

Haloalkanes

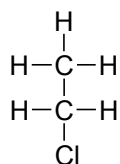
General

A haloalkane is a compound in which one or more H atoms of an alkane are replaced by halogen atoms.

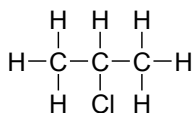
If one hydrogen atom is replaced, the general formula is $C_nH_{2n+1}X$
where X = F, Cl, Br or I

Like alcohols, haloalkanes are classified as primary, secondary or tertiary depending on the number of carbon atoms bonded to the carbon which carries the halogen.

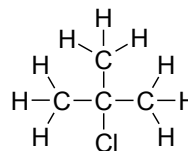
Primary:



Secondary:



Tertiary:



Check your understanding:

i) Identify the four isomers of C_4H_9Br , name them, and classify them as primary, secondary or tertiary.

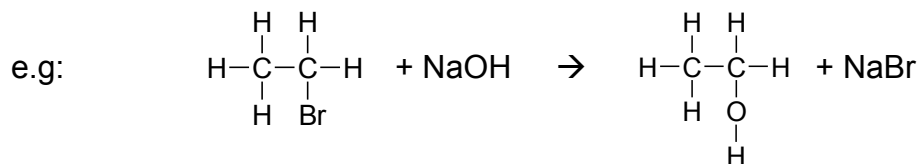
Reactions of the Halogenoalkanes

The X- group is electronegative, so the C-X bond is polar, with the C being charged $\delta+$. This makes the carbon atom susceptible to attack by reagents which are electron-pair donors.

We define **nucleophiles** as **electron-pair donors**. The electrons donated are from a lone pair on an electronegative atom.

examples of nucleophiles: $:\text{OH}^-$ $:\text{X}^-$ $\text{H}_2\text{O}:$ $:\text{NH}_3$

To illustrate the way nucleophiles can attack a $\delta+$ carbon, we will consider the **hydrolysis** of primary haloalkanes to form alcohols:

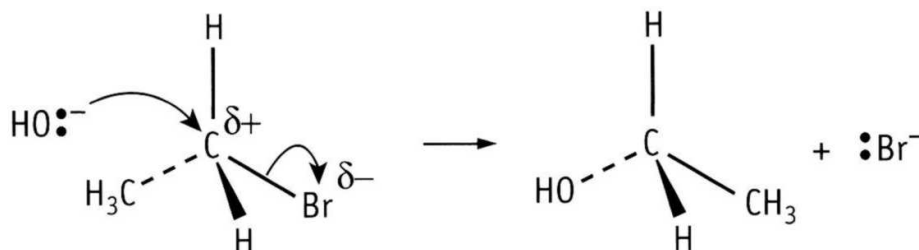


We can see that the $-\text{Br}$ has been replaced by $-\text{OH}$, so this is a **substitution** reaction.

Reagent: aqueous alkali e.g. NaOH or KOH

Conditions: the reaction mixture is heated under reflux

Mechanism for nucleophilic substitution:



Check your understanding:

ii) Draw the mechanism for the hydrolysis of 1-chloropropane using hydroxide ions.

iii) Write a balanced equation for the reaction of 1,2-dichlorocyclohexane with excess hydroxide ions, and suggest the reagents and conditions required for a second step to make cyclohexa-1,3-diene.

Rates of reaction of the different halogens

If we compare the rates of reaction of similar haloalkanes e.g. 1-chlorobutane, 1-bromobutane and 1-iodobutane we find the rates of reaction are different. Two factors affect the rate of the reaction:

- 1) The electronegativity of the halogen determines how δ^+ the carbon atom will be and therefore how strongly it will attract the nucleophilic OH^- . If this is the dominant factor, then we will see 1-chlorobutane react the fastest and 1-iodobutane react the slowest
- 2) The strength of the bond between the C and the X atom determines how much energy is required to break it and therefore what proportion of collisions between the haloalkane and the OH^- will be successful.

Bond enthalpies	(kJmol ⁻¹)
C-F	467
C-Cl	340
C-Br	280
C-I	240

If this is the dominant factor then we will see 1-iodobutane react the most quickly and 1-chlorobutane react the most slowly.

Doing the investigation

We need to see how quickly the Cl^- , Br^- or I^- appears in the solution so we can use $\text{Ag}^+_{(\text{aq})}$ ions to show this, as a silver halide precipitate will form.

$\text{Ag}^+_{(\text{aq})}$ will also react with $\text{OH}^-_{(\text{aq})}$, however, forming a $\text{AgOH}_{(\text{s})}$ precipitate so we can't use sodium or potassium hydroxide to provide the $\text{OH}^-_{(\text{aq})}$.

Instead, we can use water as the nucleophile, donating a lone pair from the oxygen atom to substitute the –OH group, although the rate will be much slower than when an alkali is present.



Haloalkanes don't dissolve in water readily, so a little ethanol can be added as a solvent. The lone pair on the O of the ethanol means that this can also act as a nucleophile, so care must be taken to use exactly the same amount of ethanol in each experiment.

Results & Conclusion

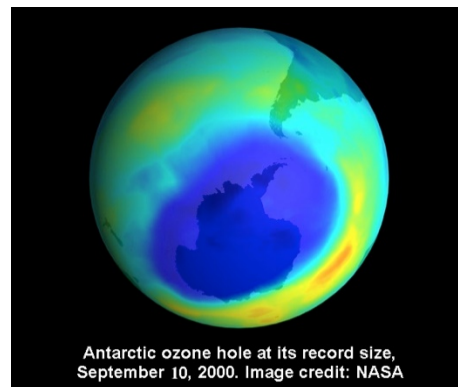
Experimental investigation shows that 1-iodobutane reacts most quickly and 1-chlorobutane most slowly. The C-F bond in fluoroalkanes is so strong that it rarely undergoes hydrolysis. These results show that the strength of the C-X bond is the factor which determines the rate of hydrolysis of the halogenoalkanes.

Ozone depletion – role of haloalkanes

Complex life on earth would not be possible, or at least would have evolved very differently, if we were fully exposed to the ultraviolet content of the sun's radiation. Exposure to increased levels of UV causes tissue damage in plants and animals, increasing melanoma risks for humans.

Ozone (O_3), represented as $\text{O}=\text{O}\rightarrow\text{O}$, is not normally present in the atmosphere close to the earth's surface, but 25km up in the stratosphere there is a layer containing ozone which is about 15km thick. This ozone absorbs ultraviolet radiation, preventing it from reaching the earth's surface.

The "hole" in the ozone layer was discovered where the layer had significantly thinned over the Antarctic, allowing harmful uv through.



The main cause of the hole in the ozone layer was found to be chlorine radicals. The presence of chlorine radicals in the stratosphere (which weren't there a few decades before!) was mainly attributed to the use of refrigerant and fire-suppressant gases called chlorinated fluorocarbons (CFCs).

CFCs have low reactivity, low toxicity and are easily condensed and evaporated (volatile). These properties made them very suitable for use as aerosol propellants and as the refrigerant liquid in fridges and air conditioners, and as blowing agents in expanded foams such as expanded polystyrene. It was originally thought that their low flammability and low toxicity made them environmentally friendly. Examples of those used include CCl_2F_2 and CCl_3F . The low reactivity makes CFCs very persistent in the atmosphere, and the extent of their use has led to significant levels in the upper atmosphere.

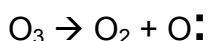
The use of CFCs was phased out in the Montreal Protocol of 1987. There is still concern about ozone depletion despite Montreal protocol and CFCs being banned and replaced in products because:

- CFCs may take a long time to reach ozone layer/long residence time
- CFCs are still being used in some countries/some products
- there are other ozone-depleting substances than CFCs

The first replacements for CFCs were hydrochlorofluorocarbons (**HCFCs**), which deplete ozone to a much lesser extent than CFCs. Hydrofluorocarbons (**HFCs**) offer a better solution: unlike CFCs and HCFCs, HFCs do not deplete ozone at all, lacking a C-Cl bond.

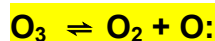
Mechanism

UV (300nm wavelength) is able to cause homolytic fission in ozone, causing the reaction

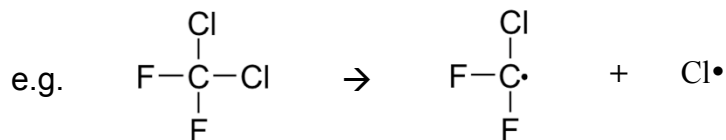


Note: the oxygen di-radical has two unpaired electrons - consider its electron arrangement $1s^2 2s^2 2p^4$ ($2p_x^2 2p_y^1 2p_z^1$) - rather than three lone pairs.

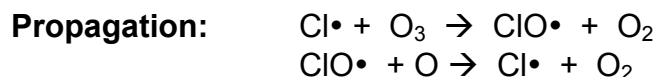
The reactive oxygen radicals react readily with oxygen molecules to form ozone, so an equilibrium is established, meaning that there are all three oxygen species present in the upper atmosphere:



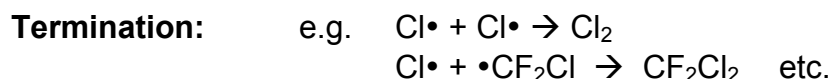
Initiation: UV light also causes homolytic fission of C-Cl bonds in CFCs in the upper atmosphere, creating chlorine radicals.



The chlorine free radical then acts as a catalyst for the decomposition of ozone, being regenerated each time it breaks down an ozone molecule.



It has been estimated that one chlorine radical can destroy approximately 1000 ozone molecules before it is terminated in a reaction with some other radical such as $\bullet\text{CF}_2\text{Cl}$ or another Cl^\bullet .

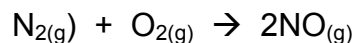


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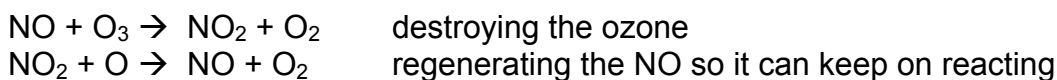
- CFCs may take a long time to reach ozone layer/long residence time
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Ozone depletion – other causes

Compounds which contains C-Cl are not the only ones which can destroy ozone. The role of nitrogen monoxide (NO) is also of concern. Thunderstorms are a major natural source of this gas, but they are also created in the upper atmosphere by the high-temperature combustion of nitrogen and oxygen from the air inside aircraft jet engines.



What happens in the stratosphere are the following propagation steps (in this case no initiation step is needed):



It is worth noting that these two reactions are the same as those occurring with the chlorine radical, so we can generalise the destruction of the ozone layer to:



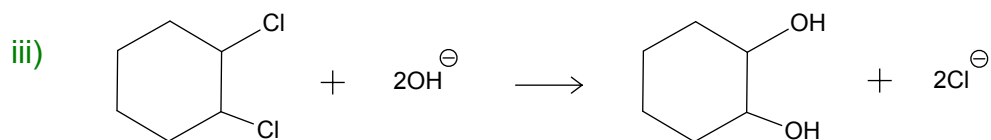
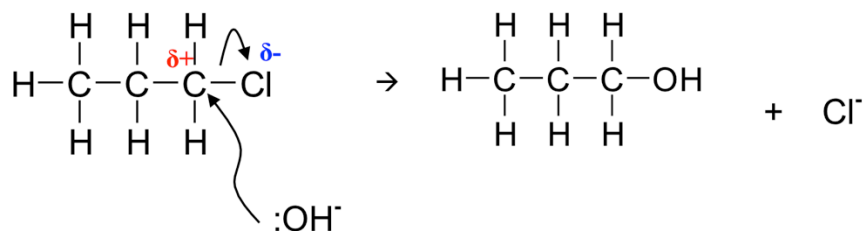
There are other possible 'R' species which can destroy ozone in the same way, and you could be expected to construct equations of the kind above, given information about these.

Check your understanding:

i) Identify the four isomers of C_4H_9Br , name them, and classify them as primary, secondary or tertiary:

1-bromobutane	$CH_2BrCH_2CH_2CH_3$	primary
2-bromobutane	$CH_3CHBrCH_2CH_3$	secondary
1-bromomethylpropane	$(CH_3)_2CHCH_2Br$	primary
2-bromomethylpropane	$(CH_3)_3CBr$	tertiary

ii) Draw the mechanism for the hydrolysis of 1-chloropropane using hydroxide ions.



Subsequent step is dehydration of the alcohol groups, refluxing with hot concentrated sulphuric or phosphoric acid:

