15 Halogen compounds

The work on aliphatic organic halogen compounds (or halogenoalkanes) in this chapter is for AS Level. Aromatic halogen compounds are revisited for the A Level examination in Chapter 31.

Formation of halogenoalkanes

As you have probably realised, organic reactions are intertwined so that the reaction of one organic compound results in the formation of a different organic compound. In summary, you need to remember the reactions and conditions for these changes.

In the case of halogenoalkanes, the following methods of formation are specified. Exemplar equations are given but you should be able to write others.

1. The free-radical substitution of alkanes by Cl_2 or Br_2 in the presence of ultraviolet light, using ethene as an example.

   $C_2H_6 + Cl_2 \rightarrow C_2H_5Cl + HCl$

   $C_2H_5Cl + Cl_2 \rightarrow C_2H_4Cl_2 + HCl$

   $C_2H_4Cl_2 + Cl_2 \rightarrow C_2H_3Cl_3 + HCl$ and so on

2. The electrophilic addition of a halogen, X_2, or a hydrogen halide, HX(g), to an alkene at room temperature.

   $CH_2{=}CH_2 + Br_2 \rightarrow CH_2BrCH_2Br$

3. The substitution of an alcohol, e.g. with HX; KBr with H_2SO_4 or H_3PO_4; or with PCl_3 and heat; or with PCl_5; or with $SOCl_2$.

   $CH_3CH_2OH + HBr \rightarrow CH_3CH_2Br + H_2O$

Halogenoalkanes behave differently depending on which other groups are attached to the carbon that the halogen is attached to (you will also see this with other functional groups).

- If there are only hydrogen atoms attached to the carbon, it is a **primary** (1°) halogenoalkane – for example CH_3CH_2Br.
- If there is one alkyl group attached as well as the halogen, it is a **secondary** (2°) halogenoalkane – for example $(CH_3)_2CHBr$
- If there are no hydrogen atoms, only alkyl groups and the halogen, it is a **tertiary** (3°) halogenoalkane – for example $(CH_3)_3CBr$.

The C–Hal bond is polar because of the difference in electronegativities of the carbon atom and the halogen atom. Except when bonded to iodine, the carbon atom is relatively positive, making it susceptible to nucleophilic attack by lone pairs of electrons or negative ions.

NOW TEST YOURSELF

1 Which of the following is(are) a secondary (2°) halogenoalkane?

$CH_2ClCH_2CH_3$ $CH_3CH_2CHBrCH_3$ $(CH_3)_2CH_2CH_2I$ $(CH_3)_2CHBrCH_2CH_3$

Nucleophilic substitution

Halogenoalkanes undergo a number of nucleophilic substitution reactions. The syllabus requires you to know about three of these using bromoethane as a starting compound. However, you should be able to recognise this type of reaction with different halogenoalkanes and different nucleophilic reagents.

Hydrolysis

When bromoethane, a primary halogenoalkane, is heated under reflux with sodium hydroxide in a solvent of aqueous ethanol, the bromine is substituted by a hydroxyl group and ethanol is formed:

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

You need to know the mechanism for this reaction, which can be represented in two ways. Figure 15.1 shows the first of these.

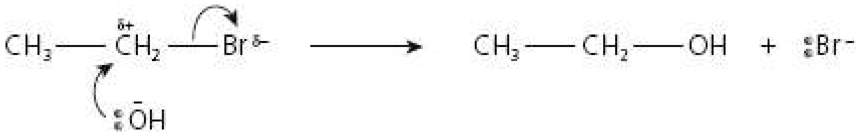

Figure 15.1

The reaction is described as S_N2, because there are two reactants in the rate-determining or slow step.

STUDY TIP

Think of S_N2 as 'Substitution Nucleophilic, 2 reactants'.

The other way of representing this reaction is to show it (Figure 15.2) as a two-stage process.

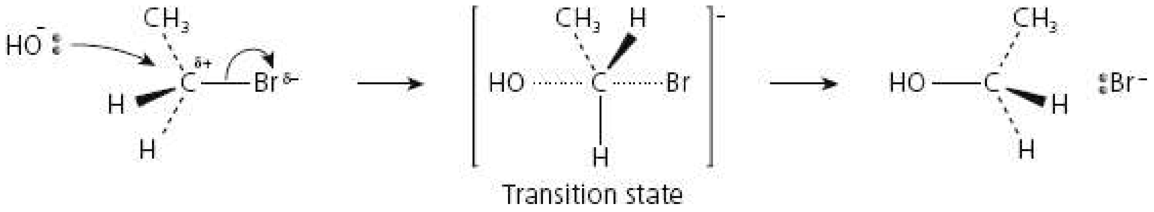

Figure 15.2

With a tertiary halogenoalkane, the mechanism is still nucleophilic substitution:

STUDY TIP

Think of S_N1 as 'Substitution Nucleophilic, 1 reactant'.

$$(CH_3)_3CBr + OH^- \rightarrow (CH_3)_3COH + Br^-$$

However, in this mechanism, only *one* molecule is present in the rate-determining step (slow step). This is an S_N1 mechanism, even though there are two stages (Figure 15.3).

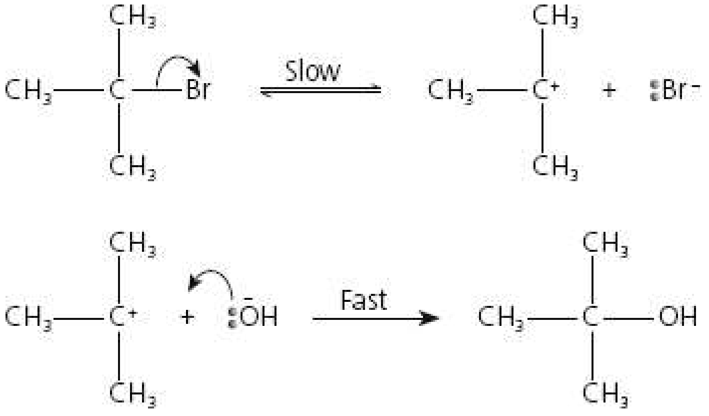

Figure 15.3

For a secondary halogenoalkane, the mechanism is a combination of S_N1 and S_N2.

It is important to remember that alkyl groups have an inductive effect and that this will influence the reaction mechanism.

There is another reaction that can take place when halogenoalkanes react with hydroxide ions – this is covered on page 99.

STUDY TIP

For a given halogenoalkane, to favour **substitution** use:

- lower temperatures
- more dilute solutions of sodium or potassium hydroxide
- more water in the solvent mixture

NOW TEST YOURSELF

2 Write equations to show the two reactions by which $(CH_3)_2CHBr$ reacts with OH^-.

Formation of nitriles

When a halogenoalkane is heated under reflux with cyanide ions dissolved in ethanol, the cyanide ion is substituted for the halogen atom and a nitrile is formed:

$$CH_3CH_2Br + CN^- \rightarrow CH_3CH_2CN + Br^-$$

This is an important reaction because a carbon atom has been added to the carbon chain and the nitrile group can be reacted further.

Secondary and tertiary halogenoalkanes react in a similar way, but the mechanism may be different.

NOW TEST YOURSELF

3 Why is the reaction of CN^- ions with halogenoalkanes important?

Formation of primary amines

When a halogenoalkane is heated with ammonia, a reflux process cannot be used because the ammonia would escape as gas. This reaction has to be carried out in a sealed tube. The reaction takes place in two steps:

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

$$CH_3CH_2NH_3^+Br^- + NH_3 \rightarrow CH_3CH_2NH_2 + NH_4^+Br^-$$

However, in a sealed tube the reaction does not stop with the formation of a primary amine. It continues replacing successive hydrogens on the nitrogen to give secondary amines and then tertiary amines, and finally a quaternary ammonium salt. Note that these reactions are *not* needed for AS Level or A Level.

Elimination of hydrogen bromide

Under similar conditions to those needed for nucleophilic substitution, it is possible to get an elimination reaction to take place. If, instead of aqueous ethanol, a concentrated hydroxide solution in pure ethanol is used, HBr is eliminated and a double bond is formed:

$$CH_3CH_2Br + OH^- \rightarrow CH_2{=}CH_2 + H_2O + Br^-$$

It is important to remember that different halogenoalkanes favour one type of reaction over the other (Table 15.1).

STUDY TIP

For a given halogenoalkane, to favour **elimination** use:

- higher temperatures
- a concentrated solution of sodium or potassium hydroxide
- pure ethanol as the solvent

Table 15.1

Halogenoalkane	Reaction favoured
Primary	Mainly **substitution**

Halogenoalkane	**Reaction favoured**
Secondary	Both
Tertiary	Mainly **elimination**

Different types of halogenoalkane

So far we have used bromoethane as the exemplar halogenoalkane and for most purposes that is fine. However, you must not forget that different halogens have different effects on the halogenoalkanes they form, not least because of the relative strengths of the C–Hal bond (Table 15.2).

Table 15.2

Bond	**Bond energy/kJ mol^{-1}**
C–F	467
C–Cl	338
C–Br	276
C–I	238

For a halogenoalkane to react, the C–Hal bond has to be broken. From Table 15.2 you can see that this is much more difficult for fluoroalkanes than for the other members of the group.

We can see this trend in a practical context when we look at the reactions of halogenoalkanes with aqueous silver nitrate in ethanol (Table 15.3).

Table 15.3

Compound	**Observation with aqueous $AgNO_3$ in ethanol**	**Colour of precipitate**
$(CH_3)_2CH–Cl$	Slight cloudiness after 1 hour	White
$(CH_3)_2CH–Br$	Cloudiness appears after a few minutes	Pale cream

Compound	**Observation with aqueous $AgNO_3$ in ethanol**	**Colour of precipitate**
$(CH_3)_2CH–I$	Thick precipitate appears within a minute	Pale yellow

NOW TEST YOURSELF

4 Explain why fluoroalkanes are more difficult to react with OH^- ions than are bromoalkanes.

REVISION ACTIVITY

a Why is a carbon–halogen bond polar?

b Why does iodoethane react faster than chloroethane with warm, aqueous sodium hydroxide?

c Put the following compounds in order of ease of hydrolysis with warm, aqueous sodium hydroxide, starting with the most reactive:

CH_3CH_2Br $(CH_3)_2CHBr$ CH_3CH_2Cl

END OF CHAPTER CHECK

By now you should be able to:

- recall the reactants and conditions by which halogenoalkanes can be produced
- classify halogenoalkanes into primary, secondary and tertiary
- describe the nucleophilic substitution reactions of halogenoalkanes with NaOH(aq); KCN in ethanol; NH_3 in ethanol; $AgNO_3$(aq) in ethanol
- describe the elimination reaction of halogenoalkanes with NaOH in ethanol to form an alkene
- describe S_N1 and S_N2 mechanisms of nucleophilic substitution, including the inductive effect of alkyl groups and that primary

halogenoalkanes react via S_N2 while tertiary halogenoalkanes react via S_N1
- describe and explain the different reactivities of halogenoalkanes with $AgNO_3(aq)$ based on the strengths of the C–X bonds