

# FACTFILE: GCE CHEMISTRY

## 2.5 HALOGENOALKANES



### Learning Outcomes

#### Students should be able to:

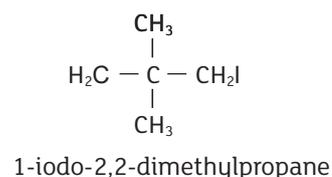
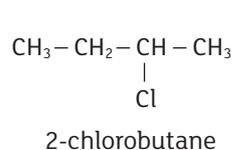
- 2.5.1** explain the variation in boiling points of halogenoalkanes with different halogen atoms;
- 2.5.2** explain the variation in boiling points of structural isomers of a halogenoalkane with the same molecular formula;
- 2.5.3** classify a halogenoalkane as primary, secondary or tertiary;
- 2.5.4** describe the laboratory preparation of a liquid organic compound, such as a halogenoalkane from the corresponding alcohol;
- 2.5.5** describe the reaction of halogenoalkanes with aqueous alkali, ammonia and potassium cyanide;
- 2.5.6** define the term nucleophile and outline the nucleophilic substitution mechanism involved in the reaction between primary and tertiary halogenoalkanes and aqueous alkali;
- 2.5.7** describe and explain, with reference to bond enthalpy, the relative rates of hydrolysis of primary halogenoalkanes with the same number of carbon atoms and different halogen atoms;
- 2.5.8** describe elimination of hydrogen halides from symmetrical and unsymmetrical halogenoalkanes using ethanolic potassium hydroxide; and

- 2.5.9** recall that chlorofluorocarbons (CFCs) are a major factor in reducing the ozone layer and allowing more harmful ultraviolet radiation to reach the Earth's surface.

### Halogenoalkanes

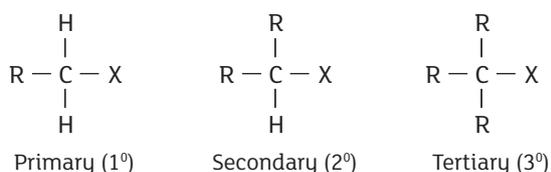
Halogenoalkanes are saturated aliphatic compounds formed by replacing a hydrogen atom on an alkane by a halogen atom. They are named according to IUPAC rules:

- Name the longest carbon chain and add the suffix -ane.
- Name the halogen atom or atoms as a prefix using fluoro, chloro, bromo or iodo.
- For several halogen atoms, indicate their numbers with di, tri, tetra etc and indicate their positions by numbering the chain so that the attachment numbers are as low as possible, listing the halogens in alphabetical order.
- Indicate the presence of any alkyl groups in the usual manner.



Halogenoalkanes can be classified as primary, secondary or tertiary:

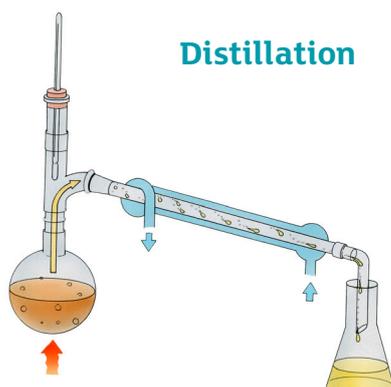
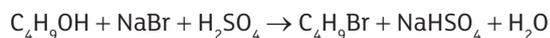
- A **primary halogenoalkane** has one carbon atom bonded directly to the carbon atom that is bonded to the halogen (except halomethanes).
- A **secondary halogenoalkane** has two carbon atoms bonded directly to the carbon atom that is bonded to the halogen.
- A **tertiary halogenoalkane** has three carbon atoms bonded directly to the carbon atom that is bonded to the halogen.



Compared to alkanes with the same number of carbon atoms, halogenoalkanes have much higher boiling points. This is due to the increased RAM of the halogen atom compared to a hydrogen atom which results in stronger van der Waals' forces between the molecules. Isomeric halogenoalkanes also vary in their boiling points; the tertiary halogenoalkane 2-bromo-2-methylpropane ( $73^\circ\text{C}$ ) has a lower boiling point than the primary 1-bromobutane ( $101^\circ\text{C}$ ). With increased branching, the molecules cannot get as close and there are fewer points of contact. This results in weaker van der Waals' forces and lower boiling points.

Halogenoalkanes can be prepared from alcohols. As the laboratory preparation of a halogenoalkane often produces a liquid product, key techniques such as reflux, distillation, use of a separating funnel and drying are used to obtain a pure sample.

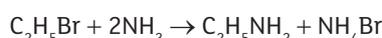
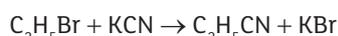
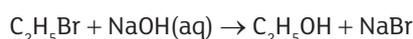
For example:



## Reactivity of halogenoalkanes

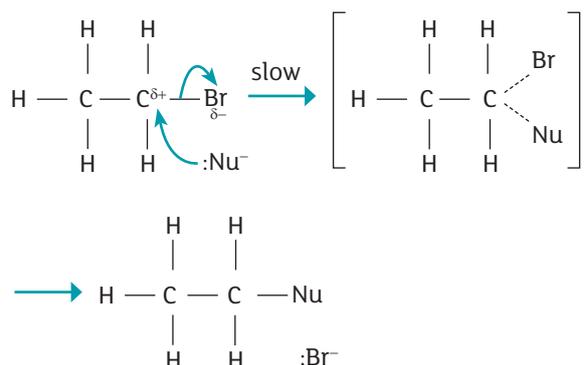
The carbon-halogen bond is polar, with a slightly positive charge ( $\delta^+$ ) on the carbon atom and it is attacked by nucleophiles. An ion or molecule with a lone pair of electrons that attacks an area of low electron density is known as a **nucleophile**.

Nucleophiles include aqueous alkali (containing hydroxide ions,  $\text{OH}^-$ ), ammonia and potassium cyanide. For example:

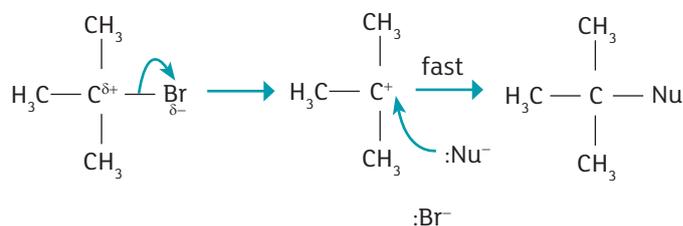


The mechanism of the reaction occurs via nucleophilic substitution and varies depending on the type of halogenoalkane.

### 1. Primary halogenoalkanes

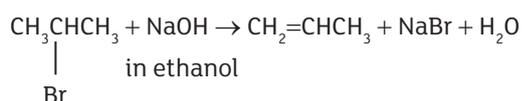


### 2. Tertiary halogenoalkanes



The rate of hydrolysis depends on the nature of the halogenoalkane, with iodoalkanes reacting faster than corresponding chloroalkanes due to the lower bond enthalpy of the C-I bond.

Halogenoalkanes can also react with alkali in **ethanol** to produce alkenes via an **elimination** reaction. For example:



A hydrogen atom is removed from one of the carbon atoms adjacent to the carbon bonded with the bromine atom as well as the bromine atom. In elimination reactions the atoms being removed are on adjacent carbon atoms, and a double bond is set up between those carbons, forming an alkene. With unsymmetrical halogenoalkanes a mixture of elimination products is obtained. For example, 2-bromobutane reacts with ethanolic NaOH to form but-1-ene (minor product) and but-2-ene (major product).

The table below summarises some of the reactions of halogenoalkanes.

Reagent	Condition	Mechanism	Product
KOH (aq)	reflux	nucleophilic substitution	alcohol
KCN	reflux	nucleophilic substitution	nitrile
NH <sub>3</sub>	Excess conc ammonia in a sealed tube	nucleophilic substitution	amine
KOH (in ethanol)	Reflux, ethanol as solvent	elimination	alkene

Chlorofluorocarbons (CFCs) are a class of compounds which were widely used as refrigerants, propellants and solvents. However, they were discovered to contribute to the depletion of ozone, O<sub>3</sub>, in the upper atmosphere resulting in increased exposure to harmful ultraviolet radiation. Their use in these applications has been phased out as a result.

## Credits

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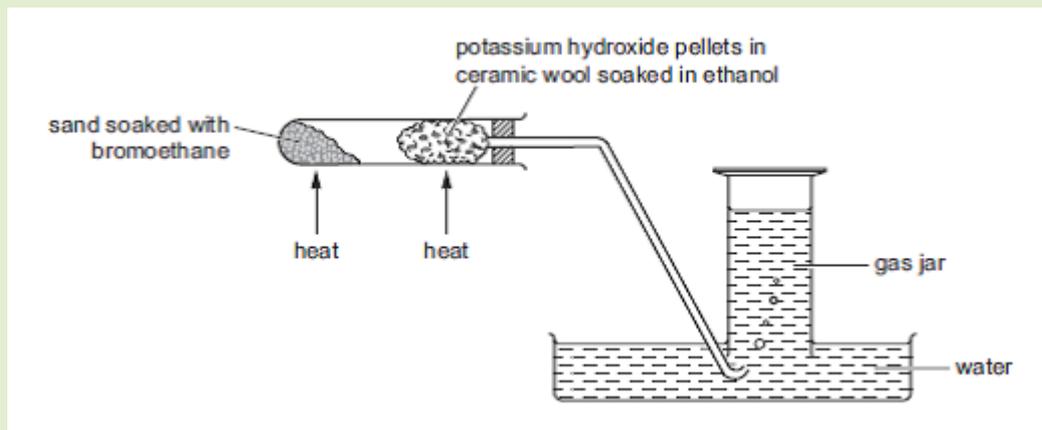
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## Revision Questions

1 Bromoethane is a colourless liquid which boils at 38 °C. 9.1 g of bromoethane dissolve in one litre of water at room temperature. It undergoes an elimination reaction with ethanolic potassium hydroxide.

(a) The following experiment shows the reaction of bromoethane with ethanolic potassium hydroxide.



(i) Write the equation for the reaction of bromoethane with ethanolic potassium hydroxide.

..... [1]

(ii) Name the gas collected in the gas jar.

..... [1]

(iii) Describe a chemical test to confirm the identity of the gas.

.....  
 ..... [2]

(iv) How does the collection of this gas prove that an *elimination* reaction has taken place?

.....  
 ..... [1]



2 There are four bromoalkanes with the formula  $C_4H_9Br$ .

(a) Complete the following table by drawing the missing structures, giving the missing name and indicating the classification for each.

(P = Primary, S = Secondary and T = Tertiary)

Structure and Name	Classification
$\begin{array}{cccc} \text{H} & \text{H} & \text{H} & \text{H} \\   &   &   &   \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{Br} \\   &   &   &   \\ \text{H} & \text{H} & \text{H} & \text{H} \end{array}$ <p>1-bromobutane</p>	P
$\begin{array}{ccc} \text{H} & \text{Br} & \text{H} \\   &   &   \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\   &   &   \\ \text{H} & \text{CH}_3 & \text{H} \end{array}$ <p>2-bromo-2-methylpropane</p>	
<p>1-bromo-2-methylpropane</p>	
<p>_____</p>	

[6]

- (b) (i) 1-bromobutane can be prepared by refluxing a mixture containing butan-1-ol, water, sodium bromide and concentrated sulfuric acid for 45 minutes. Describe the remaining steps required to produce a pure, dry sample of this halogenoalkane.

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..... [4]

Quality of written communication [2]

- (ii) 11.1 g of butan-1-ol were used to prepare 1-bromobutane and 12.3 g were obtained.



Calculate the percentage yield.

.....  
.....  
.....  
.....  
..... [3]

- 3 Which one of the following molecules can **not** act as a nucleophile?

- A.  $\text{CH}_3\text{NH}_2$   
B.  $\text{CH}_4$   
C.  $\text{H}_2\text{O}$   
D.  $\text{NH}_3$  [1]

