 **M3** is independent.

> <u>Mechanism</u> Penalise M1 if covalent KOH Penalise M3 for formal charge on C or incorrect partial charges Penalise once only for a line and two dots to show a bond. Max 2 marks <u>for the mechanism</u> for wrong reactant and/or "sticks" Ignore product

Award full marks for an E1 mechanism in which M2 is on the correct carbocation.

(c) Any one condition from this list to favour elimination;

Apply the list principle

- <u>alcohol(ic)/ethanol(ic)</u> (solvent)
- <u>high concentration</u> of KOH/alkali/hydroxide *OR* <u>concentrated</u> KOH/hydroxide *Ignore "aqueous"*
- high temperature or hot or heat under reflux or T = 78 to 100°C Ignore "excess"
- (d) (i) <u>Addition</u> (polymerisation) ONLY Penalise "additional"

1

(ii) <u>But-2-ene</u> ONLY (hyphens not essential)

Ignore references to cis and trans or E/Z Ignore butane

[12]

1

1

10

# Electron pair donor **OR**

Species which uses a pair of electrons to form a co-ordinate / covalent bond.

**QoL** Credit "lone pair" as alternative wording

(b)

(a)



- M1 Must show an arrow from the lone pair of electrons on the carbon atom of the negatively charged cyanide ion to the central C atom.
- M2 Must show the movement of a pair of electrons from the C-Br bond to the Br atom. Mark M2 independently.

Award full marks for an  $S_N$ 1 mechanism in which M1 is the attack of the cyanide ion on the intermediate carbocation.

Penalise M1 if covalent KCN is used Penalise M2 for formal charge on C or incorrect partial charges Penalise once only for a line and two dots to show a bond. Max 1 mark for the wrong reactant or "sticks"

(c) Ethylamine / CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub> is a nucleophile

# OR

Ethylamine could react further

# OR

Ethylamine could make secondary / tertiary amines

# OR

To make reaction with ammonia more likely

# OR

To minimise further substitution

# OR

The idea of releasing free amine from the salt

# OR

The idea of removing a proton from the intermediate

alkylammonium ion

# OR

The idea that ammonia acts <u>both</u> initially as a nucleophile and then as a base

Do not credit a simple reference to the equation or the mechanism requiring two moles of ammonia.

Credit "base elimination" but NOT "nucleophilic elimination" No other prefix.

HOP  
HMZH  
H
$$-c$$
  
H $-c$   
H $-c$ 

- M1 Must show an arrow from the lone pair on oxygen of a negatively charged hydroxide ion to the correct H atom
- M2 Must show an arrow from the correct C-H bond to the C-C bond and should only be awarded if an attempt has been made at M1
- M3 Is independent.

Award full marks for an E1 mechanism in which M2 is on the correct carbocation.

<u>Mechanism</u> Penalise M1 if covalent KOH Penalise M3 for formal charge on C or incorrect partial charges Penalise once only for a line and two dots to show a bond. Max 2 marks **for the mechanism** for wrong reactant or "sticks"

[8]

3

1

**11** <sup>(a)</sup>

(i)



If wrong carbocation, lose structure mark If wrong alkene, lose structure mark Can still score <sup>3</sup>/<sub>4</sub> i.e. penalise M3 Penalise M2 if polarity included incorrectly no bond between H and Br bond is shown as — or — (ii)

12

 $\oplus$ 

 $CH_3CH_2CH_2$ 

credit secondary carbocation here if primary carbocation has been used in (i)

Ignore attack on this carbocation by  $\ddot{B}r \Theta$ 1 Structure:  $H_3C - CH - CH_3$  (1)  $\begin{bmatrix} insist on \\ C - OH bond \end{bmatrix}$ (b) (i) 1 Name: propan-2-ol Not 2-hydroxypropane 1 Name of mechanism: nucleophilic substitution (both words) (ii) (NOT  $S_N 1$  or  $S_N 2$ ) 1 Mechanism:  $\begin{array}{c} M1 \\ arrow (1) \quad \swarrow^{Br} \\ H_{3}C - CH - CH_{3} \longrightarrow CH_{3}CH(OH)CH_{3} + Br\Theta \\ \Theta_{HO} \end{array}$   $\begin{array}{c} \Theta_{HO} \\ (1) \text{ arrow from} \\ \text{lone pair} \end{array}$ M1 (M2) lone pair penalise incorrect polarity on C-Br (M1) Credit the arrows even if incorrect haloalkane If S<sub>N</sub>1, <u>both marks</u> possible 2 elimination (C) (i) 1 (ii) base OR proton acceptor NOT nucleophile 1

[12]

[1]

(a)

(penalise other words before 'elimination' e.g. nucleophilic)

M1: curly arrow from lone pair of electrons on oxygen of hydroxide ion

1

		(insist on a lone pair of electrons on the oxygen atom and a negative charge, but only credit this mark if the attack is to a correct H atom)	1
	<b>M2</b> : of the	curly arrow from the middle of the C-H bond to the middle e C–C bond	
		(only credit this mark if the arrow originates from the correct C–H bond and if an attempt has been made at M1)	1
	<b>M3</b> : o the B	curly arrow from the <u>middle of the C–Br bond</u> towards/alongside ar atom	
		(credit M3 independently unless the bond breaking is contradicted by an additional arrow)	
		(penalise curly arrow if the C–Br has a formal positive charge) (credit full marks for an E1 mechanism, with M2 awarded for a correct curly arrow on the correct carbocation)	
		(award a maximum of two marks for either an incorrect haloalkane or an incorrect organic product)	
		(maximum 2 marks for use of 'sticks' for the haloalkane, unless RE from 2(b), when credit can be given)	
(b)	(i)	M1: compounds with the same structural formula	1
		M2: but the bonds/groups/atoms have different spatial arrangements or orientation or configuration/are arranged differently in space/3D (ignore reference to the same molecular formula for M1)	
	(ii)	<b>M1</b> : correct structural representation for cis-but-2-ene <u>and</u> its name or its identification as the cis isomer	1
		M2: correct structural representation for trans-but-2-ene and its name or its identification as the trans isomer (accept representations which are 90° to linear) (award one mark for two correct structures but either wrong/no names) (maximum 1 mark for an incorrect alkene)	1

(c) nucleophile or electron pair donor (penalise 'base')

14

 (d) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br + 2NH<sub>3</sub> → CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub> + NH<sub>4</sub>Br (*M1* correct product) (*M2* balanced equation using 2NH<sub>3</sub> and leading to NH<sub>4</sub>Br) (penalise M1 for use of C<sub>4</sub>H<sub>9</sub>NH<sub>2</sub> or for incorrect haloalkane, but allow consequent correct balancing of equation with 2 moles of ammonia)
 (1–)butylamine (credit 1–aminobutane and butyl–1–amine) (award QoL mark for correct spelling)

[13]

1

2

1

2-bromobutane; (a) 1 (b) Elimination; (penalise "nucleophilic" OR "electrophilic" before the word "elimination") 1 M1: curly arrow from lone pair on oxygen of hydroxide ion to H atom on correct C-H adjacent to C-Br; (penalise M1 if KOH shown as covalent with an arrow breaking the bond) 1 M2: curly arrow from single bond of adjacent C-H to adjacent single bond C-C; (only credit M2 if M1 is being attempted to correct H atom) 1 M3: curly arrow from C-Br bond to side of Br atom; (credit M3 independently unless arrows contradict) (Credit possible repeat error from 2(c)(iii) for M3) (If the wrong haloalkane is used OR but-1-ene is produced, award MAX. 2 marks for the mechanism) (If E1 mechanism is used, give full credit in which M1 and M2 are for correct curly arrows on the correct carbocation)

	(c)	(i)	(structural) isomers/hydrocarbons/compounds/they have <u>the same</u> molecular formula, but different structural formulas/different structures; 1		
			(penalise statements which are not expressed in good English and which do not refer clearly to structural <u>isomers</u> i.e. plural) (penalise statements which refer to "different (spatial) arrangements")		
			(credit" different displayed formulas") (Q of L mark)		
		(ii)	Correct structure for but-1-ene;	1	
					[7]
15					[1]
16	(a)	M1 ( H ate	curly arrow <u>from lone pair</u> on oxygen of hydroxide ion to om on C-H adjacent to C-Br		
				1	
		M2 c <u>to ac</u>	curly arrow <u>from single bond</u> of adjacent C-H Jjacent single bond C-C		
			(only credit M2 if M1 is being attempted to correct H atom)	1	
		МЗ с	curly arrow from C-Br bond to side of Br atom		
			(credit M3 independently)	1	
	(b)	MI c desi	redit a correct structure for either geometrical E-Z isomer <u>and</u> its gnation as either <i>cis</i> or <i>trans.</i>		
		OR ( (igno	credit <u>two</u> correct geometrical E-Z isomer structures ore the names)		
		OR ( pent	credit <u>two</u> correct names for <i>cis</i> pent-2-ene and <i>trans</i> -2-ene (ignore the structures)		
				1	
		M2 o nam	credit a second mark if all four parts of the required structures and es are correct.		
			(credit "linear" structures) (insist on the alkyl groups being attached clearly by C-C bonds)		
				1	

(c)	(i)	MI curly arrow from middle of C = C bond to H atom on H-Br (penalise M1 if partial negative charge or formal positive charge on H) (penalise MI if pent-2-ene is used)				
		M2 curly arrow from H-Br bond to side of Br atom	1			
		M3 correct structure for correct secondary carbocation	1			
		M4 curly arrow from lone pair on bromide ion to the positive <u>carbon</u> of carbocation, ensuring that bromide ion has a negative charge.				
		(with the exception of pent-2-ene, if the wrong alkene is used, only penalise the structure M3) (penalise the use of two dots in addition to a covalent bond, once only)				
		Unity)	1			
	(ii)	1-bromopentane	1			
	(iii)	MI 2-bromopentane is formed <i>via</i> the secondary (or 2°) carbocation				
		OR 1-bromopentane is formed <i>via</i> the primary (or 1°) carbocation M2 a secondary carbocation is more stable than a primary carbocation - award this mark only if the quality of language justifies the award.	1			
		(the argument must involve clear statements about carbocations)	1			

[12]

[1]

18

(a)

#### ignore heat

Condition mark <u>linked to correct reagent</u> but award M2 if OH<sup>-</sup> or base or alkali mentioned

<u>Reaction 3</u>: concentrated  $H_2SO_4$  OR  $H_3PO_4$  M1 (1) heat (1) M2 OR 150°C - 200°C

Condition mark <u>linked to correct reagent</u> but award M2 if  $H_2SO_4$  or  $H_3PO_4$ , but <u>not</u> concentrated

Penalise reagent and condition if dilute H<sub>2</sub>SO<sub>4</sub> / H<sub>3</sub>PO<sub>4</sub>

(b) Mechanism:





E1 mechanism possible in which M2 H 
$$- C + C + H$$

<u>Name</u>: of mechanism = elimination **(1)** NOT dehydrohalogenation Ignore "base" OR "nucleophilic" before elimination

Reason: Reaction 2 has (very) low yield (1)

QoL OR chloroethane has to be made (from ethane) OR chloroethane is expensive OR chloroethane is not redily available 4

#### (c) Mechanism:



(M3 could be awarded on protonated alcohol)  $^{\rm M3}$ 

# Name of mechanism = elimination (1) NOT dehydration alone



[15]

6





restricted rotation OR no rotation OR cannot rotate (1) (ii)



M1 and M2 independent Curly arrows <u>must</u> be from a bond or a lone pair Do not penalise sticks

Penalise M1 if Na OH precedes (penalise this once) Penalise incorrect  $\delta + \delta$  – for M2 Penalise + on C atom for M2 Only allow M1 for incorrect haloalkane

Role of the hydroxide ion: nucleophile (1) electron pair donor lone pair donor NOT nucleophilic substitution (ii) Mechanism:





Only allow M1 and M2 for incorrect haloalkane unless RE on (i)
+ charge on H on molecule, penalise M1
M3 independent
M2 must be to correct C–C
M1 must be correct H atom
Credit M1 and M2 via carbocation mechanism
No marks after any attack of C ⊕ by OH<sup>-</sup>

Role of the hydroxide ion: base (1) proton acceptor accepts H<sup>+</sup>

7

[10]
(a) (i)



If wrong carbocation, lose structure mark If wrong alkene, lose structure mark Can still score ¾ i.e. penalise M3 Penalise M2 if polarity included incorrectly no bond between H and Br bond is shown as — or — .

Ignore attack on this carbocation by  $Br^{\mathbf{\Theta}}$ 

5

(b) (i) Structure:

 $\begin{array}{c} OH \\ I \\ H_3 C - CH - CH_3 \end{array} (1) \qquad \begin{bmatrix} \text{insist on} \\ C - OH \text{ bond} \end{bmatrix}$ 

No credit for propan-1-ol even when named correctly Credit propane-2-ol

Name: propan-2-ol (1) Not 2-hydroxypropane (ii) Name of mechanism: nucleophilic substitution (1) (both words) (NOT  $S_N$ 1 or $S_N$ 2)

Mechanism:

$$\begin{array}{ccc} & M1 \\ \text{arrow} & \textbf{(l)} & \underbrace{\mathcal{T}}_{\text{Br}}^{\text{Br}} \\ & H_3 \text{C} - \text{CH} - \text{CH}_3 & \longrightarrow & \text{CH}_3 \text{CH}(\text{OH})\text{CH}_3 + & Br \Theta \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & &$$

penalise incorrect polarity on C-Br (M1) Credit <u>the arrows</u> even if incorrect haloalkane If  $S_N 1$ , <u>both marks</u> possible

- (c) (i) elimination (1) Ignore nucleophylic elimination Penalise electrophilic elimination
  - (ii) base **(1)** OR proton acceptor NOT nucleophile (base)

21

[12]

(a) Identity of X; 2-methylpropene (1)
 Absorption at 1650 cm<sup>-1</sup> indicates an alkene present (1)
 OR a chemical answer e.g. Br<sub>2</sub> (aq) brown to colourless

2

5

(b) Reagents

Step 1 KOH (allow NaOH) (1) alcoholic (1) warm (1)

 $A \rightarrow X$ 

Only allow solvent and warm if reagent correct

Step 2 HBr (1)

Mechanism:



Or a carbocation mechanism

 $X \rightarrow B$ 

Mechanism



(c) A gives three peaks (1)
 B gives one peak (1)
 Allow one for "A has more peaks

# Allow one for "A has more peaks than B" when no number of peaks is given

[15]

[1]

11

2

**2**2

23

(a) Alcohol: Reaction = Substitution (/ hydrolysis) (1)
 Ignore reference to nucleophilic, but electrophilic give zero

Alcohol: Role = nucleophile (/ lone pair donor) (1)

```
Alkene: reaction = elimination (1)
```

Ignore ref to nucleophilic or electrophilic

Alkene: base (/ proton acceptor) **(1)** *If no indication of order in (a) assume as in question. If order is wrong can still score 'role' mark.*  (b) Alcohol: Role = butan-2-ol (1) Not 2-hydroxybutane or but-2-ol

## Appropriate structure for $CH_3CH(OH) CH_2CH_3(1)$

Brackets not essential

 $S_N 2$  version S<sub>N</sub>1 version  $\overset{_{\delta_{+}}}{\mathrm{C}}-\overset{_{\delta_{-}}}{\mathrm{Br}}$  bond is polar C-Br bond is polar (1) C–Br bond breaks (1) Lone pair of OHforming carbocation / carbonium ion (1) Attacks the  $C^{\delta+}$ 

> M1 can be scored from a diagram, M2 and M3 from written explanation only



### If but-2-ene not given here it may be obtained from cis / trans isomer

H lost from different carbon atoms (1)

H removes from  $C^1$  and  $C^3$  to give two isomers (1) Draws clear Cis and trans isomers for but-2-ene

Can score these marks from a diagram



[17]

8

Name of mechanism: nucleophilic substitution (1) Mechanism:



Marks  $S_N$ 1 using same points : M2 requires

# $\begin{array}{c} {}_{\mathrm{CH}_3} = \overset{\mathrm{CH}_3}{\underset{\Phi}{\mathsf{C}}} = {}_{\mathrm{Br}}\\ {}_{\mathrm{C}}\\ {}_{\mathrm{NH}_3}\end{array}$

(b) Role of potassium hydroxide: Base (1) Mechanism:

$$\begin{array}{c} \begin{array}{c} H \\ CH_{3} - \begin{array}{c} C \\ \end{array} \\ H - \begin{array}{c} C \\ \end{array} \\ H - \begin{array}{c} C \\ \end{array} \\ H \end{array} \end{array} \begin{array}{c} \begin{array}{c} (1) \\ Br \\ \end{array} \\ H \end{array} \end{array} \begin{array}{c} CH_{3} - \begin{array}{c} H \\ CH_{3} \\ \end{array} \\ \begin{array}{c} H \\ CH_{2} \end{array} \end{array} \begin{array}{c} (1) \\ CH_{2} \\ \end{array} \end{array}$$

Mark E1 using same points

$$\begin{array}{c} M2/M3 \\ CH_3 - \begin{array}{c} H \\ C \\ \end{array} \\ \oplus \end{array} \\ \begin{array}{c} H \\ H \\ H \\ \mathcal{L}_{:OH^{-1}} \end{array}$$

Η

5

5

(a)

(a) M1 •Cl +  $O_3 \rightarrow$  •ClO +  $O_2$ 

M2 •CIO +  $O_3 \rightarrow •CI + 2O_2$ 

M1 and M2 could be in either order Credit the dot anywhere on the radical Penalise absence of dot once only Individual multiples acceptable but both need to be doubled if two marks are to be awarded Ignore state symbols

\_c\_\_c (b) Must be displayed formula 1 Does not contain CI or does not release CI (atoms/radicals) (c) or no C-CI bonds or C-F bond(s) strong / does not break / no F (atom/radicals) released 1 M1  $CHF_2CH_3 + \bullet F \rightarrow \bullet CF_2CH_3 + HF$ (d) 1 M2  $\bullet CF_2CH_3 + F_2 \rightarrow CF_3CH_3 + \bullet F$ 1 M1 and M2 could be in either order Credit the dot anywhere on the radical Penalise absence of dot once only (e) M1 moles  $CF_3CH_3 = 1410/84(.0)$  (=16.8, 16.79 mol) 1 molecules = M1 ×  $6.022 \times 10^{23} = 1.01 \times 10^{25}$  (3sf only) M2 1 Correct answer scores both marks Allow M2 for M1 × Avogadro with answer to 3 sf (but must have attempted to calculate moles for M1) Ignore incorrect units (bonds) vibrate/stretch/bend OR (as bonds) are polar (f) NOT polar molecules; 'they' = bonds 1

1

1

(a)

UV light

	$CCl_4 \longrightarrow CCl_3 + \bullet Cl$	1
(b)	$CI \bullet + O_3 \longrightarrow CIO \bullet + O_2$	-
	$CIO \bullet + O_3 \longrightarrow CI \bullet + 2O_2$	1
(c)	$M_{\rm r}$ of CF <sub>3</sub> CI = 104.5	
	Moles freon = $1.78 \times 10^{-4} \times 10^{3} / 104.5 = 1.70 \times 10^{-3}$	1
	Number of molecules = $1.70 \times 10^{-3} \times 6.02 \times 10^{23} = 1.02 \times 10^{21}$	1
	Molecules in 500 cm <sup>3</sup> = (1.02 × 10 <sup>21</sup> × 500 × 10 <sup>-6</sup> ) / 100 = 5.10 × 10 <sup>15</sup>	
	Allow answer in the range 5.10–5.13 $\times$ 10 <sup>15</sup>	
	Answer must be given to this precision	
		1 [7]
(a)	(i) Initiation Br <sub>2</sub> $\longrightarrow$ 2Br•	
	<b>First propagation</b> Br• + CHF <sub>3</sub> $\longrightarrow$ •CF <sub>3</sub> + HBr	
	Second propagation Br <sub>2</sub> + •CF <sub>3</sub> $\longrightarrow$ CBrF <sub>3</sub> + Br•	
	Termination $2 \bullet CF_3 \longrightarrow C_2F_6 \ OR \ CF_3CF_3$ $OR$ $2Br \bullet \longrightarrow Br_2$ $OR$ $Br \bullet + \bullet CF_3 \longrightarrow CBrF_3$ $Penalise \ absence \ of \ dot \ once \ only$ $Credit \ the \ dot \ anywhere \ on \ the \ radical$	4
	(ii) Ultra-violet / uv / sunlight	
	T > 100°C OR <u>high</u> temperature	1





Displayed formula required with the radical dot on carbon

1

(ii) (The) <u>C-Br</u> (bond) breaks more readily / is weaker than (the) <u>C-CI</u> (bond) (or converse)

#### OR

The <u>C–Br bond enthalpy / bond strength</u> is less than that for <u>C–CI</u> (or converse)

Requires a comparison between the two bonds

Give credit for an answer that suggests that the UV frequency / energy may favour  $\underline{C-Br}$  bond breakage rather than  $\underline{C-CI}$  bond breakage

Ignore correct references either to size, polarity or electronegativity Credit correct answers that refer to, for example "the bond between carbon and bromine requires less energy to break than the bond between carbon and chlorine"

(iii) **M1** 

 $Br \bullet + O_3 \longrightarrow Br O \bullet + O_2$ 

#### M2

 $BrO_{\bullet} + O_3 \longrightarrow Br_{\bullet} + 2O_2$ 

M1 and M2 could be in either order Credit the dot anywhere on the radical Penalise absence of dot once only Penalise the use of multiples once only

#### M3 One of the following

They / it / the bromine (atom)

- does not appear in the overall equation
- is regenerated
- is unchanged <u>at the end</u>
- has <u>not been used up</u>
- provides an alternative route / mechanism

[10]

(a)

(i)

M1 Initiation

 $Cl_2 \longrightarrow 2Cl \bullet$ 

Penalise absence of dot once only.

#### M2 First propagation

 $Cl + CHF_3 \longrightarrow CF_3 + HCl$ *Penalise + or - charges <u>every time</u>.* 

#### M3 Second propagation

 $Cl_2 + CF_3^{\bullet} \longrightarrow CCIF_3 + Cl^{\bullet}$ Credit  $CF_3^{\bullet}$  with the radical dot above / below / to either side.

#### M4 Termination (must make C<sub>2</sub>F<sub>6</sub>)

 $2 \operatorname{CF}_{3^{\bullet}} \longrightarrow \operatorname{C}_{2}\operatorname{F}_{6} \operatorname{or} \operatorname{CF}_{3}\operatorname{CF}_{3}$ Mark independently.

(ii) ultra-violet / uv / sun light

**OR** (very) high temperature

**OR** 500 °C  $\leq$  T  $\leq$  1000 °C

**OR** 773 K ≤ T ≤ 1273 K

- (b) (i) Cl• OR chlorine atom / chlorine (free-) radical / Cl (atom) Not 'chlorine' alone.
   Credit 'Cl' alone on this occasion.
  - (ii)  $2O_3 \longrightarrow 3O_2$

Or multiples.

Ignore state symbols. If the correct answer is on the line OR clearly identified below some working, then ignore any working.

**F**=

1

4

1

1

[7]

(a) Initiation → 2CI•  $Cl_2$  – Penalise absence of dot once only. **First propagation**  $CI \bullet + CH_{3}CI \longrightarrow \bullet CH_{2}CI + HCI$ Credit the dot anywhere on the radical. Second propagation  $Cl_2 + \bullet CH_2Cl \longrightarrow CH_2Cl_2 + Cl \bullet$ Termination (must make 1,2-dichloroethane)  $2 \bullet CH_2CI \longrightarrow CH_2CICH_2CI$ Penalise C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> 4 (b) (chlorine free) radical (i) Ignore formula. 1 (ii) M1  $Cl \bullet + O_3 \longrightarrow ClO \bullet + O_2$  $CIO + O_3 \longrightarrow CI + 2O_2$ M2 M1 and M2 could be in either order. Credit the dot anywhere on the radical. Penalise absence of dot once only. Individual multiples acceptable but both need to be doubled if two marks are to be awarded. 2 (a) (i) (Free-) radical substitution 30 Both underlined words are required Penalise a correct answer if contradicted by an additional answer 1

29

[7]

Initiation (ii)

(b)

F<sub>2</sub> → 2F•

Penalise absence of dot once only

#### First propagation

 $F \bullet + CH_3F$   $\longrightarrow$   $\bullet CH_2F + HF$ Penalise + or - charges every time

#### Second propagation

 $F_2 + \bullet CH_2F \longrightarrow CH_2F_2 + F \bullet$ Accept dot anywhere on CH<sub>2</sub>F radical Mark independently Termination (must make 1,2-difluoroethane)  $2 \cdot CH_{2}F \longrightarrow CH_{2}FCH_{2}F$ Use of half-headed arrows must be correct to score, but if not correct then penalise once only in this clip 4 (iii)  $CH_3 CH_3 + 5F_2 \longrightarrow CF_3 CHF_2 + 5HF$  $(C_2H_6)$  $(C_2HF_5)$ 1 1,1,1,2-tetrachloro-2,2-difluoroethane Accept phonetic spelling eg "fluro, cloro" Penalise "flouro" and "floro", since QoL OR 1,2,2,2-tetrachloro-1,1-difluoroethane Ignore commas and hyphens 1 **2**O<sub>3</sub> → **3**O<sub>2</sub> (c) (i) ONLY this equation or a multiple Ignore NO over the arrow Other species must be cancelled 1  $O + NO_2 \longrightarrow NO + O_2$ (ii) ONLY this answer and NOT multiples Ignore any radical dot on the O atom

[9]

(a)

#### (i) chlorotrifluoromethane

Spelling must be correct but do not penalise "flouro" Ignore use of 1–

1

1

(ii) CF<sub>3</sub>•

May be drawn out with dot on C OR if as shown dot may be anywhere

# (iii) An unpaired/non-bonded/unbonded/free/a single/one/lone <u>electron</u>

NOT "bonded electron" and NOT "paired electron" NOT "pair of electrons" NOT "electron <u>s</u>" Ignore "(free) radical"

1

#### (b) **M1** $Cl \bullet + O_3 \rightarrow ClO \bullet + O_2$

M2  $CIO \bullet + O_3 \rightarrow 2O_2 + CI \bullet$ 

Mark independently Equations could gain credit in either position The dot can be anywhere on either radical Penalise the absence of a dot on the first occasion that it is seen and then mark on. Do <u>not</u> make the same penalty in the next equation, but penalise the absence of a dot on the other radical. Apply the list principle for additional equations

2

## (c) (i) (If any factor is changed which affects an <u>equilibrium</u>), the (position of) <u>equilibrium</u> will <u>shift/move</u> so as to <u>oppose</u> <u>the change</u>.

#### OR

(When a system/reaction in <u>equilibrium</u> is disturbed), the <u>equilibrium</u> <u>shifts/moves</u> in a direction which tends to <u>reduce the disturbance</u>

> Must refer to <u>equilibrium</u> Ignore reference to "system" alone A variety of wording will be seen here and the key part is the last phrase. An alternative to shift/move would be the idea of <u>changing/altering</u>

the position of equilibrium

- (ii) M1 The (forward) reaction/to the right is <u>endothermic</u> or <u>takes in heat</u>
  - **OR** The reverse reaction/to the left is <u>exothermic</u> or <u>gives out heat</u>
  - M2 The <u>equilibrium moves/shifts</u> to <u>oppose the increase in</u> <u>temperature</u> M2 depends on a correct statement for M1 For M2 accept The <u>equilibrium moves/shifts</u>
    - to take in heat/lower the temperature
    - to promote the endothermic reaction and <u>take in heat</u>/ <u>lower the</u> <u>temperature</u>
    - to oppose the change and <u>take in heat/lower the</u> <u>temperature</u> (leading to the formation of more ozone)

1

- (d) Any one of
  - Pentane does not contain chlorine OR C-CI (bond)
  - Pentane is <u>chlorine-free</u>
  - Pentane does not release chlorine (atoms/radicals)
    - Ignore reference to F OR C–F OR halogen Ignore "Pentane is not a CFC" Ignore "Pentane is a hydrocarbon" Ignore "Pentane only contains C and H" Ignore "Pentane is C  $_5H_{12}$ "

[9]

(a)

Both words needed

M2  $Cl_2 \rightarrow 2Cl$ • M3  $Cl_2 + CH_4 \rightarrow CH_3 + HCl$ M4  $Cl_2 + CH^3 \rightarrow CH_3Cl + Cl_9$ M5  $CH_4 + 3Cl_2 \rightarrow CHCl_3 + 3HCl$ Penalise the absence of a radical dot once only Ignore termination steps except, if and only if <u>both</u> M3 and M4 do not score, then accept for one mark  $Cl_9 + CH_3 \rightarrow CH_3Cl$ 

1

1

1

1

(b) M1 UV (light)/ sunlight / light / UV radiation

M2	<u>C–CI</u> or <u>carbon-chlorine</u> bond breakage	
	homolysis of C-Cl	
	OR	
	equation to show a chlorine-containing organic	
	For M1 and M2, ignore use of $Cl_2$ , but credit UV and C–Cl bond	
	breakage if seen	1
		1
М3	$CI \bullet + O_3 \rightarrow CIO \bullet + O_2$	
		1
M4	$CIO \bullet + O_3 \rightarrow CI \bullet + 2O_2$	
	lanore other equations	
	Penalise the absence of a radical dot once only	
	Accept radical dot anywhere on either radical.	
		1
M5	Any <u>one</u> from	
	• Combination $2O_3 \rightarrow 3O_2$	
	<ul> <li><u>Stated</u> that Cl• / chlorine atom is regenerated / not used up</li> </ul>	
	<ul> <li><u>Stated</u> that the Cl• / chlorine atom is unaffected</li> </ul>	
	by the process.	1
	For M5 accept Cl• on <u>both sides</u> of the equation	1
M6	Stated that the role of the CI. / chlorine atom is to find an	
	alternative route <b>OR</b> lower $E_a$ / activation energy	
	a Gy	1

Halothane contains C-CI / CI (C) M1 OR Desflurane does not contain C--CI bonds / CI OR Desflurane contains C-F / F as the only halogen Mark independently. For M1, credit the idea that desflurane contains C-F bonds that are difficult to break OR that halothane contains C-Cl bonds which are easy to break. M2 Desflurane / molecules that have fluorine as the only halogen, cause no damage / do not deplete / do not react with the ozone (layer) OR

Halothane / chlorine-containing molecules, damage / deplete / react with the ozone (layer)

1