Chem Factsheet

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# Free Radical Subsitution & Polymerisation

**To succeed in this topic you need to:**
- understand the nature of the covalent bond ( Factsheet 5);
- know the reactions of alkanes (Factsheet 16);
- understand the principle of addition polymerisation (Factsheet 18).

**After working through this Factsheet you will:**
- know that free radical substitution occurs in three stages;
- know that free radicals are formed at the initiation stage by homolytic fission;
- know that there are two reactions at the propagation stage, each of which requires a free radical;
- know that termination occurs by the coupling of free radicals;
- understand the mechanism of free radical polymerisation.

*Free radical substitution reactions are shown by alkanes, e.g. methane, and alkylaromatic hydrocarbons, e.g. methylbenzene.*

A well known example is the chlorination of methane in the presence of ultraviolet light:

$$CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl$$

***Remember -*** *'Substitution' means 'replacement'. A substitution reaction should be defined as one in which an atom or group of atoms belonging to the substrate (the molecule which is being attacked) is replaced by another atom or group from the reagent.*

In a free radical substitution, the reagent provides an attacking species called a *free radical*.

***Definition*** *A free radical is an atom or group of atoms with an unpaired electron.*

An example is the chlorine free radical, supplied by the reagent $Cl_2$ (chlorine gas) when it is heated to high temperatures or exposed to ultraviolet light. This is just a chlorine atom. The electronic configuration $1s^2, 2s^2, 2p^6, 3s^2, 3p^5$ shows that there is an odd number of 3p electrons, so one of them must be unpaired. The symbol for a chlorine free radical is $Cl^{\cdot}$, where the superscript dot symbolises the unpaired electron.

***Remember -*** *A chlorine atom and a chlorine free radical are one and the same thing. We refer to a chlorine free radical, $Cl^{\cdot}$, when we want to emphasise the unpaired electron.*

Other examples of free radicals include the methyl free radical, $CH_3^{\cdot}$, and the ethyl free radical, $CH_3CH_2^{\cdot}$.

*Every free radical substitution reaction proceeds in three stages.*
- *Initiation*
- *Propagation*
- *Termination*

### Initiation

*During initiation, free radicals are formed from molecules by the homolytic fission (homolysis) of a single covalent bond.*

When a covalent bond between two atoms undergoes homolytic fission, it is broken symmetrically so that each of the bond pair of electrons goes to one of the atoms so as to give a pair of free radicals.

***Definition*** *Homolytic fission is the breaking of a covalent bond so as to produce two fragments that are the same as each other in the sense that they are both free radicals.*

In the chlorination of methane, chlorine molecules break homolytically to give chlorine free radicals:

$$Cl{-}Cl \rightarrow 2Cl^{\cdot}$$

In this equation, the movement of a single electron is symbolised by a curly half-arrow. It must start from the origin of the electron and point towards its final location.

**Exam Hint -** Take care not to use a curly arrow with a full arrowhead because this symbolises the movement of a pair of electrons.

**Notes on homolytic fission**
- The two fragments produced may not be identical. The splitting of the iodine chloridemolecule into an iodine free radical and a chlorine free radical is still an example of homolytic fission:

$$I{-}Cl \rightarrow I^{\cdot} + Cl^{\cdot}$$

- The weakest bond is always broken preferentially. In the chlorination of methane, the Cl-Cl bond, with a bond dissociation enthalpy of 242 kJ $mol^{-1}$, breaks in preference to the C-H bond ($\Delta H^{\ominus}_{diss}$ = 435 kJ $mol^{-1}$).

### Propagation

*There are two reactions at the propagation stage.*
- *In each of these, one free radical is consumed while another is formed.*
- *Each consumes a molecule of initial reactant and liberates a molecule of end product.*

In the chlorination of methane, propagation proceeds as follows.

*Reaction 1* $Cl^{\cdot} + CH_4 \rightarrow CH_3^{\cdot} + HCl$

*Reaction 2* $CH_3^{\cdot} + Cl_2 \rightarrow CH_3Cl + Cl^{\cdot}$

As for initiation, where alternative reactions are possible, energy requirements dictate what occurs. In the chlorination of methane, the following propagation reaction satisfies the basic principles:

$$Cl^{\cdot} + CH_4 \rightarrow CH_3Cl + H^{\cdot}$$

Nevertheless, it does not occur because it is energetically unfavourable. ultraviolet light provides sufficient energy to break Cl-Cl but not C-H

***Remember -*** *Hydrogen free radicals are uncommon reaction intermediates because a large amount of energy is needed to form them, i.e break a C-H bond.*

## Termination

*Termination occurs by coupling, i.e. the joining together of pairs of free radicals to give molecules.*

For the $CH_4 + Cl_2$ reaction, there are three possibilities:

$2Cl^{\cdot} \rightarrow Cl_2$

$2CH_3^{\cdot} \rightarrow CH_3CH_3$
ethane

$CH_3^{\cdot} + Cl^{\cdot} \rightarrow CH_3Cl$
chloromethane (first substitution product)

***Notes on coupling***
- Coupling is the opposite of homolytic fission.
- Coupling takes place from the start, but becomes dominant in the later stages of the reaction when the concentration of reactants has fallen to a low level.
- Although some chloromethane is formed by coupling, most of it is produced at the propagation stage.

***Exam Hint -*** *Examiners may focus on the formation of ethane at the termination stage. You can be asked to explain why, when methane is chlorinated, the product always contains a trace of ethane. Alternatively, you can be asked about evidence for a free radical mechanism, in which case you should quote the formation of ethane which could happen only by the coupling of two* $CH_3^{\cdot}$ *free radicals.*

## Further chlorination of methane

When a mixture of methane and chlorine is exposed to ultraviolet light, four reactions occur simultaneously:

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

**B** $CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl$

**C** $CH_2Cl_2 + Cl_2 \rightarrow CHCl_3 + HCl$

**D** $CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$

Consequently, the product is always a mixture of chloromethane, dichloromethane, trichloromethane and tetrachloromethane, although with a limited amount of chlorine it is predominantly chloromethane and with a large excess of chlorine it is mainly tetrachloromethane.

The reason is that, as soon as chloromethane starts to accumulate, reaction **B** commences. As soon as dichloromethane accumulates, reaction **C** begins. And so on.

***Remember -*** *The chlorination of methane does not occur in clearly defined steps and is said to be 'non-stepwise'.*

This is easily explained in mechanistic terms.

*Chlorine free radicals produced at the propagation stage (Reaction 2) can do two things.*
- *React with some more* $CH_4$ *to give more* $CH_3Cl$.
- *React with* $CH_3Cl$ *by a similar mechanism to give* $CH_2Cl_2$, *dichloromethane*

*Propagation steps:* $Cl^{\cdot} + CH_3Cl \rightarrow CH_2Cl^{\cdot} + HCl$

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

Some free radical substitutions are stepwise, e.g. the chlorination of methylbenzene in ultraviolet light.

$C_6H_5CH_3 + Cl_2 \rightarrow C_6H_5CH_2Cl + HCl$

$C_6H_5CH_2Cl + Cl_2 \rightarrow C_6H_5CHCl_2 + HCl$

$C_6H_5CHCl_2 + Cl_2 \rightarrow C_6H_5CCl_3 + HCl$

Chlorination can be stopped at the end of either intermediate step, with a good yield of $C_6H_5CH_2Cl$ or $C_6H_5CHCl_2$, when the observed increase in mass corresponds to that which is calculated.

***Exam Hint****- There are two common sorts of questions on free radical subsitution*
- *You may be asked to write mechanistic equations for a given reaction, generally for 3 marks. If so, give the equation for initiation,* both *equations for propagation, and one of the equations for termination.*
- *Alternatively, you may be asked to explain the mechanism of a particular reaction, typically for about 5 marks. In this case, you must include mechanistic equations (as before) and, to score additional marks, say that the reaction is a free radical substitution, name the three stages, and include the terms 'homolytic fission' and 'coupling' where appropriate.*

## Free radical polymerisation

Alkenic compounds (i.e. those whose molecules contain a C=C bond) can undergo addition polymerisation to give high polymers. In the presence of organic peroxide catalysts, polymerisation occurs by a mechanism very similar to that of free radical substitution.

*Free radical polymerisation takes place by a three stage mechanism.*
- *Initiation*
- *Propagation*
- *Termination*

The polymerisation of ethene to give poly(ethene) is a simple example.

$nCH_2{=}CH_2 \rightarrow -\!\left(CH_2\text{-}CH_2\right)\!-_n$

### Initiation

Free radicals ($R^{\cdot}$) are formed from the catalyst by homolytic fission. (Details are not needed.)

### Propagation

An infinite number of reactions can occur, in each of which a free radical combines with a molecule of monomer to give a larger free radical. The first of these reactions involves the free radical from the catalyst:

$R^{\cdot} + CH_2{=}CH_2 \rightarrow R\text{-}CH_2\text{-}CH_2^{\cdot}$

The π-bond of the alkene is broken homolytically. One electron joins the unpaired electron of the free radical to form a new covalent bond, while the other remains (unpaired) on the terminal carbon atom.
In the next reaction, this new free radical behaves in a similar way:

$R\text{-}CH_2\text{-}CH_2^{\cdot} + CH_2{=}CH_2 \rightarrow R\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2^{\cdot}$

The process can be repeated indefinitely to give very long chain free radicals.

### Termination

**Any** two free radicals may couple so as to give a molecule of polymer, e.g.

$R\text{-}CH_2\text{-}CH_2^{\cdot} + {}^{\cdot}CH_2\text{-}CH_2\text{-}R \rightarrow R\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}R$

Polymers are therefore formed with varying chain lenghts.

***Remember***
- *Although every propagation reaction consumes one free radical and generates another, it does not give a molecule of the final product.*
- *The product, i.e. the polymer, is formed only at the termination stage.*

## Questions

1 Write mechanistic equations for the conversion of methylbenzene to (chloromethyl)benzene.

2 Suggest why an explosion occurs when methane is chlorinated in high intensity ultraviolet light.

3 In the propagation stage of the chlorination of ethane there are two possible first reactions, as shown by Equations 1 and 2.

Equation 1 $Cl^{\cdot} + CH_3CH_3 \rightarrow CH_3CH_2^{\cdot} + HCl$

Equation 2 $Cl^{\cdot} + CH_3CH_3 \rightarrow H^{\cdot} + CH_3CH_2Cl$

(a) Use the following bond dissociation enthalpies (all in kJ $mol^{-1}$) to predict which of these equations is likely to be correct.
C-H = 412 C-Cl = 338 H-Cl = 431

(b) Explain how your prediction could be confirmed by analysis of the final product.

4 Write equations for propagation and termination reactions when propene is polymerised in the presence of a catalyst that provides free radicals, $R^{\cdot}$.

5 Explain, by referring to the mechanism of their formation, why addition polymers are assigned an *average* relative molecular mass.

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## Answers

1 *Initiation* $Cl_2 \rightarrow 2Cl^{\cdot}$

*Propagation*
$Cl^{\cdot} + C_6H_5CH_3 \rightarrow C_6H_5CH_2^{\cdot} + HCl$
$C_6H_5CH_2^{\cdot} + Cl_2 \rightarrow C_6H_5CH_2Cl + Cl^{\cdot}$

*Termination*
$2Cl^{\cdot} \rightarrow Cl_2$
$2C_6H_5CH_2^{\cdot} \rightarrow C_6H_5CH_2CH_2C_6H_5$
$C_6H_5CH_2^{\cdot} + Cl^{\cdot} \rightarrow C_6H_5CH_2Cl$

2 For two reasons. First, the chlorination of methane is exothermic. Therefore, when the reaction starts, heat is evolved and the consequent rise of temperature increases the rate of reaction. Second, many chlorine free radicals are released simultaneously, each of which can react with a molecule of methane. As a result, a lot of energy is released all at once.

3 (a) In any chemical reaction, energy is needed to break bonds but is released when bonds are formed. Energy changes are therefore as follows.
Equation 1 +412 -431 = -19 kJ $mol^{-1}$
Equation 2 +412 -338 = +74 kJ $mol^{-1}$
Because the reaction shown by Equation 1 is exothermic (while that for Equation 2 is endothermic) it is energetically favoured.
(b) If Equation 1 were correct, the product would contain traces of butane, formed by coupling of $CH_3CH_2^{\cdot}$ radicals. If Equation 2 were correct, it would contain traces of hydrogen, formed by the coupling of $H^{\cdot}$ radicals.

4 *Propagation*

$R^{\cdot} + CH(CH_3){=}CH_2 \rightarrow R\text{-}CH(CH_3)\text{-}CH_2^{\cdot}$

$R\text{-}CH(CH_3)\text{-}CH_2^{\cdot} + CH(CH_3){=}CH_2 \rightarrow R\text{-}CH(CH_3)\text{-}CH_2\text{-}CH(CH_3)\text{-}CH_2^{\cdot}$

*Termination*

$2R\text{-}CH(CH_3)\text{-}CH_2\text{-}CH(CH_3)\text{-}CH_2^{\cdot} \rightarrow R\text{-}CH(CH_3)\text{-}CH_2\text{-}CH(CH_3)\text{-}CH_2\text{-}CH_2\text{-}CH(CH_3)\text{-}CH_2\text{-}CH(CH_3)\text{-}R$

5 Termination reactions can take place at any time. Some occur before free radicals have had a chance to grow, to give short polymer chains of low $M_r$. However, some free radicals survive long enough to accept a great many monomer molecules and, when they eventually couple together, the result is a long chain polymer of high $M_r$. The product is always a mixture of low and high polymers with a range of $M_r$ values.

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