Mr Cole Science

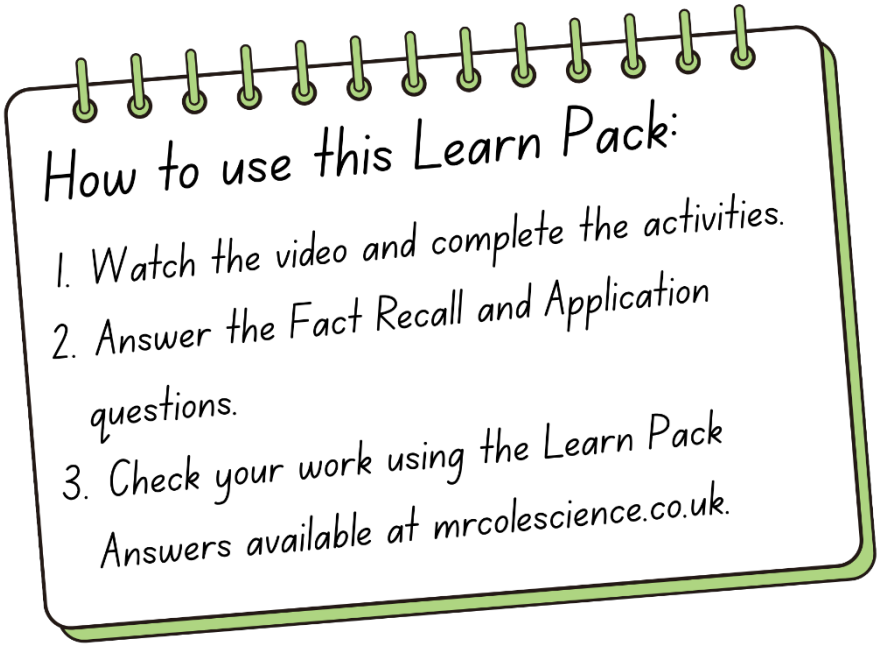
Name: _____ **Date:** _____

AQA A-LEVEL CHEMISTRY

Free Radical Substitution: Synthesising Halogenoalkanes

Learn Pack

This pack is designed to be completed alongside the video to help you build a secure understanding of this topic before moving on to revision and exam practice.



WATCH THE LESSON

Synthesis Halogenoalkanes

Halogenoalkanes are formed when one or more hydrogen atoms from an alkane are substituted for a halogen atom.

Halogenoalkanes are formed during a free radical substitution reaction.

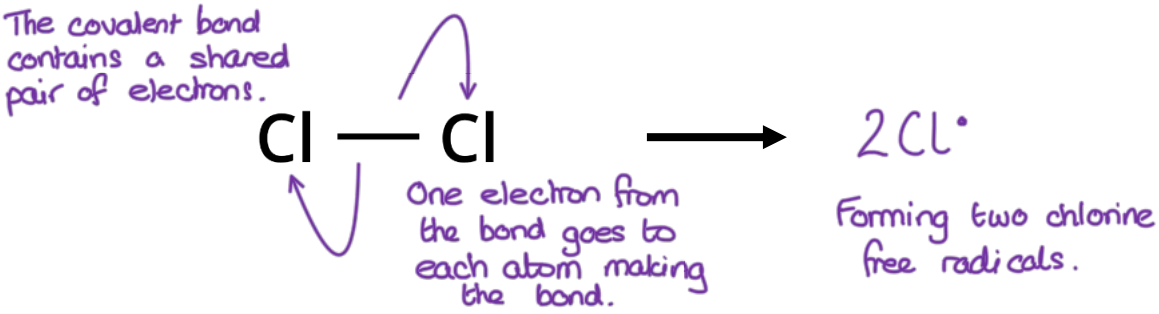
Lesson Objectives:

- Know what a free radical is and how it is represented.
- Know that the reaction of an alkane with a halogen occurs via a free-radical substitution mechanism.
- Be able to outline the stages involved in a free radical substitution reaction.
- Be able to write balanced equations for the stages in a free radical substitution mechanism.

Free Radicals

A free radical is an atom, ion or molecule that has at least one unpaired electron. Free radicals are formed when a covalent bond splits homolytically.

Annotate the diagram below to explain what happens when a covalent bond splits homolytically:



The unpaired electron makes free radicals highly reactive, so reactive that they are able to react with relatively unreactive alkane molecules via a free radical substitution reaction.

Free Radical Substitution

Reaction mechanisms show how it is that molecules react. They illustrate or explain what is happening during each stage of the reaction, ultimately showing how the products are formed.

The mechanism for free-radical substitution reactions uses a series of equations to illustrate what goes on during three stages of the reaction:

1. Initiation
2. Propagation
3. Termination.

Initiation

The initiation step involves the homolytic breaking of the halogen-halogen covalent bond to form two halogen free radicals.

$$Br_2 \rightarrow 2Br^{\bullet}$$

Identify the essential condition required for this reaction and explain why it is needed:

UV light is required to provide the energy needed to break the strong covalent bond between the halogen atoms.

Propagation

During propagation two different reactions occur. Firstly, the halogen free radical produced during initiation reacts with an alkane, producing an alkyl free radical and a hydrogen halide:

$$CH_4 + Br^{\bullet} \rightarrow {}^{\bullet}CH_3 + HBr$$

Secondly, the alkyl free radical produced during that first propagation step reacts with a halogen molecule, forming a halogenoalkane but also reforming a halogen free radical:

$${}^{\bullet}CH_3 + Br_2 \rightarrow CH_3Br + Br^{\bullet}$$

Explain why this stage is called propagation:

Because the halogen free radical used in the first propagation step is reformed allowing the reaction to continue.

Termination

This is where free radicals are removed and this can happen in one of three ways:

1. Two halogen free radicals reacting: $2Br^{\bullet} \rightarrow Br_2$
2. A halogen free radical reacting with an alkyl free radical: $Br^{\bullet} + {}^{\bullet}CH_3 \rightarrow CH_3Br$
3. Two alkyl free radicals reacting: ${}^{\bullet}CH_3 + {}^{\bullet}CH_3 \rightarrow C_2H_6$

Further Substitution

If the halogen is in excess, then further substitution reactions are likely to occur, meaning more than one halogen atom from the starting substance will be swapped out and replaced with a halogen:

$$CH_4 + 3Br_2 \rightarrow CHBr_3 + 3HBr$$

In A-Level Chemistry you are always expected to provide balanced symbol equations.

Explain the easy way to balance overall equations for free radical substitution reactions:

For every atom of hydrogen that is being substituted you need one molecule of the halogen and will form one molecule of the hydrogen halide.

It's important to note that these further substitutions don't all occur at the same time. This means that it's not only alkanes that can undergo free radical substitution reactions with halogens; halogenoalkanes can undergo them too.

Explain how this affects each stage in the reaction below:

Initiation:

There is no change at all since initiation only involves the halogen.

Propagation:

You start with the halogenoalkane instead but the principle is the same; remove H to form free radical and HX and then the free radical reacts with X_2 to complete the substitution and form $X^{\bullet}$

Termination:

Essentially stays the same only the alkyl free radical will contain one or more halogen atoms.

Practise Questions – Fact Recall

1. What is a free radical?

An atom, ion or molecule that has at least one unpaired electron.

2. How are free radicals represented?

With a dot to represent the unpaired electron eg. $Br^{\bullet}$

3. State the essential condition required for free radical substitution.

UV light

4. What are the three stages, in order, for a free radical substitution reaction.

Initiation, Propagation and Termination.

5. What happens during a termination step?

Two free radicals combine to form a molecule.

Practise Questions – Application

1. Write two equations to show what happens during the propagation stage for chloromethane reacting to form dichloromethane:

$CH_3Cl + Cl^{\bullet} \rightarrow {}^{\bullet}CH_2Cl + HCl$

${}^{\bullet}CH_2Cl + Cl_2 \rightarrow CH_2Cl_2 + Cl^{\bullet}$

2. Write an initiation equation for bromomethane reacting to form bromofluoromethane:

$F_2 \rightarrow 2F^{\bullet}$

Next Steps

Check your work using the Learn Pack Answers: