SL IB Chemistry

Your notes

Electron Sharing Reactions

Contents

Radicals

Your notes

Radicals

- Reaction equations tell you about the amount of reactants and products, including their stoichiometry, in a reaction
- Reaction mechanisms tell you about how the reaction actually takes place
  - Mechanisms involve the movement of electrons and a variety of chemical species
- One group of chemical species involved in reaction mechanisms are **radicals**

What are radicals?

- A radical is a chemical species that has an **unpaired electron**
- They can be described as:
  - **Atomic** - a single atom with an unpaired electron
  - **Polyatomic / molecular** - a group of atoms bonded together with no overall charge, that contains an unpaired electron
  - **Anionic** - an atom or molecule that gains one electron to become an anion **AND** has one atom with an unpaired electron
  - **Cationic** - an atom or molecule that loses one electron to become a cation **AND** has one atom with an unpaired electron
- The sole requirement for a radical is the unpaired electron
  - They can exist independent of the charge on the chemical species, e.g. cations must have a corresponding anion and vice versa

Examples of radicals table

name	formula	atomic	polyatomic / molecular	anionic / cationic
benzene	$\bullet C_6H_6^-$		✓	anionic
bromine	$Br\bullet$	✓		
ethanol	$C_2H_5OH^+\bullet$		✓	cationic
hydrogen	$H\bullet$	✓		
hydroxyl	$OH\bullet$		✓	
methyl	$\bullet CH_3$		✓	

nitric oxide	NO•		✓	
propane	$\bullet C_3H_8^+$		✓	cationic
superoxide	$O_2^-\bullet$		✓	anionic

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- Radicals are indicated by the **dot (•)** in the formula of the chemical species
  - When the radical is made of several atoms, the radical dot should be shown on the atom with the unpaired electron
  - This is most obviously seen in displayed formulae

The methyl radical

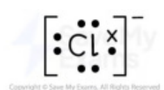
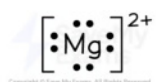
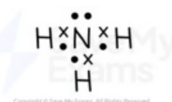
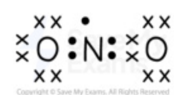
Worked example

Which of the following species are radicals?

1. Cl^-
2. F
3. Mg^{2+}
4. NH_3
5. NO_2

Answer:

- Draw the Lewis formulas, including all valence electrons, of each species:

				
Cl^-	F	Mg	NH_3	NO_2

- Identify the species that have an unpaired electron
  - The species that are radicals are:
    - **F**
    - **NO_2**

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Reactivity of radicals

- The unpaired electron of a radical makes them highly reactive
- It causes them to have a high enthalpy
- In terms of energetics, it is favourable for radicals to react and form products with a lower enthalpy which can be achieved by:
  - Taking an electron from another species - although this creates other radical species because the resulting other species will have an unpaired electron
  - Combining with another radical to form a covalent bond
- Their high reactivity means that radicals are, typically, not long lasting

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Homolytic Fission

Homolytic Fission

- In a reaction mechanism, curly arrows show the movement of electrons
- A single-headed curly arrow shows the movement of a **single electron**
  - These arrows can be called single barbed arrows, fish-hook arrows or half-curly arrows

What is homolytic fission?

- **Homolytic fission** is breaking a covalent bond in such a way that each atom takes an electron from the bond to form two radicals
  - **Remember:** A radical is a chemical species that contains an unpaired electron
- The homolytic fission of halogens is the **initiation step** (first step) in a sequence of steps that form a chain reaction

Homolytic fission of a chlorine-chlorine bond

The covalent bond breaks evenly and each chlorine atom receives one electron resulting in the formation of two chlorine radicals, Cl•

- The mechanism of homolytic fission can also be represented using Lewis formulas:

Mechanism of homolytic fission using Lewis formulas

The mechanism of homolytic fission using Lewis formulas shows the specific movement of electrons

- When drawing mechanisms, ensure:
  - That the curly arrows start at an electron-rich region
    - In this case, the curly arrows should start from the middle of the covalent bond
  - That the curly arrows finish at their correct destination
    - In this case, each curly arrow should finish at a chlorine atom

Types of homolytic fission

- Since bond breaking is an **endothermic** process, energy is required for homolytic fission to occur
- The amount of energy required depends on the strength of the covalent bond being broken
  - **Thermolytic fission**: For weaker bonds, simply heating the compound could provide sufficient energy

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$$X{:}X \xrightarrow{\text{heat}} X\bullet + X\bullet$$

- **Photolytic fission**: For stronger bonds such as halogen bonds, exposing the compound to high-energy UV light provides the required energy

$$X{:}X \xrightarrow{\text{UV light}} X\bullet + X\bullet$$

Halogenation of Alkanes

Your notes

Halogenation of Alkanes

Stability of alkanes

- Alkanes are relatively stable / unreactive due to the strengths of the C–C and C–H bonds and their non-polar nature

Strength of bonds

- Alkanes consist of carbon and hydrogen atoms which are bonded together by **single bonds**
- Unless a lot of heat is supplied, it is difficult to break these **strong** C-C and C-H covalent bonds
- This decreases the alkanes' reactivities in chemical reactions

Lack of polarity

- The **electronegativities** of the carbon and hydrogen atoms in alkanes are almost the same
- This means that both atoms share the electrons in the covalent bond almost equally

Pauling electronegativity values for the elements

H 2.1																	He –
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne –
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.2	S 2.5	Cl 3.0	Ar –
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr 3.0
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe 2.6
Cs 0.7	Ba 0.9	La–Lu 1.1–1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Ti 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn –
Fr 0.7	Ra 0.9	Ac–No 1.1–1.7															

The Pauling Scale shows that the difference in electronegativity between carbon and hydrogen is only 0.4

- As a result of this, alkanes are **nonpolar** molecules and have no partial positive or negative charges (δ^+ and δ^- respectively)

Structural formula of ethane showing bond polarities

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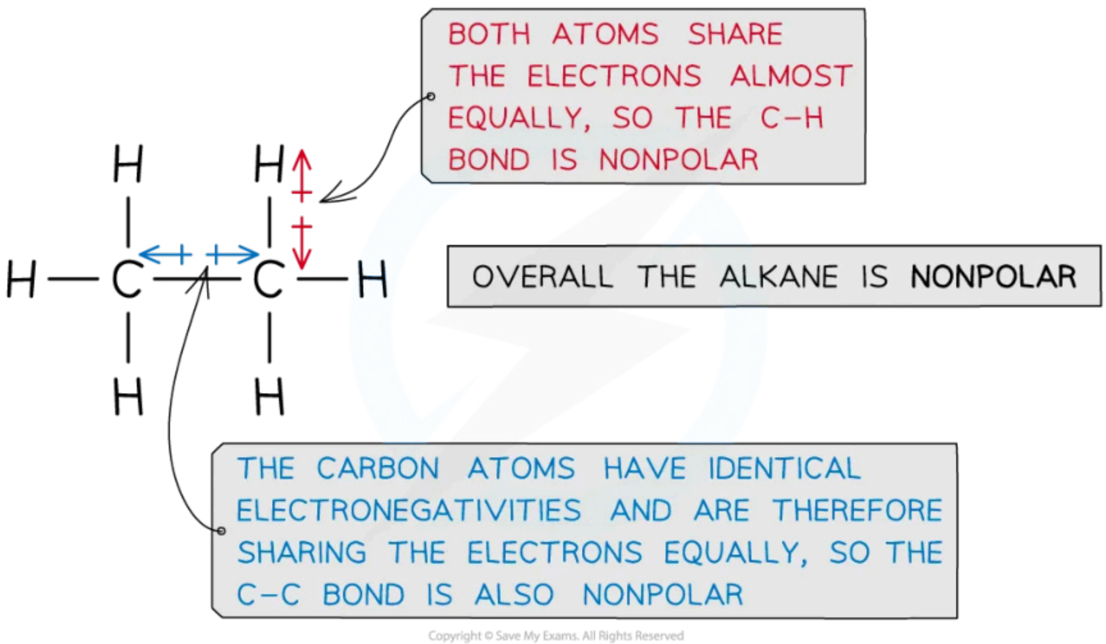


Ethane is an example of an alkane that lacks polarity due to almost similar electronegativities of the carbon and hydrogen atoms

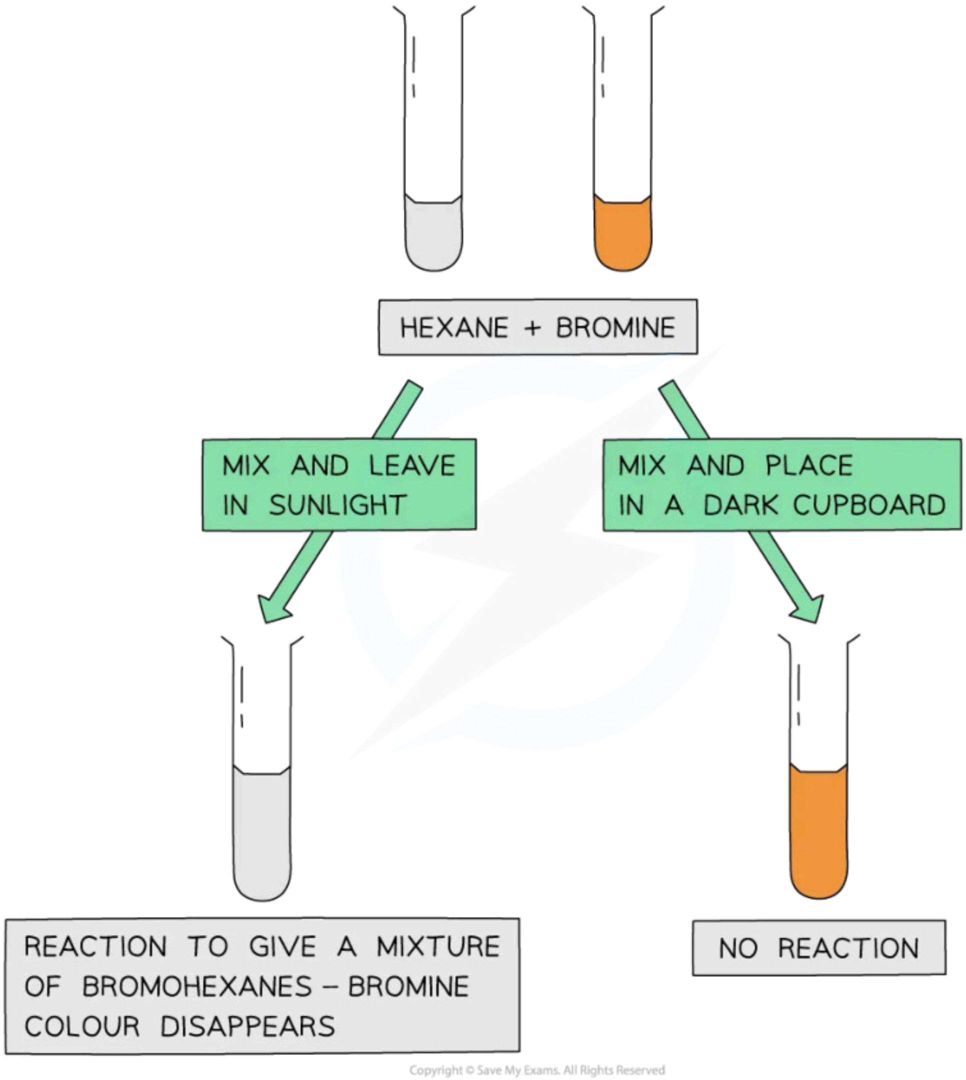
- Alkanes, therefore, do not react with **polar reagents**
  - They have no electron-deficient areas to attract **nucleophiles**
  - And also lack electron-rich areas to attract **electrophiles**
- Alkanes only react in combustion reactions and undergo substitution by radicals

Free-radical substitution of alkanes

- Alkanes can undergo **free-radical substitution** in which a hydrogen atom gets **substituted** by a halogen (chlorine/bromine)
- Since alkanes are very unreactive, **ultraviolet** light **(sunlight)** is needed for this substitution reaction to occur

Proving that energy from UV light is required for radical reactions with halogens

Your notes



The fact that the bromine colour has disappeared only when mixed with an alkane and placed in sunlight suggests that the ultraviolet light is essential for the free radical substitution reaction to take place

- The free-radical substitution reaction consists of three steps:
  - In the **initiation step**, the halogen bond (Cl-Cl or Br-Br) is broken by **UV energy** to form two radicals
    - For more information about the initiation step, see our revision note about Homolytic Fission
  - These radicals create further radicals in a chain reaction called the **propagation step**
  - The reaction is terminated when two radicals collide with each other in a **termination step**

Propagation step

- The **propagation step** refers to the **progression** (growing) of the substitution reaction in a chain reaction
  - **Radicals** are very reactive and will attack the unreactive alkanes

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- A C-H bond breaks **homolytically** (each atom gets an electron from the covalent bond)
- An **alkyl** free radical is produced
- This can attack another halogen molecule to form the **halogenoalkane** and **regenerate** the halogen radical
- This radical can then **repeat** the cycle

- For example, the chlorination of ethane is:

CH_3CH_3	+	$Cl\bullet$	→	$\bullet CH_2CH_3$	+	HCl
ethane		chlorine radical		alkyl (ethyl) radical		

$\bullet CH_2CH_3$	+	Cl_2	→	CH_3CH_2Cl	+	$Cl\bullet$
ethyl radical		chlorine molecule		halogenoalkane (chloroethane)		chlorine radical regenerated

- This reaction is not very suitable for preparing specific halogenoalkanes as a **mixture** of substitution products is formed
- If there is enough halogen present, all the hydrogens in the alkane will eventually get substituted
- For example, the chlorination of ethane could continue:

CH_3CH_2Cl	+	$Cl\bullet$	→	$\bullet CH_2CH_2Cl$	+	HCl
halogenoalkane (chloroethane)		chlorine radical		radical		

$\bullet CH_2CH_2Cl$	+	Cl_2	→	$ClCH_2CH_2Cl$	+	$Cl\bullet$
radical		chlorine molecule		disubstituted halogenoalkane		chlorine radical regenerated

- This process can repeat until hexachloroethane, C_2Cl_6, is formed

Termination step

- The **termination step** is when the chain reaction **terminates** (stops) due to two free radicals reacting together and forming a single unreactive molecule
  - Multiple products are possible
- For example, the single substitution of ethane by chlorine can form:

$\bullet CH_2CH_3$	+	$Cl\bullet$	→	CH_3CH_2Cl
ethyl radical		chlorine radical		chloroethane
$\bullet CH_2CH_3$	+	$\bullet CH_2CH_3$	→	$CH_3CH_2CH_2CH_3$
ethyl radical		ethyl radical		butane
$Cl\bullet$	+	$Cl\bullet$	→	Cl_2
chlorine radical		chlorine radical		chlorine molecule

Examiner Tip

- Make sure you practice and are able to write out these equations, especially the **propagation** steps
- Students frequently get the propagation steps wrong, by showing the formation of a hydrogen radical produced in propagation
  - This step ($CH_3CH_3 + Cl\bullet \rightarrow CH_3CH_2Cl + H\bullet$) does not happen:
- Do not fall into this trap!

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