13.2 Characteristic organic reactions

Name: _____ Class: _____ Date: _____ **Total: 22 marks**

KEY WORDS addition • fission • electrophile • homolytic fission • nucleophile

Objective

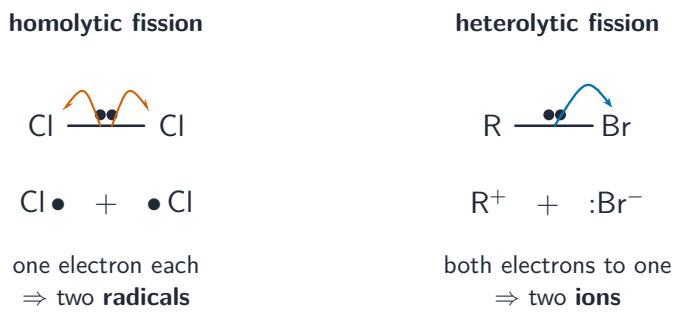
Build the skills to answer exam questions on **characteristic organic reactions** – bond **fission**, **nucleophiles** and **electrophiles**, the reaction types, and mechanism terms.

You must be able to:

- use the terms homologous series, saturated/unsaturated, and homolytic/heterolytic fission
- define nucleophile, electrophile, and the reaction types (addition, substitution, etc.)
- describe the free-radical steps and name the main mechanisms

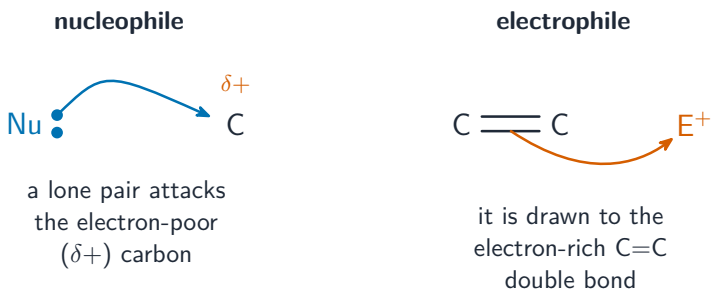
1 Key knowledge and worked examples

Breaking bonds



*Homolytic: one electron to each atom (two **free radicals**). Heterolytic: both electrons to one atom (two ions)*

Nucleophiles and electrophiles



A nucleophile donates a lone pair to an electron-poor centre; an electrophile accepts an electron pair from an electron-rich region (e.g. C=C)

A **nucleophile** donates an electron pair. It need not be negative: neutral ammonia has a nitrogen lone pair. An **electrophile** accepts an electron pair.

Reaction and mechanism types

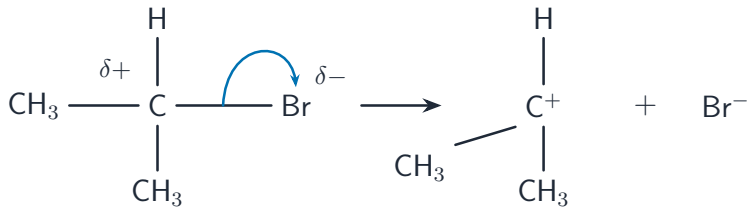
addition (two → one), **substitution** (swap), **elimination** (lose a small molecule → double bond), **hydrolysis** (split by water), **condensation** (join + lose a small molecule). Free-radical reactions go by **initiation → propagation → termination**. Main mechanisms: free-radical substitution, electrophilic addition, nucleophilic substitution, nucleophilic addition. A **curly arrow** shows a pair of electrons moving.

Worked classification. Ethene plus HBr makes bromoethane by addition; bromoethane plus hydroxide replaces Br with OH by substitution; ethanol losing water to make ethene is elimination. Ester plus water giving acid and alcohol is hydrolysis, while acid plus alcohol giving ester and water is condensation. Classify from the structural change and the role of water.

Follow the electron pair in a substitution

A full curly arrow starts on a bond or a lone pair and shows **two** electrons moving. A half-headed arrow shows one electron moving in a radical step. Do not start an arrow at a positive charge.

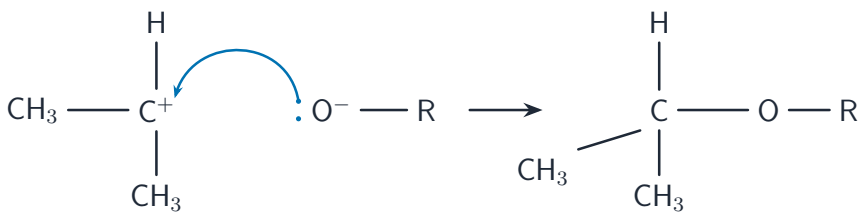
Original application: 9701/24 N25 Q3(b)(ii). The question states an S_N1 mechanism for 2-bromopropane with $(CH_3)_2CHO^-$. Follow the stated mechanism. First show the $\delta+$ carbon and $\delta-$ bromine, then move the C–Br pair to bromine. This gives a carbocation and Br^-.



Bond pair moves to Br; the carbon intermediate has a positive charge.

Full curly arrow from the C–Br bond to Br; the intermediate carbon has a positive charge.

Next, move a lone pair on the nucleophile's oxygen to the positive carbon. A new C–O bond forms. In the figure, R means $CH(CH_3)_2$.



An oxygen lone pair forms the C–O bond. Here R = $CH(CH_3)_2$.

The arrow begins at the lone pair; it shows electron movement, not the movement of an entire molecule.

For the worksheet's 2-bromo-2-methylpropane case, the same two-stage pattern gives a tertiary carbocation, then attack by OH^-. Three alkyl groups help stabilise the positive charge by their electron-releasing effect. A primary carbocation is much less stable. In the worksheet's 1-bromobutane S_N2 case, attack and C–Br breaking occur together in one stage, without a carbocation intermediate. Draw both pair-moving arrows in that stage.

■ Identify radical stages from what they do

For methane and chlorine under UV light: initiation $Cl_2 \rightarrow 2Cl\cdot$ makes radicals. Propagation $Cl\cdot + CH_4 \rightarrow HCl + \cdot CH_3$, followed by $\cdot CH_3 + Cl_2 \rightarrow CH_3Cl + Cl\cdot$, consumes and regenerates one radical in each step. Termination $\cdot CH_3 + Cl\cdot \rightarrow CH_3Cl$ consumes two radicals without making a new radical.

2 Practice

2.1 Define a **nucleophile**. [1]

2.2 Name the type of bond fission that produces two free radicals. [1]

3 Exam-style questions

3.1 Heterolytic fission of a covalent bond produces: [1]

- ☐ **A** two free radicals
- **B** two ions
- **C** two atoms
- **D** a double bond

3.2 A reaction in which a small molecule is removed to form a C=C double bond is: [1]

- ☐ **A** addition
- **B** substitution
- **C** elimination
- **D** hydrolysis

3.3 (a) State the difference between homolytic and heterolytic fission. [2]

(b) Name the three steps of a free-radical mechanism. [3]

3.4 Explain why a C=C double bond is attacked by electrophiles. [2]

3.5 2-bromo-2-methylpropane, $(CH_3)_3CBr$, reacts with warm aqueous sodium hydroxide.

(a) Name the type of reaction and its mechanism. [2]

(b) Explain what is meant by a *nucleophile*, and state which species is the nucleophile here. [2]

(c) The C–Br bond breaks heterolytically. Explain the term *heterolytic fission* and name the two species formed. [3]

(d) 1-bromobutane reacts by a different mechanism under the same conditions. Name that mechanism, and explain the difference in terms of the stability of the intermediate. [4]

Solutions

Each answer shows the steps, then the **result**.

2.1

- an electron-pair donor; its lone pair forms a bond to an electron-poor centre

2.2

- homolytic fission

3.1 B

- Heterolytic fission gives both electrons to one atom, producing two ions

3.2 C

- Removing a small molecule to form a double bond is elimination

3.3

(a)

- homolytic – the bond splits evenly, one electron to each atom (two radicals); heterolytic – both electrons go to one atom (two ions)

(b)

- initiation; propagation; termination

3.4

- the C=C bond is an electron-rich region (high electron density); electrophiles are electron-deficient and are attracted to it

3.5

(a)

- Nucleophilic substitution; by the S_N1 mechanism

(b)

- A nucleophile is an electron-pair donor that attacks an electron-deficient, $\delta+$ carbon; here it is the hydroxide ion, OH^-

(c)

- In heterolytic fission **both** bonding electrons go to one of the two atoms, so the bond breaks unevenly; it gives a bromide ion, Br^- and a tertiary carbocation, $(CH_3)_3C^+$

(d)

- S_N2. The tertiary carbocation is stabilised by the electron-releasing inductive effect of **three** alkyl groups, which spread the positive charge; a primary carbocation has only one such group, so it is far less stable and does not form readily; the hydroxide

therefore attacks the $\delta+$ carbon directly in a single step, from the side opposite the bromine