Chem Factsheet
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The reaction mechanism for a free radical substitution reaction

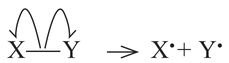
> A reaction mechanism is a step by step sequence of elementary reactions by which the overall chemical change occurs.

Each step typically shows how electrons move to either break an existing covalent bond (a shared pair of electrons) or form a new covalent bond (or a lone pair).

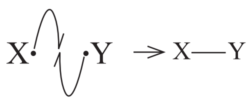
The electron movements are represented by (a) a **fish-hook curly arrow** for the movement of a single electron or (b) a **double-headed curly arrow** for the movement of a pair of electrons.

(a) a fish-hook curly arrow (b) a double-headed curly arrow

Type (a) is involved in this Chem Factsheet. Here an electron pair in a bond is split such that each of the bond atoms (X and Y) gains one of the electrons to form **free radicals** (*uncharged* atoms or groups of atoms with an unpaired electron represented by ●). This type of bond breaking is called **homolytic fission**.



Conversely, the unpaired electrons on two free radicals can combine to form a new bond.



Depending on your specification, it may be acceptable to show the changes without the fish-hook arrows but be careful to show the unpaired electrons on the correct atoms.

A **substitution reaction** is one where one group or atom is replaced by another group or atom. In general, two particles give two particles.
e.g. $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$
e.g. $CH_3CH_2Br + OH^- \rightarrow CH_3CH_2OH + Br^-$.

Such reactions are usually associated with **saturated** molecules – molecules which contain *single* bonds only.

Hence, the mechanism to be studied here, **free radical substitution**, involves the **replacement** of H atoms in **saturated** alkanes or haloalkanes by halogen atoms with the involvement of **free radical intermediates**.

The Mechanism

The overall reaction involves the substitution of a hydrogen atom in a C-H bond by a halogen atom (X; usually Cl or Br), promoted by the presence of u.v. radiation. The C-H bond may be in an alkane or a haloalkane and can be generalised as follows.

$$—\overset{|}{\underset{|}{C}}—H + X_2 \xrightarrow{U.V} —\overset{|}{\underset{|}{C}}—X + HX$$

The three "incompletely labelled" bonds remain the same throughout the reaction. Hence, for any given exam question, decide what needs to be bonded in these three positions and leave them unchanged during your description of the mechanism!

e.g. 1 If the 3 spare bonds are all to H atoms and X is Cl, then the equation represents the reaction of methane to form chloromethane.

e.g. 2 If 2 of the 3 spare bonds are to H atoms with the third to Br, and X is Br, then the equation represents the reaction of bromomethane to form dibromomethane.

e.g. 3 If 2 of the 3 spare bonds are to H atoms with the third to an ethyl group, and X is Cl, then the equation represents the reaction of propane to form 1-chloropropane.

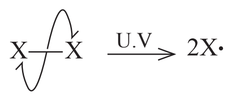
The mechanism for free radical substitution involves three stages.

(a) **INITIATION** – a *small percentage* of the halogen molecules (X_2) in the reaction mixture are converted to free radicals (halogen atoms, X•) by homolytic bond fission using energy provided by u.v. radiation. $X_2 \xrightarrow{U.V} 2X\bullet$

This is the preferred bond fission because, as the following table shows, X-X bonds a weaker than the alternatives, C-H and C-C bonds.

Bond	Cl-Cl	Br-Br	C-H	C-C
Bond energy (kJ mol^{-1})	+243	+193	+413	+347

This stage can also be represented using fish-hook curly arrows but this is rarely expected in answers to exam questions.

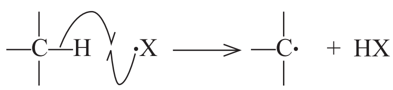


Note: The u.v. does not need to be applied continuously. One short flash will create enough Cl• free radicals to allow the next steps to occur.

(b) **PROPOGATION** – There are two propagation steps. In the first, a free radical from the initiation stage reacts with the second reactant (containing C-H) to form the first of the overall products, HX, along with a new free radical where the unpaired electron is on the C atom which was bonded to the substituted H atom.

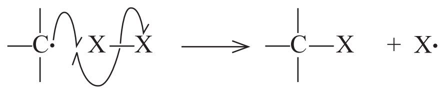
$$—\overset{|}{\underset{|}{C}}—H + X\bullet \longrightarrow —\overset{|}{\underset{|}{C}}\bullet + HX$$

Note: the unpaired electron is now on the C atom.
Again, should it be required, fish-hook arrows can be used to show this step.



In the second propagation step, this new free radical then reacts with a halogen molecule (Rem: only a few were converted to free radicals during initiation) to form the second substitution product (C-X) and *regenerate* a halogen free radical.

$-\dot{C}- + X_2 \longrightarrow -C{-}X + X\cdot$ or, using fish-hook arrows



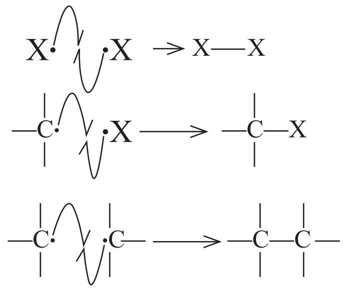
The regeneration of the halogen free radical means that these two steps can repeat and repeat (a **chain reaction**), each time producing the two overall reaction products. This can continue until the reactants are consumed or termination reactions (see below) occur to remove the free radicals that are essential for the repetition of the propagation steps to continue.

(c) **TERMINATION** – as suggested above, these are processes that can bring the overall reaction to a halt. They involve the combination of any two free radicals to form a neutral molecule which is not capable of continuing the reaction. There are three possible termination reactions.

$2X\cdot \longrightarrow X_2$ or

$-C\cdot + X\cdot \longrightarrow -C{-}X$ or

$-C\cdot + \cdot C- \longrightarrow -C{-}C-$ or



Note: Termination reactions are usually less significant than depletion of reactants because free radical concentrations are very low resulting in a very small chance that any two will collide and react.

Note: The detection of small amounts of molecules with twice as many C atoms as the original reactant provide very strong evidence for this mechanism.

Practice Questions

1. Apply the generalised mechanism to give a mechanism for the reaction of fluorine with trifluoromethane (CHF_3) to form tetrafluoromethane (CF_4).
2. Apply the generalised mechanism to give a mechanism for the reaction of 1,2-dichloroethane with bromine to give 1-bromo-1,2-dichloroethane.
3. In terms of the free radical substitution mechanism, explain why the reaction of methane with chlorine results in a mixture of products.

Answers

1. For CHF_3 as starting material the 3 "incompletely labelled" bonds will all be C-F bonds and the reacting halogen will be F_2. Hence the overall reaction equation is

$$F{-}C(F)(F){-}H + F_2 \xrightarrow{U.V} F{-}C(F)(F){-}F + HF$$

and the reaction mechanism is

initiation: $F_2 \xrightarrow{U.V} 2F\cdot$

propogation 1: $F{-}C(F)(F){-}H + F\cdot \longrightarrow F{-}C(F)(F)\cdot + HF$

propogation 2: $F{-}C(F)(F)\cdot + F_2 \longrightarrow F{-}C(F)(F){-}X + F\cdot$

terminations: $2F\cdot \rightarrow F_2$

${}_3FC\cdot + F\cdot \rightarrow CF_4$

${}_3FC\cdot + \cdot CF_3 \rightarrow CF_3\,CF_3$

2. For $ClCH_2CH_2Cl$ as starting material the 3 "incompletely labelled" bonds will be C-H, C-Cl and C-CH_2Cl. The reacting halogen is Br_2. Hence the overall reaction equation is

$$ClCH_2{-}C(Cl)(H){-}H + Br_2 \xrightarrow{U.V} ClCH_2{-}C(Cl)(H){-}Br + HBr$$

and the reaction mechanism is

initiation: $Br_2 \xrightarrow{U.V} 2Br\cdot$

propogation 1: $Cl{-}C(CH_2Cl)(H){-}H + Br\cdot \longrightarrow Cl{-}C(CH_2Cl)(F)\cdot + HBr$

propogation 2: $Cl{-}C(CH_2Cl)(H)\cdot + Br_2 \longrightarrow Cl{-}C(CH_2Cl)(H){-}Br + Br\cdot$

terminations: $2Br\cdot \rightarrow Br_2$

$ClCH_2\dot{C}HCl + Br\cdot \rightarrow ClCH_2CHBrCl$

$ClCH_2\dot{C}HCl + ClCH_2\dot{C}HCl \rightarrow ClCH_2{-}C(H)(Cl){-}C(H)(Cl){-}CH_2Cl$

3. Methane converts first of all to chloromethane (CH_3Cl) since C-H in methane becomes C-Cl. However, CH_3Cl also has a C-H bond which can react with further Cl free radicals to form dichloromethane, CH_2Cl_2. Since they both have C-H bonds, this and its product ($CHCl_3$) can react again finally producing CCl_4. Thus, depending on the availability of chlorine molecules to react, a mixture of CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4 will result.

Note: the proportion of CCl_4 will increase as the ratio of chlorine to methane increases.

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