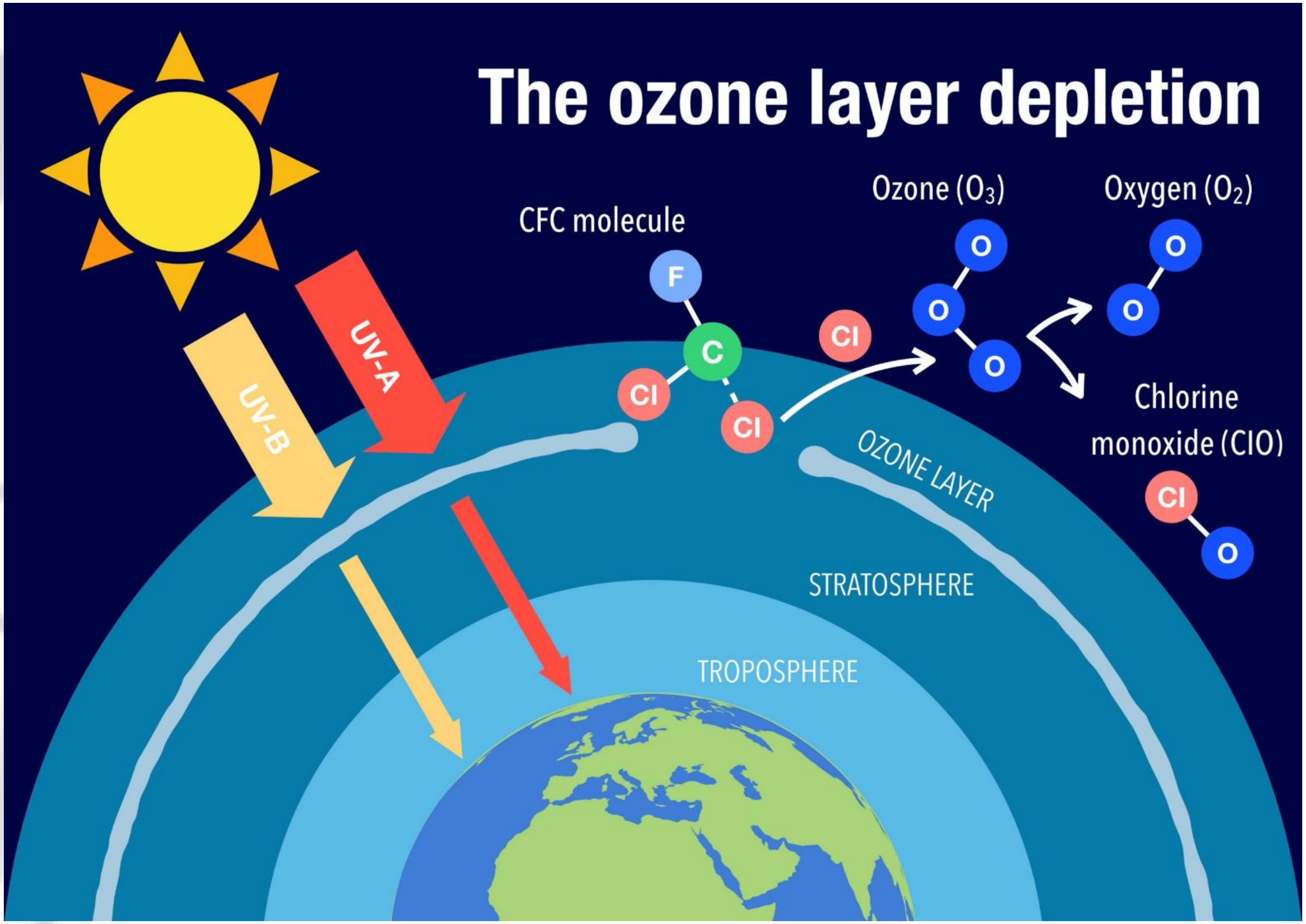
Halogenoalkanes



Learning Objectives

- Recall the synthesis of chloroalkanes
- Understand environmental concerns about haloalkanes and understand the mechanism of ozone depletion
- Know less environmentally damaging substitutes for haloalkanes

Success Criteria

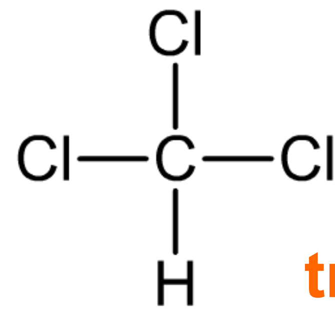
- Write equations for the synthesis of chloroalkanes and other halogenoalkanes.
- Gives some examples of halogenoalkanes and their uses.
- Outline and draw the mechanisms for synthesis of halogenoalkanes and ozone depletion.
- Suggest examples of less environmentally damaging substitutes for haloalkanes.

Keywords

- Halogenoalkane (haloalkane)
- Chlorofluorocarbons (CFCs)
- Primary, secondary, tertiary haloalkanes
- Free radical substitution
- Electrophilic addition
- Initiation, propagation, termination
- Radicals
- Ozone depletion
- Hydrofluorocarbons (HFCs)

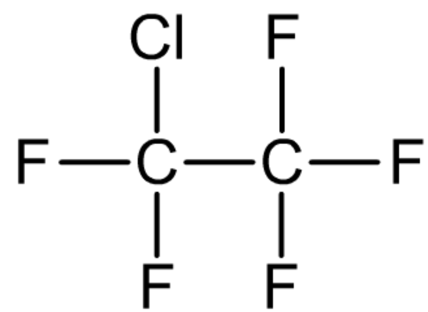
What are halogenoalkanes?

Halogenoalkanes are similar to alkanes but with one or more of the hydrogen atoms replaced by a halogen.



trichloromethane

Halogenoalkanes can contain more than one type of halogen. For example, **CFCs (chlorofluorocarbons)** contain both chlorine and fluorine atoms.



chloro-pentafluoroethane

Some halogenoalkanes are useful themselves, but many are valuable **intermediates** in the production of other molecules.

Naming halogenoalkanes

A prefix is added to the name of the alkane depending on what halogens are attached.

halogen	prefix
fluorine	fluoro-
chlorine	chloro-
bromine	bromo-
iodine	iodo-

no. halogen atoms	prefix
one	–
two	di-
three	tri-
four	tetra-
five	penta-

Another prefix is used to indicate how many atoms of each halogen is present.

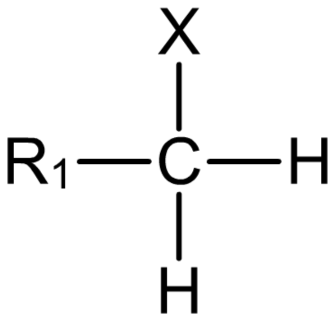
Numbers are used, where necessary, to indicate to which carbon atom(s) each halogen is attached.

What's the halogenoalkane?

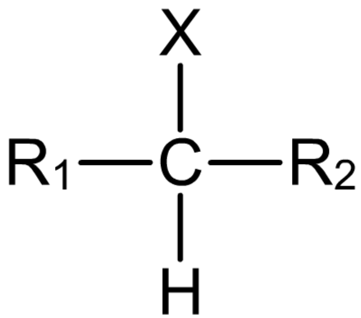
Primary, secondary and tertiary

A chain of carbon atoms can be represented by R when drawing the structure. This is referred to as an **R group**.

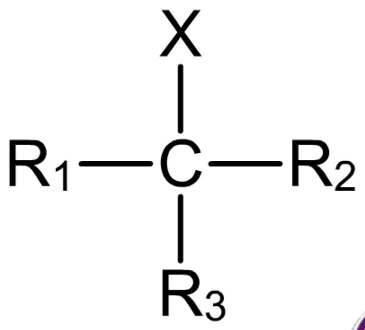
- **Primary (1°) halogenoalkanes** have one R group attached to the carbon linked to the halogen.



- **Secondary (2°) halogenoalkanes** have two R groups attached to the carbon linked to the halogen.



- **Tertiary (3°) halogenoalkanes** have three R groups attached to the carbon linked to the halogen.



Primary, secondary or tertiary?

How are halogenoalkanes made?

There are several ways by which halogenoalkanes can be made, including:

- **free radical substitution** of an alkane:

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$

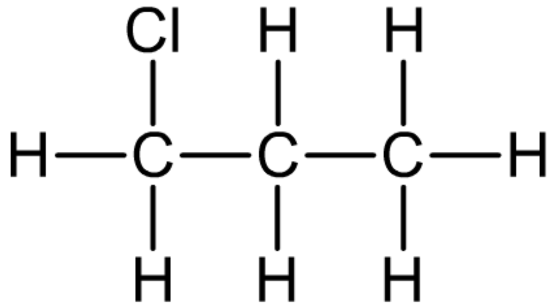
- **electrophilic addition** of HX or X_2 to an alkene:

$$C_2H_4 + HBr \rightarrow C_2H_5Br$$

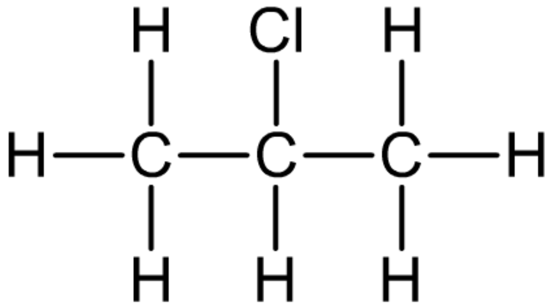
$$C_2H_4 + Br_2 \rightarrow C_2H_4Br_2$$

Other products of chain reactions

If an alkane is more than two carbons in length then any of the hydrogen atoms may be substituted, leading to a mixture of different isomers. For example:



1-chloropropane

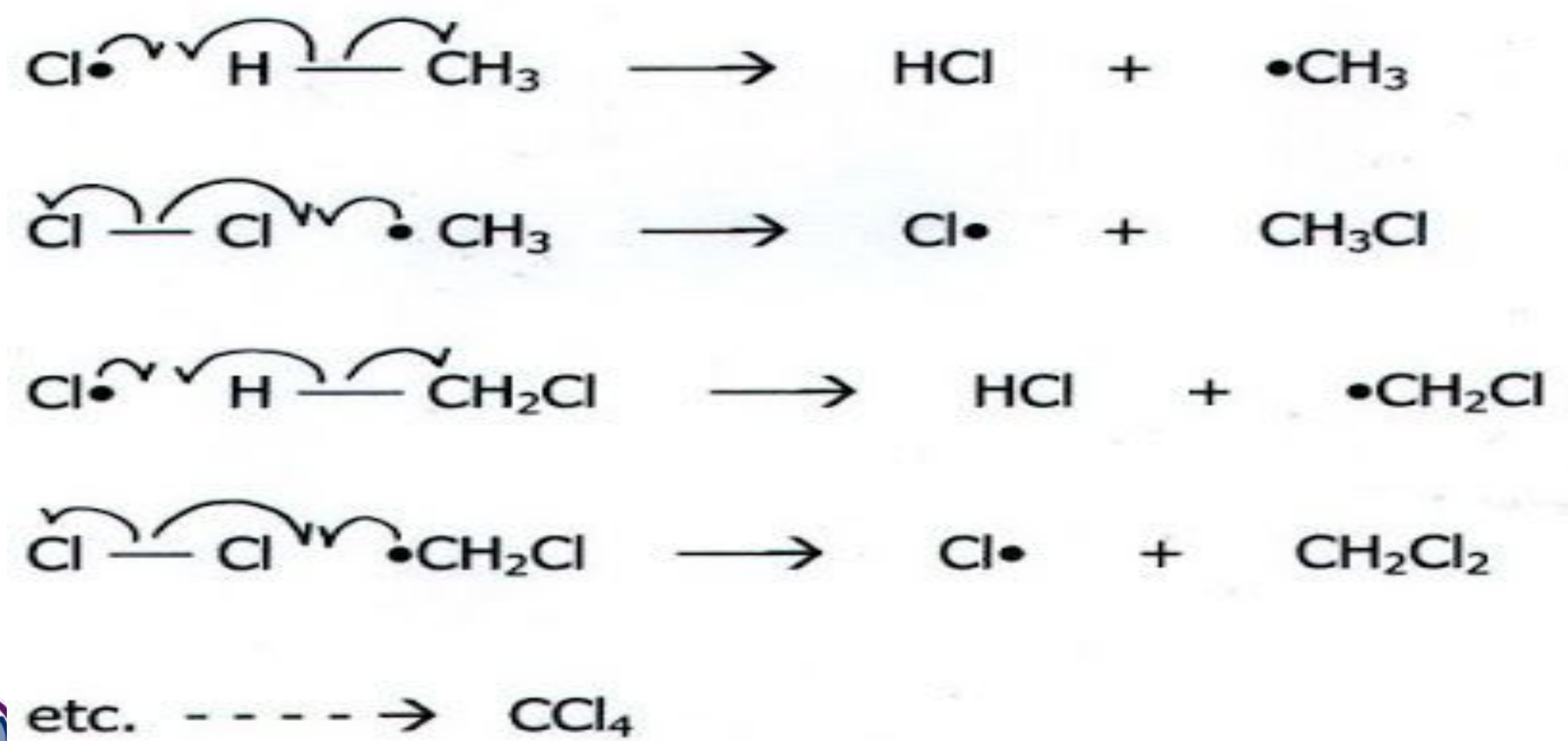


2-chloropropane

The mixture of products is difficult to separate, and this is one reason why chain reactions are not a good method of preparing halogenoalkanes.

Further substitution in chain reactions

Some chloromethane molecules formed during free radical substitution between methane and chlorine will undergo further substitution to form dichloromethane. Further substitution can occur until all hydrogens are substituted.



USES OF HALOGENOALKANES

Synthetic The reactivity of the C-X bond means that halogenoalkanes play an important part in synthetic organic chemistry. The halogen can be replaced by a variety of groups via nucleophilic substitution.

Polymers Many useful polymers are formed from halogeno hydrocarbons

Monomer	Polymer	Repeating unit
chloroethene	poly(chloroethene) PVC	$-(CH_2-CHCl)_n-$
	USED FOR PACKAGING	
tetrafluoroethene	poly(tetrafluoroethene) PTFE	$-(CF_2-CF_2)_n-$
	USED FOR NON-STICK SURFACES	

USES OF HALOGENOALKANES

Chlorofluorocarbons - CFC's

dichlorofluoromethane $CHFCl_2$ refrigerant

trichlorofluoromethane $CFCl_3$ aerosol propellant, blowing agent

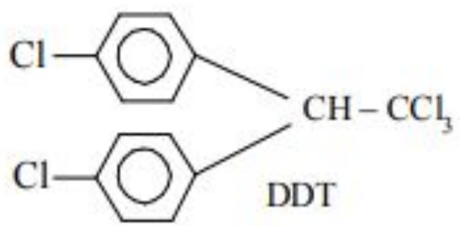
bromochlorodifluoromethane $CBrClF_2$ fire extinguishers

CCl_2FCClF_2 dry cleaning solvent, degreasing agent

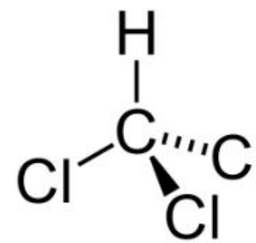
All are chosen because of their LOW REACTIVITY, VOLATILITY, NON-TOXICITY

Benzene hexachloride (BHC) pesticide

Dichlorodiphenyltrichloroethane (DDT) Mosquito control



Chloroform used to extract and purify **penicillin.**



Was used as anesthesia but found to be carcinogenic, very harmful to organs

Free radical substitution: $Cl_2 + CH_4$

Chain initiation

The chain is initiated (started) by UV light breaking a chlorine molecule into free radicals.

$$Cl_2 \longrightarrow 2Cl\bullet$$

Chain propagation reactions

These are the reactions which keep the chain going.

$$CH_4 + Cl\bullet \longrightarrow CH_3\bullet + HCl$$

$$CH_3\bullet + Cl_2 \longrightarrow CH_3Cl + Cl\bullet$$

Chain termination reactions

These are reactions which remove free radicals from the system without replacing them by new ones.

$$2Cl\bullet \longrightarrow Cl_2$$

$$CH_3\bullet + Cl\bullet \longrightarrow CH_3Cl$$

$$CH_3\bullet + CH_3\bullet \longrightarrow CH_3CH_3$$

$$CH_3 + Cl_2 \xrightarrow[h\nu]{520\text{-}670K \text{ or}} CH_3\text{-}Cl + HCl$$

Methane — Methyl Chloride

Step 1: Initiation

$$Cl\text{—}Cl \xrightarrow[h\nu/\ 520\text{-}670K]{\text{Homolytic fisssion}} \dot{C}l + \dot{C}l$$

Free radicals

Step 2: Propagation

$$CH_3\text{-}H + \dot{C}l \longrightarrow .CH_3 + H\text{-}Cl$$

Methyl free radical

$$\cdot CH_3 + Cl\text{—}Cl \longrightarrow CH_3\text{-}Cl + \cdot Cl$$

Step 3: Termination

$$\cdot Cl + \cdot Cl \longrightarrow Cl_2$$

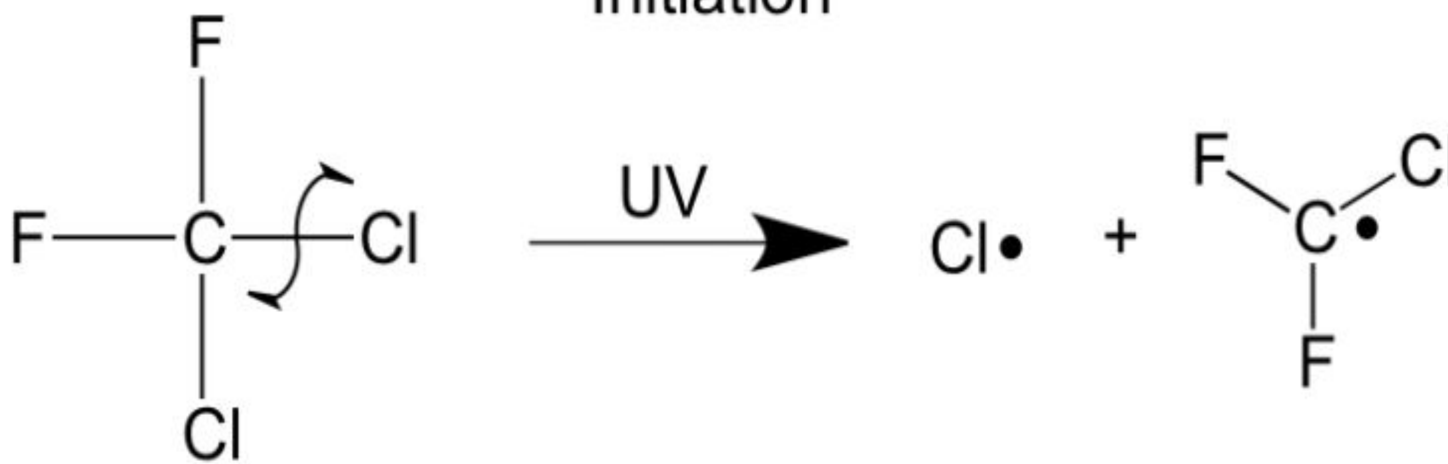
$$\cdot CH_3 + \cdot CH_3 \longrightarrow CH_3\text{—}CH_3$$

Chain reactions and ozone

Ozone Equilibrium

$$O_2 + O \xrightleftharpoons{UV} O_3$$

Initiation



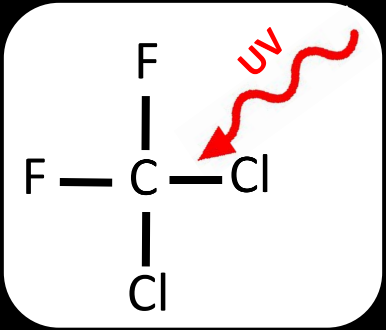
CFC

Free Radicals

<u>CFCs</u>

Chlorofluorocarbons (CFCs) break down ozone (O_3) in the **<u>atmosphere</u>**

CFCs are molecules that have had all their hydrogens replaced by **<u>chlorine</u>** and **<u>fluorine</u>**. They are stable molecules but are broken down by UV.



C-Cl bonds are broken down by **<u>UV radiation</u>** in the atmosphere. **<u>Radicals</u>** are formed catalysing the break down of ozone.

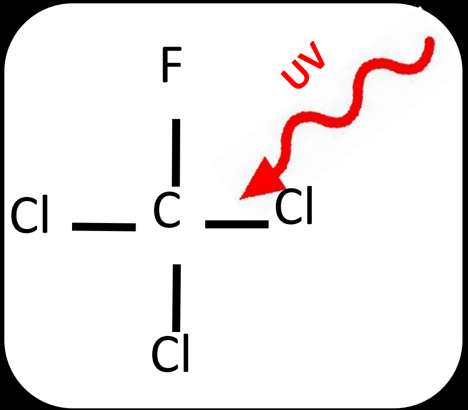
C-Cl bonds are broken easiest by UV as they have the lowest **<u>bond enthalpy</u>**. A C-F bond is less likely to be broken as it is a stronger bond.

How CFCs destroy ozone

CFCs break down to form chlorine radicals that catalyse the break down of ozone

Initiation

Sunlight breaks the C-Cl bond in a CFC molecule and produces 2 radicals which will react with ozone molecules (O_3)



$$CCl_3F_{(g)} + hv \rightarrow \bullet CCl_2F_{(g)} + Cl\bullet_{(g)}$$

1. $Cl\bullet_{(g)} + O_{3(g)} \rightarrow O_{2(g)} + ClO\bullet_{(g)}$
2. $ClO\bullet_{(g)} + O_{3(g)} \rightarrow 2O_{2(g)} + Cl\bullet_{(g)}$

Propagation

1. The Cl• reacts with O_3 to form the ClO• intermediate and O_2.
2. The ClO• reacts with more O_3 to make O_2 and Cl•. As Cl• is reformed it acts as a **catalyst**

Termination

2 radicals react For **example** forming Cl_2.

$$Cl\bullet_{(g)} + Cl\bullet_{(g)} \rightarrow Cl_{2(g)}$$

Overall

$$2O_{3(g)} \rightarrow 3O_{2(g)}$$

Cl• is the catalyst


CFC
The COMET Program

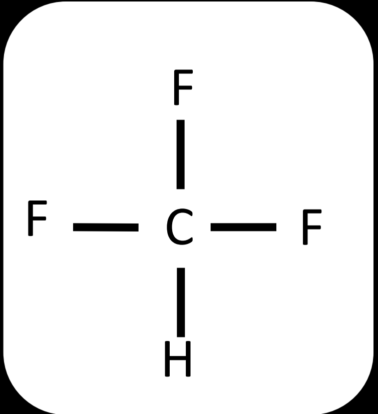
Restricting use of CFCs

Average Bond Dissociation Energie

H—H	436	C—H	410
H—C	410	C—C	350
H—F	570	C—F	450
H—Cl	432	C—Cl	330

CFCs are banned now

CFCs are stable, unreactive, non-toxic chemicals that were used in fridges as a **refrigerant**, and as a **propellant** in deodorants.



It was demonstrated by scientists that CFCs were damaging the **ozone layer**. Despite the advantages, the risks outweigh the benefits.

REMEMBER

Ozone **absorbs** most harmful UV radiation that causes **skin cancer**

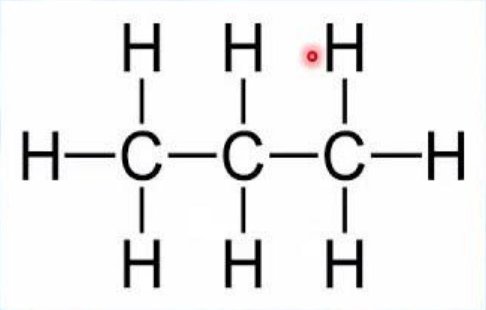
Today we use alternatives that are safer. We use **HFCs** (hydrofluorocarbons) and hydrocarbons as they don't have chlorine in.

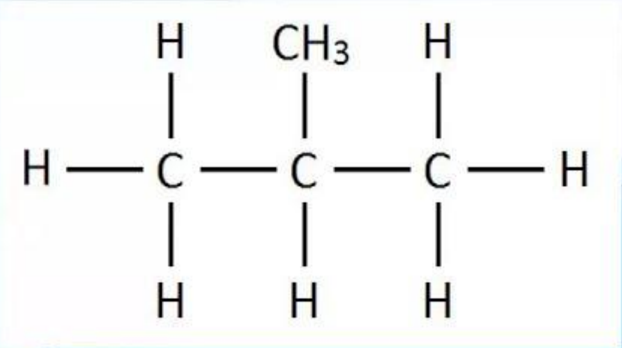
Replacements of CFCs

CFCs	Replacements	Uses
CFC-12 (CCl_2F_2), CFC-13($CClF_3$), HCFC-22 ($CHClF_2$), CFC-113 ($Cl_2FCCClF_2$), CFC-114 ($CClF_2CClF_2$), CFC-115 (CF_3CClF_2) etc.	HFC-23 (CHF_3), HFC-134a (CF_3CFH_2), HFC-507 (a 1:1 azeotropic mixture of HFC 125 (CF_3CHF2) and HFC-143a (CF_3CH_3) etc.	Refrigeration & air-conditioning.
CFC-114 ($CClF_2CClF_2$) etc.	HFC-134a (CF_3CFH_2), HFC-227ea (CF_3CHFCF_3) etc.	Propellants in medicinal aerosols.
CFC-11 (CCl_3F); CFC 113 ($Cl_2FCCClF_2$); HCFC-141b (CCl_2FCH_3) etc.	HFC-245fa ($CF_3CH_2CHF_2$); HFC-365 mfc ($CF_3CH_2CF_2CH_3$) etc.	Blowing agents for foams.

Alternatives to CFCs

- Hydrocarbons such as propane and 2-methylpropane are used as refrigerants.
- The presence of a C-H bond instead of a C-Cl bond make these compounds decompose less easily because the C-H bond is stronger than the C-Cl bond.
- However, they are flammable.





Free radical reactions: true or false?

Reflection

- What has been learned
- What remained unclear
- What is necessary to work on