# Reactivity 3.3 Answers

**IB CHEMISTRY SL** 













# Reactivity 3.3.1 and 3.3.2

### Understandings:

- A radical is a chemical entity that has an unpaired electron. Radicals are highly reactive (3.3.1).
- Radicals are produced by homolytic fission, e.g. of halogens, in the presence of ultraviolet (UV) light or heat (3.3.2).

#### Learning outcomes:

- Identify and represent radicals (3.3.1).
- Explain, including with equations, the homolytic fission of halogens, known as the initiation step in a chain reaction (3.3.2).

#### Additional notes:

• The use of a single-barbed arrow (fish hook) to show the movement of a single electron should be covered.

### Linking questions:

- Structure 2.1 How is it possible for a radical to be an atom, a molecule, a cation or an anion? Consider examples of each type.
- Reactivity 1.2 Why do chlorofluorocarbons (CFCs) in the atmosphere break down to release chlorine radicals but typically not fluorine radicals?
- Structure 2.2 What is the reverse process of homolytic fission?
- Structure 2.2 Chlorine radicals released from CFCs are able to break down ozone, O<sub>3</sub>, but not oxygen, O<sub>2</sub>, in the stratosphere. What does this suggest about the relative strengths of bonds in the two allotropes?

### Homolytic bond fission

- In homolytic bond fission, (also known as homolytic bond cleavage), a covalent bond between two atoms in a molecule breaks with each atom taking one electron from the bond.
- The breaking of the bond requires energy in the form of UV radiation or heat.
- Homolytic fission results in the formation of radicals (or free radicals) which are highly reactive species with unpaired electrons.
- For example, the covalent bond between two atoms of X breaks with each atom taking one electron from the bond.



- The single-barbed arrows (known as fish hooks) show the movement of a single electron.
- The radicals formed are represented with a single dot such as X•.

### Homolytic fission of the halogens

• The bond between the two atoms in chlorine, Cl<sub>2</sub>, can undergo homolytic fission in the presence of ultraviolet (UV) radiation.

$$: \underbrace{\dot{C}}_{i} \xrightarrow{} \underbrace{\dot{C}}_{i} : \xrightarrow{uv} : \underbrace{\ddot{C}}_{i} \cdot + \cdot \underbrace{\ddot{C}}_{i} :$$

• The products of the fission are two chlorine radicals, represented as CI.

 $Cl_2 \rightarrow 2Cl \bullet$  or  $Cl_2 \rightarrow Cl \bullet + Cl \bullet$ 

- The formation of radicals is the first step, known as the initiation step, in the freeradical substitution reactions of the alkanes.
- The bond between the two atoms in Bromine, Br<sub>2</sub>, can also undergo homolytic fission in the presence of UV radiation.

$$:\underline{Br} \xrightarrow{\mathbf{UV}} \underline{Br} : \xrightarrow{\mathbf{UV}} :\underline{Br} \cdot + \cdot \underline{Br} :$$

• The products of the fission are two bromine radicals, represented as Br•.

 $Br_2 \rightarrow 2Br \bullet$  or  $Br_2 \rightarrow Br \bullet + Br \bullet$ 

Exercise: Outline the type of bond fission taking place in the reaction below.

$$X: Y \longrightarrow X \cdot + Y \cdot$$

The type of bond fission is homolytic. The bond between X and Y breaks and each atom takes one electron from the bond. Two radicals are produced: X• and Y•.

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### Reactivity 3.3.3

### **Understandings:**

 Radicals take part in substitution reactions with alkanes, producing a mixture of products.

# Learning outcomes:

• Explain, using equations, the propagation and termination steps in the reactions between alkanes and halogens.

### Additional notes:

• Reference should be made to the stability of alkanes due to the strengths of the C–C and C–H bonds and their essentially non-polar nature.

# Linking questions:

• Reactivity 2.2 Why are alkanes described as kinetically stable but thermodynamically unstable?

# Radical substitution reactions of the alkanes

- Alkanes undergo radical substitution reactions which take place in three stages: initiation, propagation and termination.
- Example methane and chlorine react as follows in the presence of UV light as follows.

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

#### Initiation

- The bond between the chlorine atoms undergoes homolytic fission in the presence of UV light.
- Each chlorine atom takes one electron from the single bond resulting in the production of reactive chlorine radicals with unpaired electrons.

$$CI_2 \to 2CI \bullet$$

# Propagation

- The first propagation step shows methane reacting with a chlorine radical to produce a methyl radical and hydrogen chloride.
- The second step shows the methyl radical reacting with a chlorine molecule to produce chloromethane and a chlorine radical.

$$CH_4 + CI \bullet \rightarrow \bullet CH_3 + HCI$$

$$\bullet CH_3 + CI_2 \rightarrow CH_3CI + CI \bullet$$

• Two more propagation steps are shown below.

 $CH_3CI + CI \bullet \rightarrow \bullet CH_2CI + HCI$ 

$$\bullet CH_2CI + CI_2 \rightarrow CH_2CI_2 + CI \bullet$$

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#### Termination

• In the termination step, radicals pair up to form molecules.

$$CI \bullet + CI \bullet \rightarrow CI_2$$
$$\bullet CH_3 + \bullet CH_3 \rightarrow C_2H_6$$
$$\bullet CH_3 + CI \bullet \rightarrow CH_3CI$$

**Exercise:** Ethane, C<sub>2</sub>H<sub>6</sub>, reacts with bromine to form bromoethane, C<sub>2</sub>H<sub>5</sub>Br, in a radical substitution reaction. Write initiation, propagation and termination steps for the reaction.

Initiation (occurs in the presence of UV radiation)

 $Br_2 \rightarrow 2Br_{\bullet}$ 

Propagation

 $Br\bullet + C_2H_6 \rightarrow \bullet C_2H_5 + HBr$ 

 $\bullet C_2H_5 + Br_2 \rightarrow C_2H_5Br + Br \bullet$ 

Termination

 $\bullet C_2H_5 + \bullet C_2H_5 \rightarrow C_4H_{10}$ 

 $Br\bullet + Br\bullet \to Br_2$ 

 $\bullet C_2H_5 + Br \bullet \to C_2H_5Br$