Curly Arrows in Organic Chemistry

As you progress through Organic Chemistry, **mechanisms** become very important to help us understand **what is happening to the electrons** in organic reactions. As with many of the skills that you learn in chemistry, you learn them so that you can predict outcomes in new situations.

If you have read our primer on **Reactions Kinetics**, you will know that organic mechanisms were developed from rates experiments.

An organic mechanism shows the steps that a reaction follows as the reactants in the overall equation become products. In many cases, reactions do not take place in a single step. If you are currently just starting out in organic chemistry, you may not have covered some advanced reaction kinetics and so the fact that many reactions take place in multiple steps may be new to you.

Here is a good example that you will study early in A level Chemistry.

$$CH_{4(g)} + Cl_{2(g)} \rightarrow CH_3Cl_{(g)} + HCl_{(g)}$$

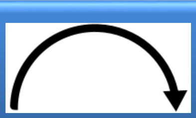
This reaction seems so simple on the surface of it. Methane and chlorine in; chloromethane and hydrogen chloride out.

However, this reaction takes place in no less than 4 stages. That means that this reaction has a four-stage mechanism.

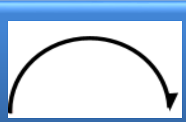
Clearly, there has been a rearrangement of atoms and so there must have been some bonds broken and some bonds made. We are going to develop a way of showing this in a diagrammatic way.

To do this we are going to make it clear how the electrons on atoms and between atoms (bonds) move around. This involves something called a **curly arrow**.

A **double headed arrow** represents the movement of **2 electrons**



A **single headed arrow** represents the movement of **1 electron**



Things to understand about these arrows.

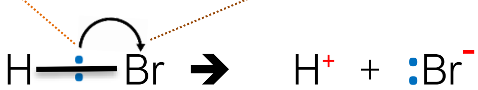
1. The start of the arrow must be drawn where the electrons **begin** their movement.
2. The end of the arrow must be drawn where the electrons **finish** their movement.
3. Electrons begin their movement from 2 possible places: ATOMS* or BONDS
4. Electrons finish their movement in 2 possible places: ATOMS* or BONDS

* could also be ions

For example:

Start of the arrow placed here because this is where the pair of electrons are leaving from, *i.e.* the bond.

Head of the arrow placed here because this is where the pair of electrons 'land'.



Heterolytic fission.

You need to look at a step in a mechanism and decide what has changed between the reactants and the products. Ask yourself:

i. Have bonds been made?
ii. Have bonds been broken?
iii. Have ionic charges been made?
iv. Have ionic charges been destroyed?

Now ask yourself how you are going to shuffle the electrons around to allow those changes to happen. Finally, add the curly arrows to show the movement.

Below are a series of **generalised mechanism steps**. Draw the curly arrows for each process.

There are some useful hints that help you predict the movement of the electrons.

A chemical species that is represented as a **cation** (generally given the symbol E^+) or a **partially positively charged species,** *e.g.* $C^{\delta+}$—$X^{\delta-}$ is an electron deficient particle which attracts a pair of electrons towards itself to **produce a new bond**. We call these particles, ELECTROPHILES

A particle that has a lone pair of electrons, (generally given the symbol $Nu:^-$), or possesses a **double bond** is an electron rich particle which can use a pair of electrons to attack an electron deficient species to produce a new bond. We call these particles, NUCLEOPHILES. Nucleophiles attack carbons atoms with **a** $\delta+$ (by being attached to an electronegative atom such as oxygen or a halogen atom).

Remember, curly arrows must only begin from the middle of a bond or from an atom, ion or radical. Curly arrows must only end in the place where the bond will form or on an atom, ion or radical.

Anything else is wrong. Be careful with those arrows!

Now have a go at adding curly arrows to the following general examples.

1. A—B → A^+ + $:B^-$ — Heterolytic fission.

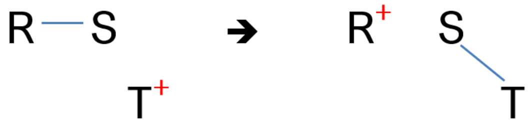
2. C—D → C• + •D — Homolytic fission.

3. $E:^-$ F^+ → E—F

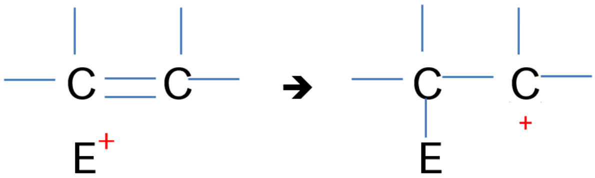
4. G• H—I → G—H + •I — Free radical substitution

5. $Nu:^-$ $C^{\delta+}$—$X^{\delta-}$ → Nu—C + $^-:X$ — Nucleophilic substitution

6.



7.

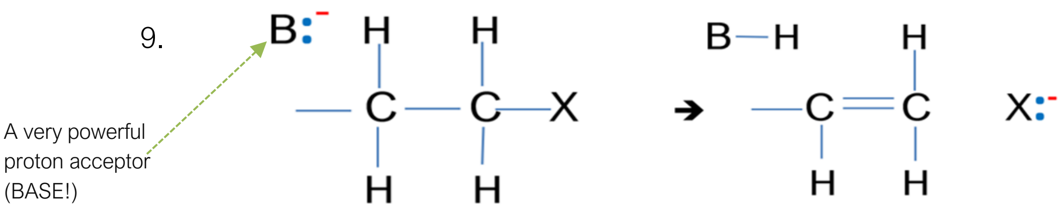


Electrophilic addition (first step)

8.

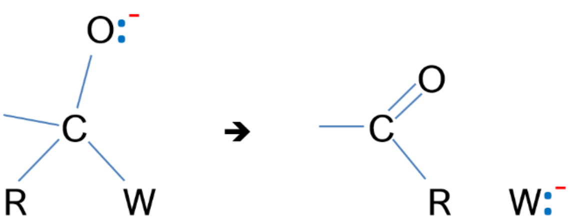
Nucleophilic addition (first step)

9.



elimination

10.



elimination

One final tip that is useful to remember:

> In **all** chemical reactions (including overall equations, ionic equations, half-equations, redox equations, mechanisms etc,) the sum of charges on the left of the arrow must equal the sum of the charges on the right of the arrow. Remembering this might help you avoid a careless error at some point.

In another coloured pen, draw the **curly arrows on the products** that would turn them back into **reactants**. 2 worksheets for the price of one!