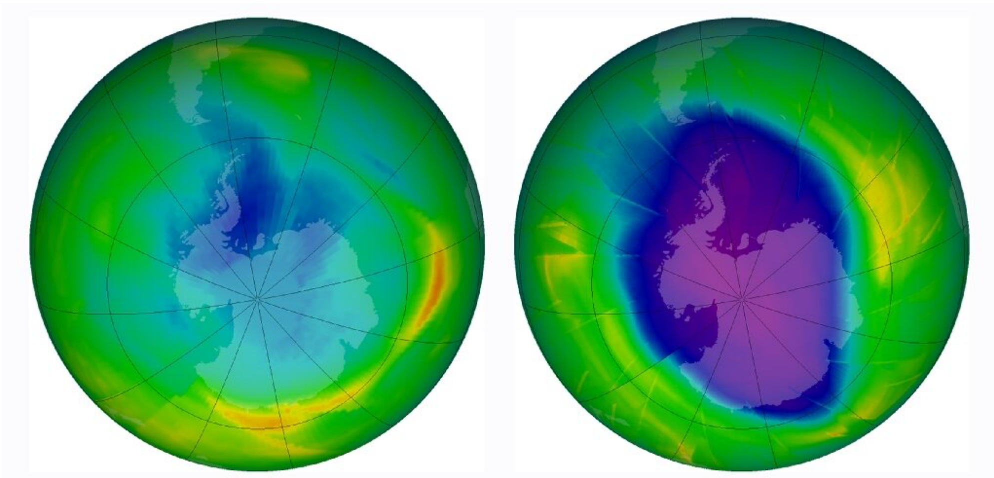
HALOGENOALKANES



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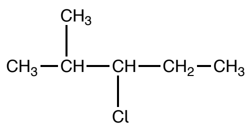
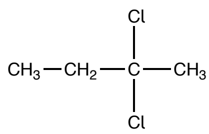
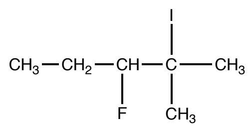
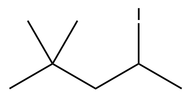
INTRODUCTION

- Halogenoalkanes are similar to alkanes but with one or more halogen atoms (F, Cl, Br, I) bonded to C atoms in place of H atom(s).
- They can be made from alkanes by free radical substitution reactions.
- They are much more reactive than alkanes and provide many routes into the synthesis of useful organic compounds.

TASK 1 – Drawing and naming halogenoalkanes

structure				
name				

NUCLEOPHILIC SUBSTITUTION REACTIONS

- In a **substitution** reaction, the halogen atom is replaced by another atom/group.
- Halogenoalkanes are susceptible to attack by **nucleophiles** (lone pair donors) such as OH^-, CN^- and NH_3
- This is because the C-halogen bond is polar with the C atom being $\delta+$
- The C-halogen bond is polar because the halogen atom is more electronegative than the carbon atom.
- The rate of the reaction is affected by the strength of the C-halogen bond. The weaker the bond, the faster the reaction.

rate of reaction

fastest ← **slowest**

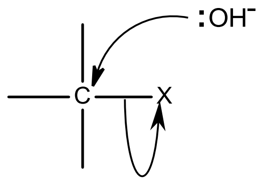
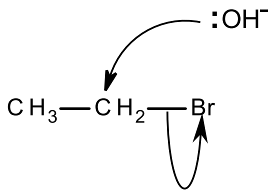
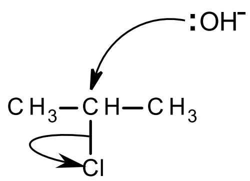
iodoalkanes > bromoalkanes > chloroalkanes > fluoroalkanes

C–halogen bond strength

weakest bond → **strongest bond**

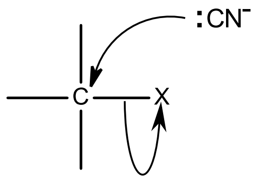
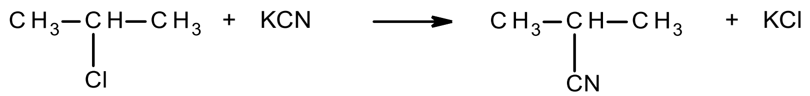
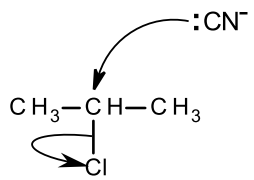
C–I > C–Br > C–Cl > C–F

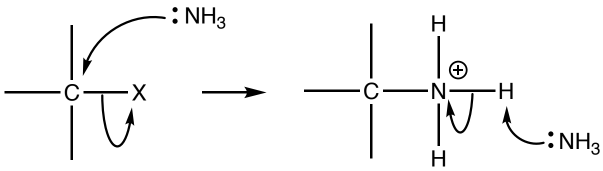
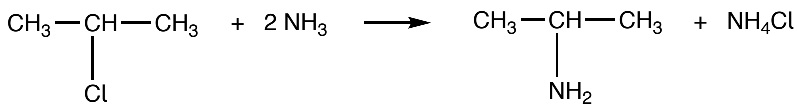
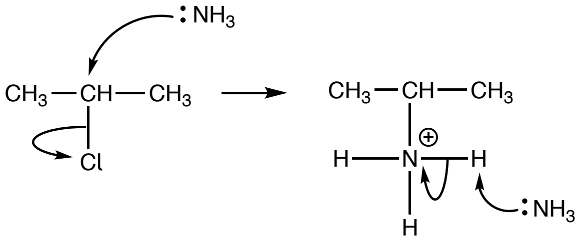
NUCLEOPHILIC SUBSTITUTION 1 – reaction with warm, aqueous NaOH

Reagent	NaOH
Conditions	aqueous, warm
What happens	halogen atom is replaced by OH group
Overall equation	R—X + NaOH ⟶ R—OH + NaX
Mechanism	**nucleophilic substitution** 
Example 1	e.g. bromoethane + aqueous NaOH $CH_3—CH_2—Br$ + NaOH ⟶ $CH_3—CH_2—OH$ + NaBr **nucleophilic substitution** 
Example 2	e.g. 2-chloropropane + aqueous NaOH $CH_3—CH(Cl)—CH_3$ + NaOH ⟶ $CH_3—CH(OH)—CH_3$ + NaCl **nucleophilic substitution** 
Example 3	e.g. 1-bromopropane + aqueous NaOH

Example 4	e.g. 2-iodo-3-methylbutane + aqueous NaOH

NUCLEOPHILIC SUBSTITUTION 2 – reaction with KCN

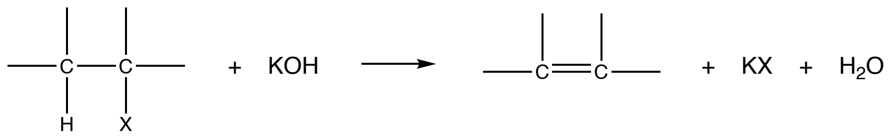
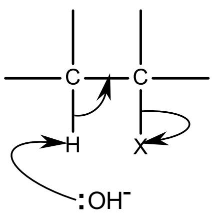
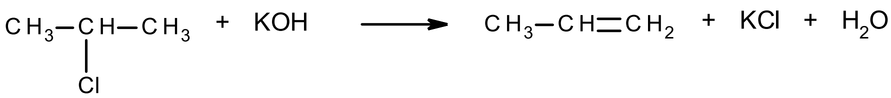
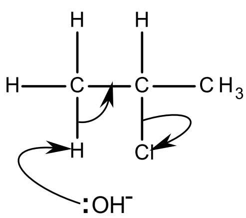
Reagent	KCN
Conditions	Aqueous ethanol, warm
What happens	halogen atom is replaced by CN group
Overall equation	R—X + KCN ⟶ R—CN + KX
Mechanism	**nucleophilic substitution** 
Example 5	e.g. 2-chloropropane + KCN in aqueous ethanol  **nucleophilic substitution** 
Example 6	e.g. 1-bromobutane + KCN in aqueous ethanol

NUCLEOPHILIC SUBSTITUTION 3 – reaction with NH_3	
Reagent	NH_3
Conditions	Excess concentrated ammonia dissolved in ethanol at pressure in a sealed container
What happens	first molecule of NH_3: the halogen atom is replaced by NH_3 group second molecule of NH_3: removes H^+ from added NH_3
Overall equation	$R{-}X + 2\,NH_3 \longrightarrow R{-}NH_2 + NH_4X$
Mechanism	**nucleophilic substitution** 
Example 7	e.g. 2-chloropropane + excess conc NH_3  **nucleophilic substitution** 
Example 8	e.g. 2-bromo-3-methylbutane + excess conc NH_3

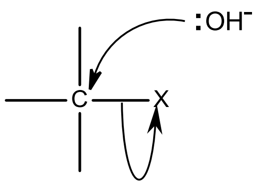
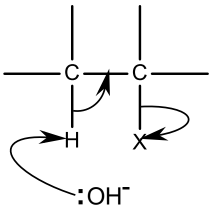
ELIMINATION REACTIONS

- When halogenoalkanes react with OH^- ions, an elimination reaction can compete with the nucleophilic substitution reaction.
- Elimination is favoured if hot, ethanolic KOH is used instead of warm, aqueous NaOH.
- The change from NaOH to KOH is simply about solubility, with KOH being more soluble than NaOH in ethanol. The key changes are the solvent (from water to ethanol) and the higher temperature.
- In elimination, an H and X are removed from adjacent C atoms giving an alkene.
- This reaction can give a mixture of alkenes, either because the H can come from different adjacent C atoms, or because the alkenes formed have *E/Z* stereoisomerism.
- If there is no H on a C atom adjacent to the C-X then no elimination is possible.
- In elimination, the OH^- ion acts as a base. In substitution, the OH^- ion acts as a nucleophile.

ELIMINATION – reaction with hot, ethanolic KOH

Reagent	KOH
Conditions	Ethanolic, hot
What happens	The halogen atom and one H atom from an adjacent C atom is removed giving an alkene (note that elimination cannot happen if there is no H on an adjacent C atom). A mixture of alkenes could be formed depending on which of the adjacent C atoms the H is lost from.
Overall equation	
Mechanism	**elimination** 
Example 9	e.g. 2-chloropropane + hot, ethanolic KOH  **elimination** 

Example 10	e.g. 2-bromobutane + hot, ethanolic KOH (to give but-2-ene)

COMPETING REACTIONS WITH OH^-		
Mechanism name	Nucleophilic substitution	Elimination
Solvent	Water	Ethanol
Temperature	Warm	Hot
Reagent	NaOH	KOH (more soluble than NaOH)
Role of OH^-	Nucleophile	Base
Products	Alcohol	Alkene(s)
Outline of mechanism		

TASK 2 – Competing reactions

2-bromo-2-methylbutane reacts with hydroxide ions to form an alcohol and two alkenes.

ALCOHOL	
Structure of alcohol	
Name of alcohol	
Balanced equation	
Name of mechanism	
Outline of mechanism	
Role of OH^- ion	
Reagent and conditions to favour this reaction	

ALKENE 1	
Structure of alkene	
Name of alkene	
Balanced equation	
Name of mechanism	
Outline of mechanism	
Role of OH^- ion	
Reagent and conditions to favour this reaction	

ALKENE 2	
Structure of alkene	
Name of alkene	
Balanced equation	
Name of mechanism	
Outline of mechanism	
Role of OH^- ion	
Reagent and conditions to favour this reaction	

TASK 3 – Reactions of halogenoalkanes

1)	**bromoethane + aqueous NaOH**
	balanced equation (showing structural formulae)
	name of organic product
	name of mechanism
	mechanism outline
2)	**2-bromopropane + ethanolic KOH**
	balanced equation (showing structural formulae)
	name of organic product
	name of mechanism
	mechanism outline
3)	**chloroethane + NH_3 (excess of NH_3)**
	balanced equation (showing structural formulae)
	name of organic product
	name of mechanism
	mechanism outline

4)	chloromethane + chlorine (with uv light, excess of chloromethane)
	balanced equation (showing structural formulae)
	name of organic product
	name of mechanism
	mechanism outline

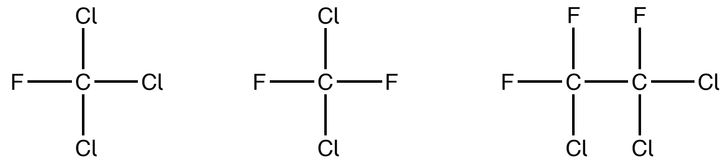
5)	1-chloropropane + KCN
	balanced equation (showing structural formulae)
	name of organic product
	name of mechanism
	mechanism outline

CFCs and the OZONE LAYER

What are CFCs?

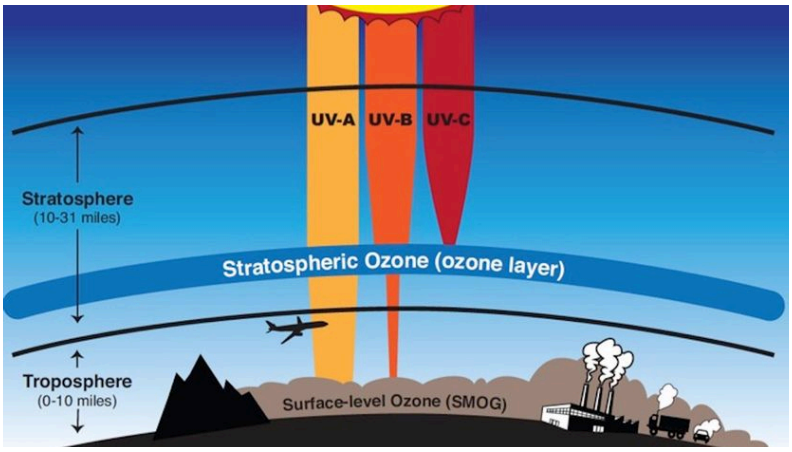
- CFCs are chlorofluorocarbons.
- CFCs were used as
  - coolant in refrigerators
  - propellant in aerosols
  - degreaser for circuit boards

e.g.



What is ozone?

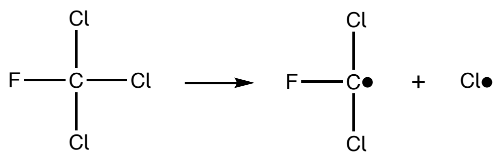
- Ozone is a form of oxygen, O_3
- There is a "layer" of ozone in the stratosphere (a region where there is a higher concentration of ozone)
- The ozone layer absorbs harmful UV radiation. This radiation can damage DNA and cause, for example, skin cancer.



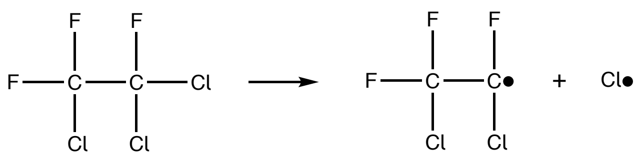
What CFCs do to the ozone layer

- CFCs escape and rise into the stratosphere.
- CFCs break down in the stratosphere to form Cl● free radicals by the breaking of a C–Cl bond. The energy comes from UV light. For example

e.g.



e.g.



- These Cl● free radicals catalyse the destruction of ozone in a free radical chain reaction.

$$Cl\bullet + O_3 \rightarrow ClO\bullet + O_2$$

$$ClO\bullet + O_3 \rightarrow Cl\bullet + 2O_2$$

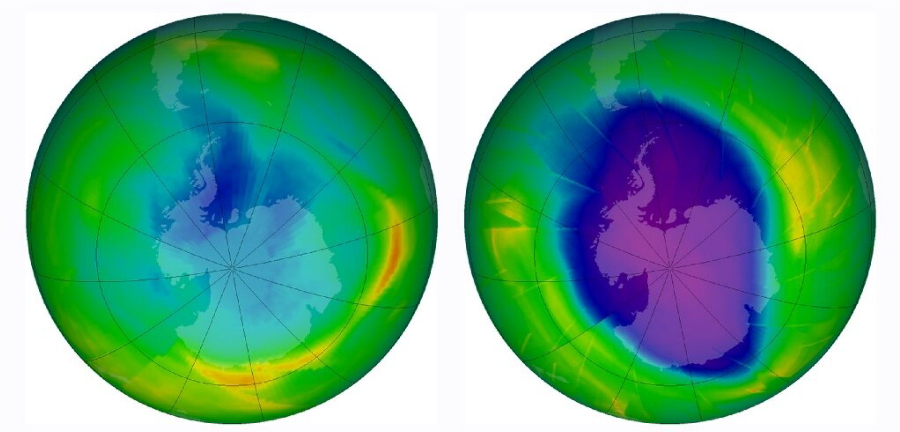
$$\text{Overall} \quad 2O_3 \rightarrow 3O_2$$

- One Cl● free radical can catalyse the destruction of a huge number of ozone molecules.

Ozone depletion

- The concentration of ozone in the ozone layer fell significantly as CFCs went into large scale use.
- The fall in concentration was particularly significant over the Earth's poles. These areas are often referred to as "holes" in the ozone layer.
- Chemists suspected that the large-scale use of CFCs would lead to depletion of the ozone layer. In 1974, Molina and Rowland published research to show how CFCs would damage the ozone layer.
- In the early 1980s, evidence started to appear to show that the ozone layer was being depleted, in particular near the Earth's poles. Since then, skin cancer has become a much greater problem, especially in countries nearer the poles such as Australia.
- In 1995 Molina and Rowland won the Nobel Prize for Chemistry for their work on ozone and CFCs.

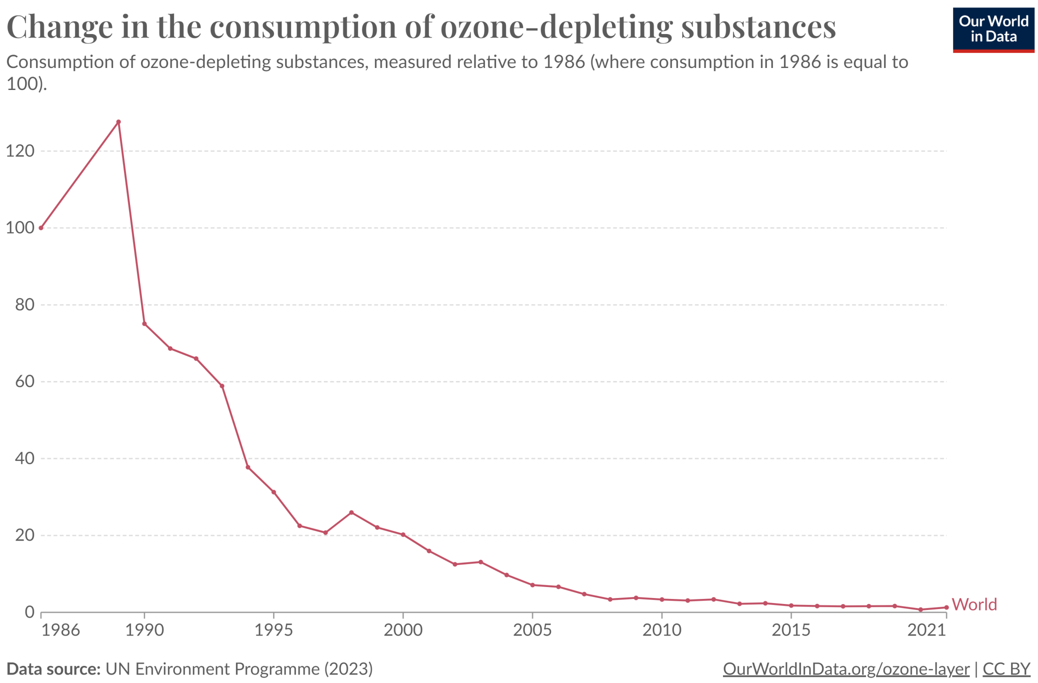
Antarctica ozone "hole"



1979 2009

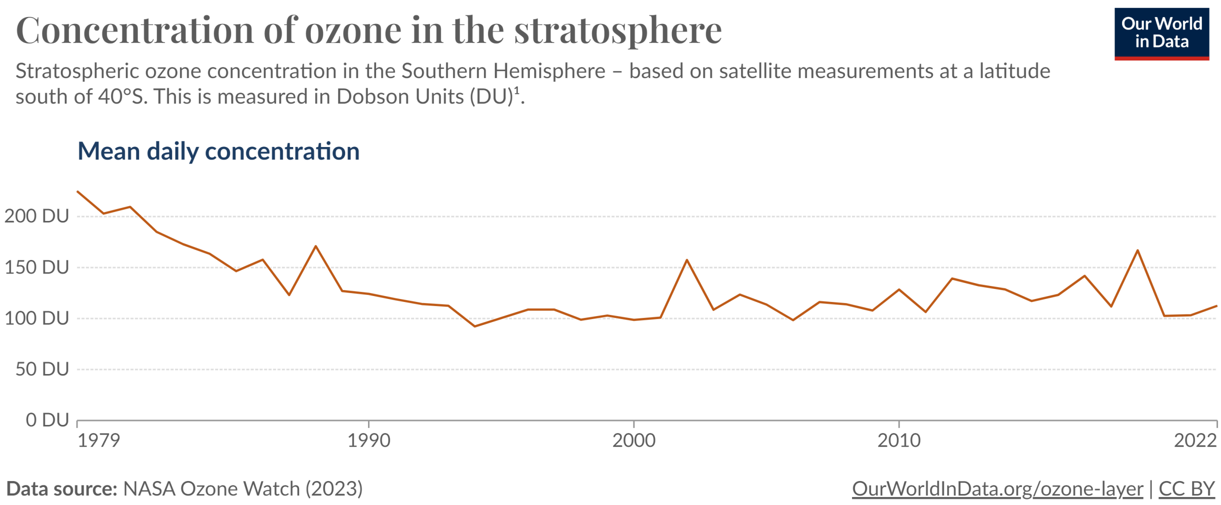
Montreal Protocol

- In 1987, several countries (including the UK) signed the Montreal Protocol to ban the use of CFCs.
- More countries have since banned their use and so the use of CFCs has fallen dramatically.
- The banning of the use of CFCs is one of the most effective environmental actions ever.



The ozone layer since the banning of CFCs

- The concentration of ozone in the atmosphere has stopped falling in recent years. The
- There are still some CFCs in use, for example in old refrigerators. While the CFCs are properly removed and disposed of from many old refrigerators, this is not always the case and so some are still being emitted into the atmosphere.
- It is predicted that the ozone concentration will start to rise again over time, but we have stopped its depletion.



Alternatives to CFCs

- CFCs have been replaced by chemicals that do not contain chlorine, e.g.
  - 1,1,1,2-tetrafluoroethane as the coolants in refrigerators, CF_3CH_2F
  - butane as the propellant in aerosols, $CH_3CH_2CH_2CH_3$
- They cannot break down to produced chlorine free radicals as they do not contain any chlorine atoms.
- It should noted that all the CFC replacements are greenhouse gases (as are CFCs) and so they are not without some problems still.

TASK 4 – CFCs & OZONE

1 **a** Write an equation to show the formation of ozone destroying free radicals from CFC-12, CF_2Cl_2

………

b Write a pair of equations to show how free radicals from part **a** destroy ozone molecules.

………

………

2 **a** Write an equation to show the formation of ozone destroying free radicals from CFC-114, CF_2ClCF_2Cl

………

b Write a pair of equations to show how free radicals from part **a** destroy ozone molecules.

………

………

c Explain why one free radical from part **a** can destroy very many ozone molecules.

………

………

3 R-134a (CF_3CH_2F) is commonly used as a refrigerant in place of CFCs. Explain why this compound cannot destroy ozone.

………

………