CHAPTER 16: Halogen Derivatives

Learning outcomes:

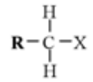
(a) *recall the chemistry of halogenoalkanes as exemplified by*
  (i) *the following nucleophilic substitution reactions of bromoethane: hydrolysis, formation of nitriles, formation of primary amines by reaction with ammonia.*
  (ii) *the elimination of hydrogen bromide from 2-bromopropane.*
(b) *describe the mechanism of nucleophilic substitution (by both S_N1 and S_N2 mechanisms) in halogenoalkanes.*
(c) *interpret the different reactivities of halogenoalkanes(with particular reference to hydrolysis and to the relative strengths of the C-Hal bonds).*
(d) *explain the uses of fluoroalkanes and fluorohalogenoalkanes in terms of their relative chemical inertness.*
(e) *recognise the concern about the effect of chlorofluoroalkanes on the ozone layer.*

16.1 Introduction to Halogenoalkaes

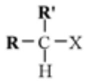
What are halogenoalkanes?

1) *Halogenoalkanes*(or alkyl halides) are compounds in which one or more hydrogen atoms in an alkane have been replaced by halogen atoms (fluorine, chlorine, bromine or iodine).

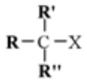
2) Halogenoalkanes can be classified as **primary**, **secondary** or **tertiary** depending on the number of alkyl groups(R groups) attached to the carbon atom holding the halogen atom.



primary (1°)
(1 R group or 2 H atoms)

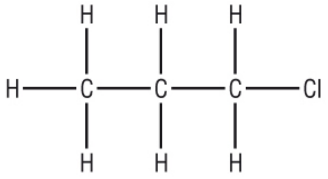


secondary (2°)
(2 R groups or 1 H atom)

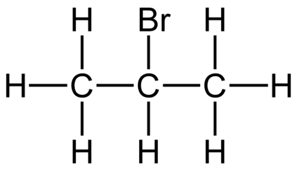


tertiary (3°)
(3 R groups or no H atoms)

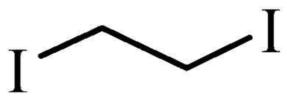
3) Some examples of halogenoalkanes:



Chloropropane,
$CH_3CH_2CH_2Cl$

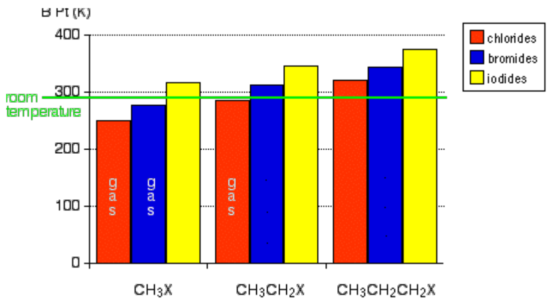


2-bromopropane,
$CH_3CHBrCH_3$



1,2-diiodoethane, ICH_2CH_2I

Physical properties of halogenoalkanes



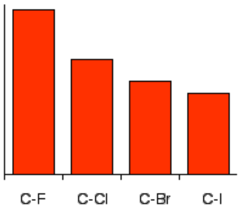
1) i. Boiling point of the halogenoalkanes increases as the molecular size increases. This is because there are **more electrons** in larger molecules and **more temporary dipoles** can be set up, resulting in stronger van der Waal's forces.

ii. Primary halogenoalkanes have higher boiling point compared to secondary and tertiary halogenoalkanes of the same molecular weight. This is because the **surface area of primary halogenoalkanes is higher**, more temporary dipoles can be set up, resulting in stronger van der Waal's forces.

2) i. Halogenoalkanes are **insoluble in water but soluble in organic solvents**.
   ii. This is because when dissolved in water(polar solvents), the energy needed to break the hydrogen bonds between water molecules is too high. The energy released when halogenoalkane-water attraction is set up is not enough to compensate it. This makes the structure to gain energy overall, making it less stable.
   iii. While when it is dissolved in organic solvents, the halogenoalkane-solvent attraction is strong enough to compensate the energy needed to break the weak van der Waal's forces between organic molecules.

16.2 Reactions of Halogenoalkanes

Chemical reactivity of halgenoalkanes



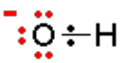
1) **Fluoroalkanes are the least reactive while iodoalkanes are the most reactive**. This is because the carbon-halogen bond strength decreases from fluorine to iodine as the size of the halogen atoms increases.

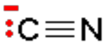
2) Since reactions of halogenoalkanes involve the breaking of the carbon-halogen bond, it follows that carbon-iodine bonds are the easiest to break, making them the easiest to react.

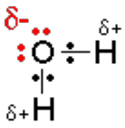
Nucleophilic substitution

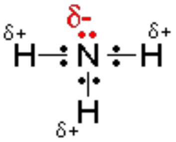
1) The signature reaction of halogenoalkanes is **nucleophilic substitution**. Nucleophilic substitution is the **substitution of an atom by a nucleophile**.

2) A nucleophile is a species(an ion or a molecule) which is strongly attracted to a region of positive charge in something else. It normally carries **either a partial or fully negative charge on the molecule**. Some example of nucleophiles are shown below:









3) Nucleophilic substitution is possible due to **polarity of the carbon-halogen bond**. Halogens are more electronegative than carbon, therefore the electron pair in the carbon-halogen bond will be attracted towards the halogen end, leaving the halogen slightly negative and the carbon slightly positive.

4) Since nucleophiles are negative, it is attracted to the positive carbon and this initiates the substitution to occur.

5) For carbon-iodine bond, although there is no polarity, it is still possible because the nucleophile can induce a dipole in the bond due to the electrons repelling each other.

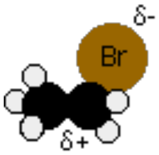
6) Nucleophilic substitution is done via two mechanisms, the **S_N1 or S_N2** mechanism.
-Primary halogenoalkanes will use S_N2.
-Tertiary halogenoalkans will use S_N1.
-Secondary halogenoalkanes will use both.

The S_N2 mechanism

1) In S_N2 mechanism, the 'S' stands for substitution, the 'N' stands for nucleophilic and the '2' stands for the **initial step(rate-determining step) involves two species(the halogenoalkane and the nucleophile)**.

2) The general mechanism of an S_N2 reaction, using bromoethane, CH_3CH_2Br as a typical primary halogenoalkane and Nu^- as a general nucleophile:

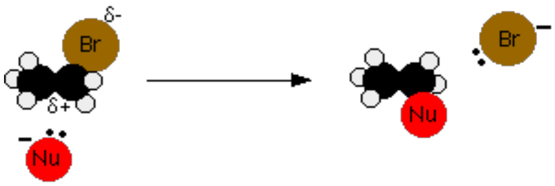
i. The carbon-bromine bond in bromoethane is polarised due to the electronegativity difference between the two atoms. Carbon carries a partial positive charge while bromine carries a partial negative charge.



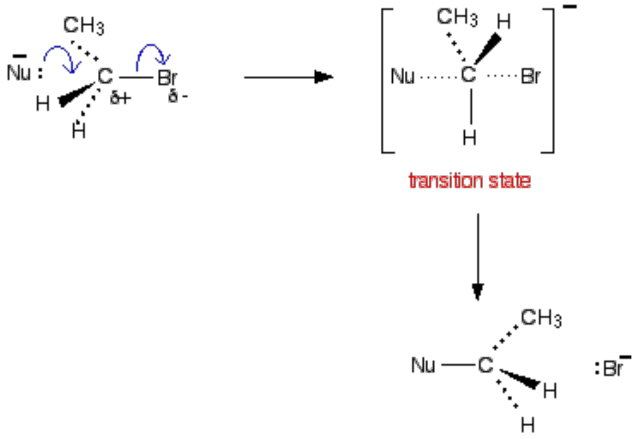
ii. The nucleophile, **Nu^- is attracted towards the positive carbon**, beginning to form a co-ordinate bond with it. Meanwhile, the negative bromine atom is **repelled further** due to the approaching nucleophile.

iii. Eventually, there is a state, called the **transition state** where the carbon-bromine bond is just at the point of breaking and the carbon-nucleophile bond is just at the point of forming. The transition state has **five groups** attached to the central carbon atom.

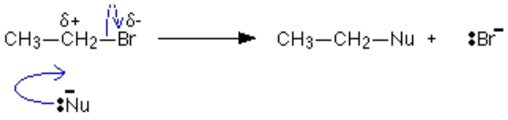
iii. The movement goes on until the Nu^- is firmly attached to the carbon, and the bromine has been expelled as a Br^- ion. The nucleophile has substituted the bromine.



3) In the examination, the mechanism can be written like this:



....or a more simplified version:

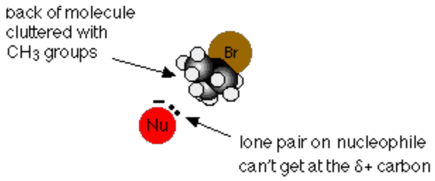


4) Note:

i. When the nucleophile approaches the halogenoalkane, it approaches **from the opposite side of bromine** because the negative bromine hinders the attack from its side.

ii. It is crucial to get the orientation of the atoms right, the molecule has been inverted at the end of the reaction. This is called the **inversion of configuration**(product has a configuration opposite to the reactant).

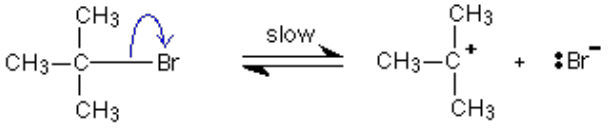
5) It is unlikely for tertiary halogenoalkanes to react by SN2 mechanism. This is because SN2 mechanism involves the nucleophile approaching and forming bond from the opposite side of the halogen. In the case of tertiary halogenoalkane, it is unlikely because the opposite of the halogen is cluttered with CH_3 group(s).



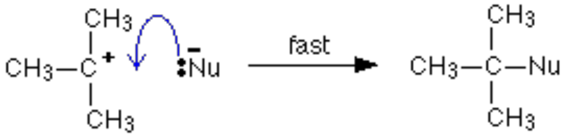
The S_N1 mechanism

1) In S_N1 mechanism, the '1' stands for the **initial step(rate-determining step) involves one species only(the halogenoalkane)**. The overall rate of reaction is governed by the rate of the first step.

2) The general mechanism of an S_N2 reaction, using 2-bromo-2-methylpropane, $(CH_3)_3Br$ as a typical tertiary halogenoalkane and Nu^- as a general nucleophile:
   i. The reaction happens in two stages. In the first stage, a small proportion of the halogenoalkane **ionises to give a carbocation and a bromide ion**.



   ii. Once the carbocation is formed, it will **react immediately** when it comes into contact with a nucleophile, Nu^-. The lone pair of the nucleophile is **strongly attracted** towards the positive carbon, and moves towards it to create a new bond.



3) Tertiary halogenoalkanes react via S_N1 because the **tertiary carbocation intermediate formed is relatively stable**. If primary halogenoalkanes were to react in the same manner, the primary carbocation formed would be relatively unstable, resulting in high activation energy of the reaction.

4) Secondary halogenoalkanes can react using **both S_N1 and S_N2** mechanisms because:
   i. The opposite of the halogen is not cluttered by CH_3 group(s).
   ii. The secondary carbocation formed is more stable than primary carbocation.

Summary of reactions that halogenoalkanes undergo

1) i. Substitution with hydroxide ions, OH^-.
   ii. Substitution with cyanide ions, CN^-.
   iii. Substitution with ammonia, NH_3.
   iv. Elimination

Substitution with hydroxide ions, OH^- (Hydrolysis)

1) **Reagent : Aqueous sodium hydroxide, NaOH or water**
Condition : Heat under reflux
Product : Alcohols

2) When aqueous sodium hydroxide, NaOH is heated with bromoethane under reflux, the bromine is substituted by hydroxide ion, OH. Ethanol is produced.

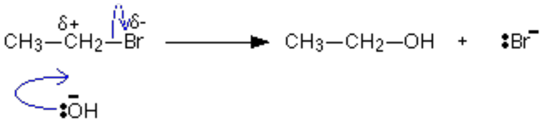
$$CH_3CH_2Br + NaOH \rightarrow CH_3CH_2OH + NaBr$$

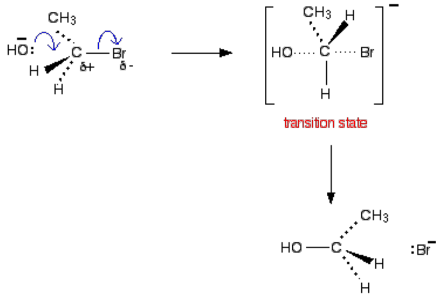
...or the ionic equation:

$$CH_3CH_2Br + OH^- \rightarrow CH_3CH_2OH + Br^-$$

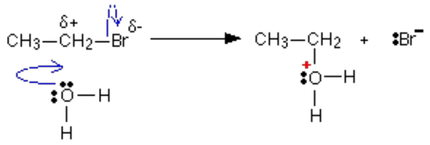
3) Heating under reflux means heating with a condenser placed vertically in the flask to prevent loss of volatile substances from the mixture.

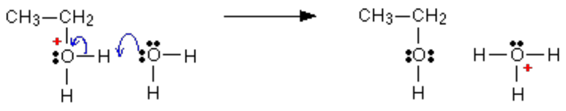
4) The mechanism of this reaction is the same as the ones mentioned before for primary halogenoalkanes, the nucleophile here is hydroxide ion, OH^-.





5) Water can also be used as the nucleophile in this reaction. However, hydrolysis using water occurs much slower. This is because the negatively-charged OH^- is a more effective nucleophile than water. The mechanism is as shown:





6) For a particular alkyl group R, the rate of hydrolysis decreases in the order:

R–I > R–Br > R–Cl > R–F
most reactive — least reactive

...as the strength of carbon-halogen bond increases progressively from iodine to fluorine. In fact, the carbon-fluorine bond is so strong that fluoroalkanes do not undergo hydrolysis.

Substitution with cyanide ions, CN^-

1) **Reagent : Potassium cyanide, KCN <u>in ethanol</u>**
Condition : Heat under reflux
Product : Nitriles

2) When ethanolic potassium cyanide, KCN is heated with 2-bromo-2-methylpentane under reflux, the bromine is substituted by cyanide ion, CN^-. 2-methyl-2-propanenitrile is produced.

$$(CH_3)_3Br + KCN \rightarrow (CH_3)_3CN + KBr$$

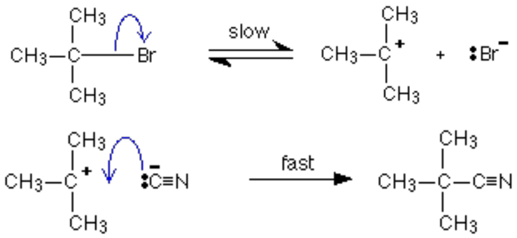
...or the ionic equation:

$$(CH_3)_3Br + CN^- \rightarrow (CH_3)_3CN + Br^-$$

3) The mechanism of this reaction is the same as the ones mentioned before for tertiary halogenoalkanes, the nucleophile here is cyanide ion, CN^-.

Step 1: Ionisation of the halogenoalkane

Step 2: Rapid attack by CN^-



4) This is a very useful reaction in organic synthesis.
   i. It serves as a means of **increasing the length of carbon chain**(a step-up reation).
   ii. The nitrile produced can be converted to carboxylic acid by heating under reflux with acid or alkali(hydrolysis reaction)

$(CH_3)_3CN + 2H_2O + H^+ \rightarrow (CH_3)_3COOH + NH_4^+$; acidic hydrolysis
$(CH_3)_3CN + H_2O + OH^- \rightarrow (CH_3)_3COO^- + NH_3$; alkaline hydrolysis

Substitution with ammonia, NH_3

1) **Reagent : Excess ammonia, NH_3 <u>in ethanol</u>**
Condition : Heat in sealed tube
Product : Amines

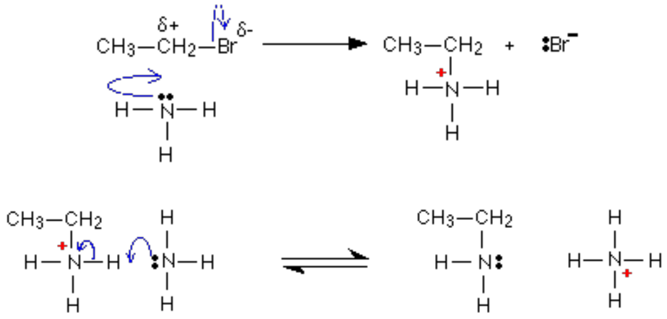
2) When ethanolic ammonia, NH_3 is heated with bromoethane in a sealed tube, the bromine is substituted by amine group, $-NH_2$. The reaction occurs in two stages. In the first stage, a salt, ethylammonium bromide is formed.

$$CH_3CH_2Br + NH_3 \rightarrow CH_3CH_2NH_3^+Br^-$$

...In the second stage, a reversible reaction occurs between this salt and the excess ammonia. Ethylamine, a primary amine is formed.

$$CH_3CH_2NH_3^+Br^- + NH_3 \rightleftharpoons CH_3CH_2NH_2 + NH_4Br$$

3) The mechanism of the reaction is shown below, ammonia is behaving as a nucleophile.

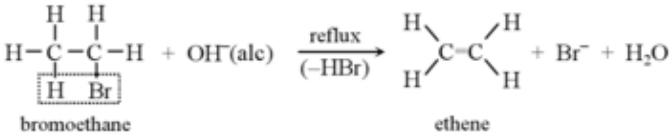


4) If the ammonia used is not in excess, a complicated mixture containing secondary and tertiary amine is obtained. This is because ethylamine is a good nucleophile and it can attack the unreacted bromoethane.

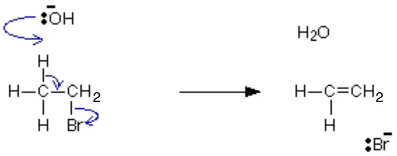
Elimination

1) **Reagent : Sodium hydroxide, NaOH in ethanol**
Condition : Heat under reflux
Product : Alkenes

2) In this alcoholic condition, the hydroxide ion, OH^- acts as a **base** rather than a nucleophile. Hence it will accept a proton(hydrogen ion) from the carbon atom next door to the one holding the bromine. The resulting re-arrangement of the electrons expels the bromine as a bromide ion and produces ethene.



3) The mechanism of the reaction is shown below:



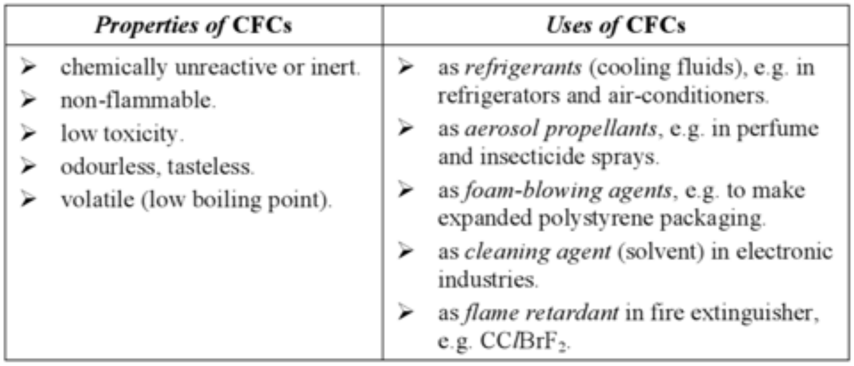
4) In unsymmetrical halogenoalkanes, a mixture of products of different isomers is produced due to the choice of hydrogen being removed.

16.3 Uses of Halogenoalkanes

The use of CFCs

1) CFCs are chlorofluorocarbons, compounds containing carbon with chlorine and fluorine atoms attached. Two common CFCs are CFC-11(CCl_3F) and CFC-12(CCl_2F_2).

2) Some properties and uses of CFCs:

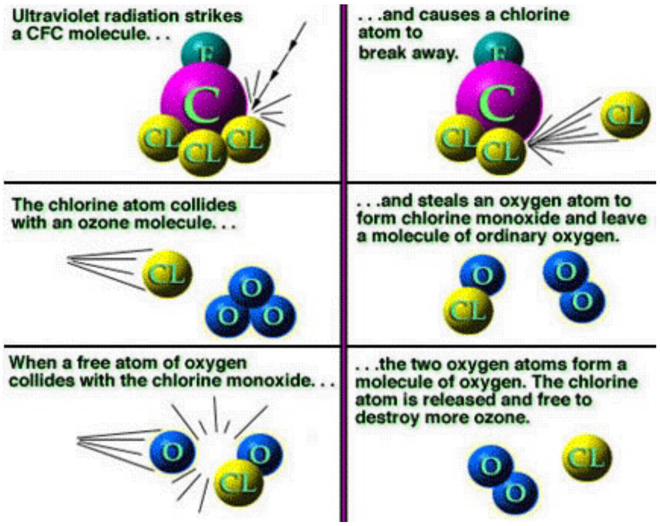


Properties of **CFCs**	*Uses of* **CFCs**
➢ chemically unreactive or inert. ➢ non-flammable. ➢ low toxicity. ➢ odourless, tasteless. ➢ volatile (low boiling point).	➢ as *refrigerants* (cooling fluids), e.g. in refrigerators and air-conditioners. ➢ as *aerosol propellants*, e.g. in perfume and insecticide sprays. ➢ as *foam-blowing agents*, e.g. to make expanded polystyrene packaging. ➢ as *cleaning agent* (solvent) in electronic industries. ➢ as *flame retardant* in fire extinguisher, e.g. $CClBrF_2$.

CFCs and the environment

1) CFCs have many uses in our daily life. However, due to their stability and inertness, they are also large responsible for the **destruction of the ozone layer**. Ozone layer prevents harmful ultraviolet radiation from reaching us.

2) Destruction of the ozone layer involves the **conversion of ozone molecule, O_3 to oxygen molecule, O_2**. The detailed mechanism is as shown below:



3) Possible solutions to protect the ozone layer:
   i. Reduce the use of CFCs. For example, replace aerosol spray with manual pump spray.
   ii. Collect and recycle CFCs for future use.
   iii. Find alternatives for CFCs.

4) Possible alternatives for CFCs:
   i. Use HCFCs(CFCs with at least one hydrogen atom, for example, CF_3CHCl_2)
      - HCFCs have smaller effect on ozone depletion because they are more readily destroyed in the troposphere.
      - However, a disadvantage of using it is, it is flammable. Also, it could potentially form toxic chemicals in the troposphere.
   ii. Use LPG(liquid petroleum gas) as propellant in aerosol sprays.
   iii. Use air-blowing agent in packaging and building industries.
   iv. Use water-based cleaning system in electronic industries.