Haloalkanes
AS & A Level

Model Answers 1

Level	A Level
Subject	Chemistry
Exam Board	OCR
Module	Core Organic Chemistry
Topic	Haloalkanes
Paper	AS & A Level
Booklet	Model Answers 1

Time allowed: **49 minutes**

Score: **/36**

Percentage: **/100**

Grade Boundaries:

A*	A	B	C	D	E
>85%	73%	60%	47%	34%	21%

Which compound does **not** react with nucleophiles?

A. CH_3CH_2CHO

B. CH_3CHCH_2

C. $CH_3CH_2COCH_3$

D. $CH_3CH_2CH_2Cl$ **[1]**

- A nucleophile is an atom or molecule that donates an **electron pair** to make a covalent bond.
- They do this by bonding with the **positively charged** or **partially** positively charged parts of molecules.
- A, C and D all have partial charges on the molecules due to the presence of **electronegative** atoms such as oxygen and chlorine, so the molecules are polar.
- Molecule B is a hydrocarbon with no other element attached, the charge is evenly spread throughout the molecule so it will therefore not react with nucleophiles.

A chemist compares the rates of hydrolysis of 1-chloropropane and 1-bromopropane in ethanol.

Which reagent in aqueous solution should be used?

A. Silver chloride

B. Silver nitrate

C. Potassium chloride

D. Potassium nitrate **[1]**

- Ag^+ ions react with halide ions to form the **halogen precipitates** Ag*Cl* and AgBr in aqueous solution.
- Silver nitrate is a soluble salt which releases Ag^+ ions in aqueous solution and is regularly used to test for halogens.
- A is incorrect as silver chloride is **insoluble** hence does not release silver ions.
- C and D are incorrect as these compounds do not contain silver.

When heated with NaOH(aq), 1-iodobutane is hydrolysed at a much faster rate than 1-chlorobutane.

Which statement explains the different rates?

A. The C–I bond enthalpy is greater than the C–C*l* bond enthalpy.

B. The C–I bond is less polar than the C–C*l* bond.

C. The C–I bond has a C atom with a greater $\delta+$ charge than in the C–C*l* bond.

D. The C–I bond requires less energy to break than the C–C*l* bond. **[1]**

- Both molecules are primary haloalkanes hence the structure of the molecule has no effect on the rate of reaction.
- The other factor which affects the rate of reaction in the hydrolysis of haloalkanes is the identity of the halogen.
- The strength of the halogen-carbon bond decreases as we move down Group 7 due to **increasing** atomic distances.
- Hence 1-chlorobutane reacts slower than 1-iodobutane as iodine sits **below** chlorine in Group 7, so less energy to break the C-I bond than the C-C*l* bond.
- A is incorrect as the opposite of this statement is the case.
- B and C are incorrect as bond polarity doesn't influence the rate of reaction.

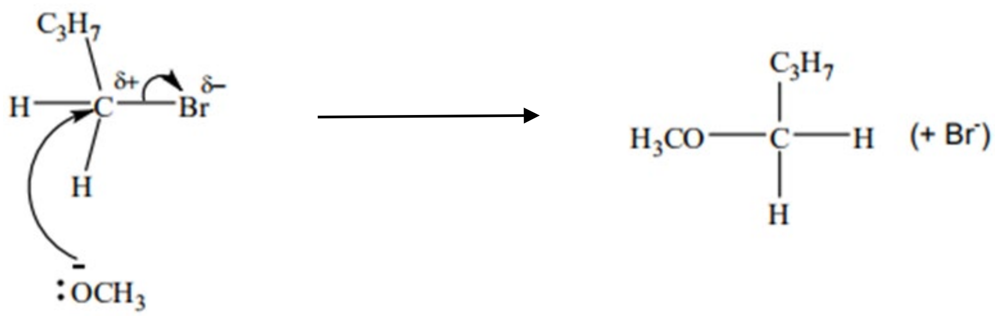
1-Bromobutane, $CH_3CH_2CH_2CH_2Br$, reacts with methoxide ions, CH_3O^-, by nucleophilic substitution.

(a) Suggest how the methoxide ion can act as a nucleophile. [1]

A nucleophile acts to **donate a lone pair of electrons**

(b) Using the 'curly arrow' model, suggest the mechanism for this reaction.

Show any relevant dipoles. [3]



An **induced dipole** occurs between the C-Br bond, producing a partially positive charge on C and a partially negative charge on Br

The nucleophile (OCH_3), which has a lone pair of electrons then attacks the positive carbon atom, depicted by the curly arrow to show the movement of a pair of electrons to form a covalent bond.

The bond between the C and Br then breaks and Br^- is formed.

(c) 1-Iodobutane also reacts with methoxide ions.

Indicate, by placing a tick in one of the boxes, how the use of 1-iodobutane would affect the rate of reaction compared with that of 1-bromobutane.

1-Iodobutane does not change the rate	
1-Iodobutane increases the rate	
1-Iodobutane decreases the rate	

Explain your answer. [1]

C-I bonds are **weaker** than **C-Br bonds** due to iodine having a larger atomic radius than bromine, so the shared pair of electrons are further from the positive nuclei, requiring less energy to break the bond.

1-iodobutane increases the rate.

(d) The ethanoate ion, CH_3COO^- also acts as a nucleophile when reacting with 1-bromobutane in a substitution reaction.

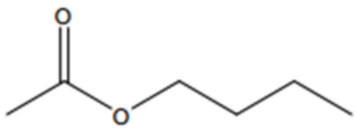
Draw the skeletal formula and give the name of the organic product formed in this reaction.

skeletal formula

[2]

An **ester** would be formed from the reaction.

In this particular case between 1-bromobutane and ethanoic acid, butyl ethanoate would be formed with structure:



(e) 1-Bromobutane (M_r, 136.9) can be made from a reaction of butan-1-ol, C_4H_9OH, as shown in the equation below.

$$C_4H_9OH + KBr + H_2SO_4 \rightarrow C_4H_9Br + KHSO_4 + H_2O$$

(i) Calculate the atom economy for the formation of 1-bromobutane in this reaction. [1]

$$Atom\ economy = \frac{Mr\ of\ 1-bromobutane}{Total\ Mr\ of\ all\ products\ formed} \times 100$$

$$= \frac{136.9}{136.9 + 18 + 136.2} \times 100$$

$$Atom\ economy\ \% = 47\ \%$$

(ii) Suggest a reactant, other than a different acid, that could be used to improve the atom economy of making 1-bromobutane by the same method. [1]

An element under Group 1 which is **less heavy than Potassium** can be used

Examples would be **NaBr** or **LiBr**

(iii) A student prepares a sample of 1-bromobutane.

5.92 g of butan-1-ol are reacted with an excess of sulfuric acid and potassium bromide. After purification, 9.72 g of 1-bromobutane arecollected.

Calculate the percentage yield.

Give your answer to **three** significant figures. [3]

$$Moles\ of\ butan-1-ol = \frac{5.92\ g}{74} = 0.08\ moles$$

Since 1:1 mole ratio

$$Moles\ of\ 1-bromobutane\ formed = 0.08\ moles$$

$$Mass\ of\ 1-bromobutane\ formed = 0.08 \times 136.2 = 10.952\ g$$

Since actual mass of 1-bromobutane collected = 9.72 g,

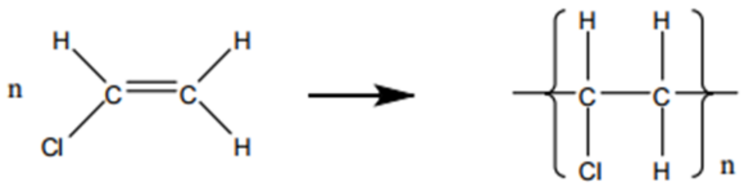
$$\%\ yield = \frac{Actual}{theoretical} \times 100\% = \frac{9.72}{10.952} \times 100\% = 88.8\ \%$$

[Total 12 Marks]

Chloroethene, CH_2CHCl, can be polymerised to form poly(chloroethene).

(a) Write an equation, using displayed formulae, to show the formation of this polymer. [2]

Chloroethene undergoes addition polymerisation to form polychloroethene whereby monomers bond together without the loss of any atoms. Alkene monomers are able to form polymers due to their double bonds, which are unsaturated and can therefore be added to:



(b) Incineration of plastics containing poly(chloroethene) produces waste gases that can damage the environment.

Incineration carried out in the presence of oxygen produces carbon dioxide, carbon monoxide and hydrogen chloride as waste gases and one other non-toxic product.

(i) Write an equation for the incineration of the monomer, chloroethene, with oxygen. [1]

Products formed are CO_2, CO, HCl and water from combustion

$$CH_2CHCl + 2O_2 \rightarrow CO + CO_2 + HCl + H_2O$$

(ii) Chemists have developed ways of removing hydrogen chloride from these waste gases. Sodium hydrogencarbonate, $NaHCO_3$(s), is frequently used in industry for this purpose.

Explain how sodium hydrogencarbonate removes hydrogen chloride. [1]

Sodium hydrogencarbonate is a base which **neutralises** HCl (an acid)

(c) Carbon dioxide is a greenhouse gas that is linked to global warming.

The greenhouse effect of carbon dioxide in the atmosphere is dependent on two factors. What are these **two** factors? [2]

CO_2 is a greenhouse gas which enhances the greenhouse effect. Abundance of these 'greenhouse' gases in the atmosphere affects the quantity of absorbed infrared radiation from the sun.

The **greenhouse** effect of CO_2 in the atmosphere is dependent on the following factors:

- The abundance of CO_2 in the atmosphere
- The ability for CO_2 to absorb infrared radiation
- CO_2 residence time. This is defined as the amount of CO_2 in the atmosphere, divided by the rate at which it is removed from the atmosphere, i.e. how long CO_2 remains in the atmosphere).

(d) Chemists are trying to minimise climate change as a result of global warming.

One way is to use Carbon Capture and Storage (CCS). One method of CCS is to react the carbon dioxide with metal oxides.

(i) Write an equation to illustrate this method of CCS. [1]

A metal oxide and CO_2 would form a **carbonate**

$$CaO + CO_2 \rightarrow CaCO_3$$

(ii) State one other method of CCS. [1]

CO_2 can be stored in:

- Deep oceans
- Geological formations
- Deep in rocks
- Oil wells
- Gas fields

[Total 8 Marks]

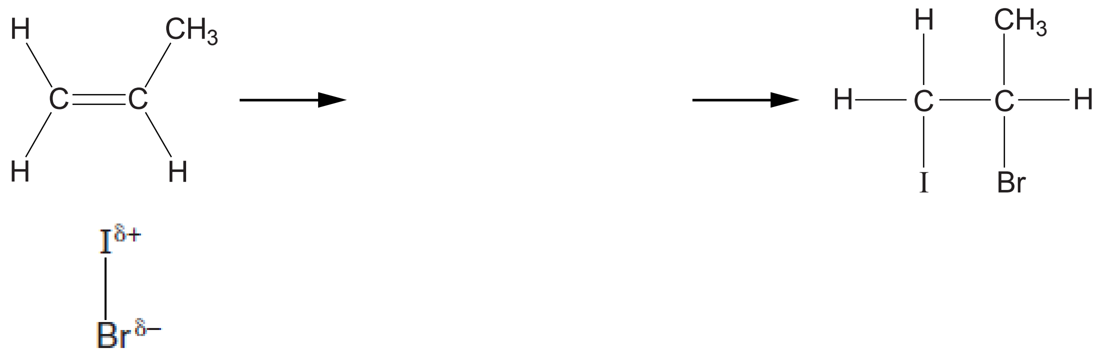
Iodine monobromide, IBr, has a permanent dipole.

Alkenes react with IBr in a similar way to the reactions of alkenes with HBr.

(a) Propene reacts with IBr to make two possible organic products.

One of these products is 2-bromo-1-iodopropane.

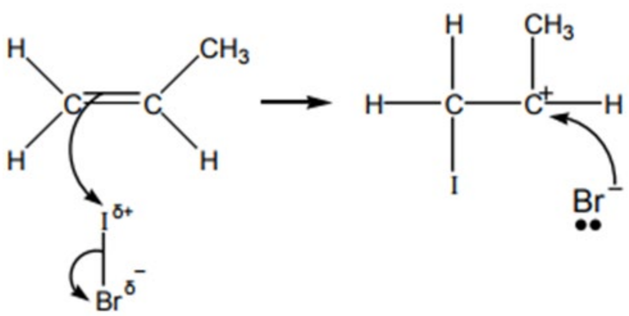
(i) Using the curly arrow model, complete the mechanism to make 2-bromo-1-iodopropane.



[3]

This is an electrophilic addition reaction.

Bromine is more electronegative than iodine, hence the permanent dipole shown in the question ($I^{\delta+}$- $Br^{\delta-}$). Therefore, the $I^{\delta+}$ acts as an electrophile and accepts a pair of electrons from the C=C (an electron dense area). This causes the I-Br bond to break, forming a Br^- nucleophile and a carbocation intermediate. The electron pair on the Br^- create a bond with the C^+, as shown in the mechanism below:

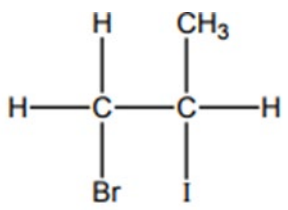


(ii) What is the name of this mechanism? [1]

Electrophilic addition

(iii) Draw the structure of the other possible organic product of the reaction of propene with IBr. [1]

Depending on which side the double bond breaks and thus which C atom in propene becomes the cation, there are two possible products. The second is:



(b) Methane reacts with IBr to form many products.

Two of these products are iodomethane and hydrogen bromide.

(i) Suggest the essential condition needed for this reaction. [1]

Ultraviolet or UV light.

High energy UV radiation in sunlight provides the initial energy for the reaction.

(ii) The mechanism of the reaction involves three steps, one of which is called termination.

Describe the mechanism of the reaction that forms iodomethane and hydrogen bromide.

Include in your answer:

- the name of the mechanism
- the names for the **other two** steps of the mechanism
- equations for these two steps of the mechanism
- the type of bond fission
- one equation for a termination step.

Your answer should link the named steps to the relevant equations. [7]

The mechanism of a reaction between iodomethane and HBr is a **free radical substitution.**

The **initiation** step forms the free radicals (atoms with single unpaired electrons):

$$IBr \rightarrow Br + I$$

Homolytic fission is the **breaking of covalent bonds** which **forms two radicals** with **one electron from the bond pair going to each atom**

The **propagation** steps involve radicals reacting to produce further radicals in a chain reaction:

$$Br + CH_4 \rightarrow HBr + CH_3$$

$$CH_3 + IBr \rightarrow CH_3I + Br$$

The **termination** steps remove free radicals from the system, without replacing them with new ones:

$I + CH_3 \rightarrow CH_3I$
OR $Br + Br \rightarrow Br_2$
OR $I + I \rightarrow I_2$
OR $Br + CH_3 \rightarrow CH_3Br$
OR $CH_3 + CH_3 \rightarrow C_2H_6$

[Total 13 Marks}