A-LEVEL CHEMISTRY • EXERCISE SHEET

13.2 Characteristic organic reactions

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

KEY WORDS addition 加成 • fission 断裂 • electrophile 亲电试剂 • homolytic fission 均裂 • nucleophile 亲核试剂

Objective

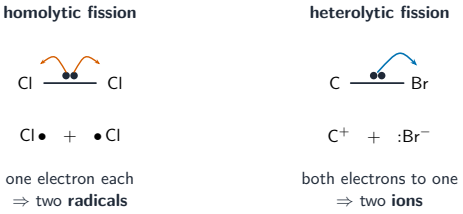
Build the skills to answer exam questions on **characteristic organic reactions** — bond **fission** 断裂, **nucleophiles** 亲核试剂 and **electrophiles** 亲电试剂, the reaction types, and mechanism terms.

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

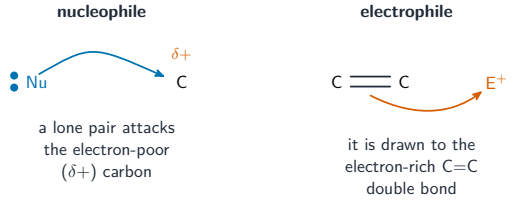
1 Worked examples

Breaking bonds



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

Nucleophiles and electrophiles



A nucleophile (lone pair) attacks an electron-poor centre; an electrophile is drawn to an electron-rich one (e.g. C=C)

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.

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

2.1 a species with a lone pair that is attracted to (attacks) an electron-poor / positive 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.