Free Radical Substitution

Halogenoalkanes can be formed from alkanes and is a big exam favourite. A halogenoalkane is just an alkane with a halogen attached such as CH_3Cl.

For example:

$$CH_4 + Cl_2 \xrightarrow{UV} CH_3Cl + HCl$$

All we are doing is substituting (**swapping**) a hydrogen atom in methane for a Cl atom to make the halogenoalkane (and HCl) using **free radicals**. It is called a **free radical substitution** reaction.

✓ Ultra-violet light (UV) is always used in this process and is a big clue as to what is going on.

What is a free radical?

A free radical is simply an atom or group with **one** unpaired electron.

Electrons "like" to be paired up. As radicals have an unpaired electron, they are very unstable or reactive. A few examples of radicals (the "big dot" represents the unpaired electron):

$$\bullet CH_3 \qquad \bullet O \qquad \bullet Cl$$

How you write or draw these radicals doesn't matter too much, you can have the "dot" on either side of the atom or group.

Free Radical Substitution

The bulk of the questions are focused on how you go from reactants to products.

There are **three** steps: **initiation** (starting the process), **propagation** (a chain reaction) and **termination** (ending the process).

The first and last steps normally don't cause many problems but the propagation step is normally where students go wrong.

Initiation

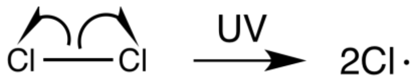
To start the process, you need to generate a free radical. A compound with a weak single bond is used as it can be easily broken into two atoms. As we are making a halogenoalkane, a halogen is used (often chlorine).

UV (ultraviolet light) is used in this step which has enough energy to break the weak bond.

Fission

This bond breaking process is called **homolytic fission** (fission just means to break) as the products are both of the **same species** i.e. two radicals.

- ✓ They do not have to be the same radical, just two radicals. When radicals are involved it is always homolytic fission.



- ✓ In electrophilic and nucleophilic reactions both electrons go to the same atom to make two **different** ions e.g. Cl^- and Cl^+, so it is called **heterolytic fission**. Basically, everything **except** radicals is heterolytic.

- ✓ I have used 'half' arrows to show **one** electron going to each chlorine atom. Remember that a 'normal' arrow represents the movement of two electrons as in electrophilic and nucleophilic reactions. It is only with radicals that you move only one electron.

Propagation

This is where the substitution takes place, in **two steps,** and is a **chain reaction**. In propagation you will make the halogenoalkane and also regenerate the Cl radical.

Step 1

The first step involves removing a hydrogen from CH_4 to generate a new radical (the CH_3 radical):

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

Step 2

The second step generates the halogenoalkane and regenerates the Cl radical. The Cl radical is acting as a catalyst and is **regenerated** as catalysts are never used up in the reaction. Propagation is therefore a chain reaction and can be repeated:

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

The mistake a lot of students make in this second step is to take another chlorine radical and react it with the CH_3 radical to make the halogenoalkane. This seems fine in principle but this would actually be an example of a termination step as there would be no radicals left.

So you need to use $\mathbf{Cl_2}$ here and not the chlorine radical!

The propagation steps cause all the problems in this topic. A few things that might help you remember the steps:

- In both steps, a radical is added to a neutral molecule, which makes another radical and neutral molecule.
- If you combine both propagation steps, you will get the **full chemical equation**. This means radicals must be on opposite sides of both equations to cancel out, as there are no radicals in the full equation.
- Both the **reactants and products are split over the two steps** i.e. use one of each in step 1 and then again in step 2.
- **HCl** (H-halogen) is always made in step one. Therefore, the other product must be made in step 2.
- The **Cl radical must be regenerated** as it is the catalyst and a chain reaction.

Termination

The termination step ends the whole process and is very easy. You are trying to stop the reaction so you need to **remove the radicals**.

All you have to do is take **any two radicals** and join them together to end up with a **neutral** molecule. There should be **three** possible equations:

For example:

$$\cdot CH_3 + Cl\cdot \longrightarrow CH_3Cl$$

$$\cdot CH_3 + CH_3\cdot \longrightarrow C_2H_6$$

$$\bullet Cl + Cl\bullet \longrightarrow Cl_2$$

Further reactions

Another exam favourite is to ask about further reactions that could occur.

In our example above we made CH_3Cl by substituting a chlorine for a hydrogen.

As we have three hydrogens remaining in the product we could do the reaction again and swap another chlorine for another hydrogen to give CH_2Cl_2.

And we could keep going until all the hydrogens have been replaced, forming $CHCl_3$ and finally CCl_4.

$$\mathbf{CH_4 \rightarrow CH_3Cl \rightarrow CH_2Cl_2 \rightarrow CHCl_3 \rightarrow CCl_4}$$

✓ Just swapping an H for a Cl every time until there are no H’s left.

Conditions

Whether you get further substitution or not depends on the conditions:

- if you use **excess methane** you will only get the single substituted product as there is not enough chlorine to react further i.e. $CH_4 \rightarrow CH_3Cl$ ONLY.

- if you use **excess chlorine** then you are very likely to get multiple products.

Side products

Generation of multiple products could be classed as side products. Also, any of the products generated in the termination step.

Other Starting Materials

In the example above we started with **methane** and added **chlorine**. This was the simplest example possible.

In exam questions they often change the alkane and sometimes the halogen. They could start with any alkane or a **halogenoalkane**. They might use **bromine** instead of chlorine. There are examples of even more bizarre reactants such as **I-Cl** instead of a halogen.

You have to stick to the same principles. It doesn't matter what they start with, all you are doing is swapping one hydrogen atom for one halogen atom. The three steps are still the same.