

Exercise walk-through

13.2

Characteristic organic reactions

A-Level Chemistry

Track the bonding electrons

Your turn

A Cl–Cl bond breaks under ultraviolet light. Each chlorine receives one bonding electron. Name the fission and draw the products.

Now a C–Br bond breaks with both bonding electrons going to Br. State the charges produced and name the fission.

Follow the two bonding electrons; use dots for unpaired electrons and signs for charges.

Bond fission

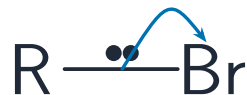
- **homolytic fission** – one electron each $\rightarrow$ two **free radicals**
- **heterolytic fission** – both electrons to one atom $\rightarrow$ two ions

homolytic fission



one electron each
 $\Rightarrow$ two **radicals**

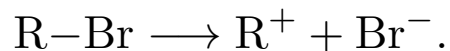
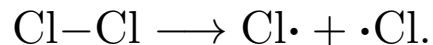
heterolytic fission



both electrons to one
 $\Rightarrow$ two **ions**

One electron or an electron pair?

Fission	Electron allocation	Products
Homolytic	one to each atom	two radicals
Heterolytic	both to one atom	a cation and an anion



A full curly arrow moves two electrons. A half-headed arrow moves one electron.
R represents the organic group.

Classify by electron-pair behaviour

Your turn

Compare OH^- , NH_3 and H^+ . Which can donate a lone pair to an electron-poor carbon? Which accepts a pair from an alkene?

Explain why charge alone is an incomplete test.

Nucleophiles and electrophiles

nucleophile



a lone pair attacks
the electron-poor
($\delta+$) carbon

electrophile



it is drawn to the
electron-rich C=C
double bond

- a **nucleophile**
(lone pair) attacks an
electron-**poor** centre

- an **electrophile** is
drawn to an electron-**rich**
centre (C=C)

Reaction types: **addition** ,
substitution ,
elimination ,
hydrolysis .

A neutral species can be a nucleophile

Species	Relevant feature	Behaviour
OH^-	oxygen lone pair	electron-pair donor
NH_3	nitrogen lone pair	electron-pair donor
H^+	accepts a pair	electron-pair acceptor

Use precise definitions

A nucleophile	donates an electron pair to an electron-poor centre.
A electrophile	accepts an electron pair from an electron-rich region.

The $\text{C}=\text{C}$ π bond is an electron-rich region. Ammonia shows why a nucleophile need not be negative.

Mechanisms

free-radical substitution
– alkanes

electrophilic addition
– alkenes

nucleophilic substitution
– halogenoalkanes

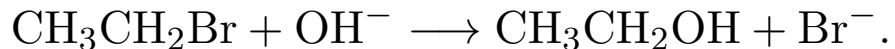
nucleophilic addition
– carbonyls

Free-radical steps: **initiation** → **propagation** → **termination** . A full **curly arrow** shows a **pair** of electrons moving.

Classify what changes in each equation

Your turn

Name each reaction type. Identify the bond or group change that supports your choice.



Use the structural change as evidence

Example	Reaction type	Evidence
Ethene + HBr	addition	C=C opens; two join as one
Bromoethane + OH ⁻	substitution	Br is replaced by OH
Ethanol to ethene	elimination	water lost; C=C forms

Nucleophilic substitution combines the electron-pair behaviour with the group replacement. A reagent name alone is not the reaction type.

Water consumed or water formed?

Hydrolysis versus condensation

Ester + water $\longrightarrow$ carboxylic acid + alcohol:

hydrolysis, because water is used to break the molecule apart.

Carboxylic acid + alcohol $\longrightarrow$ ester + water:

condensation, because joining the molecules forms a small molecule.

Check the role of water. Its presence somewhere in a reaction mixture does not by itself establish hydrolysis.

Original exam: follow the stated mechanism

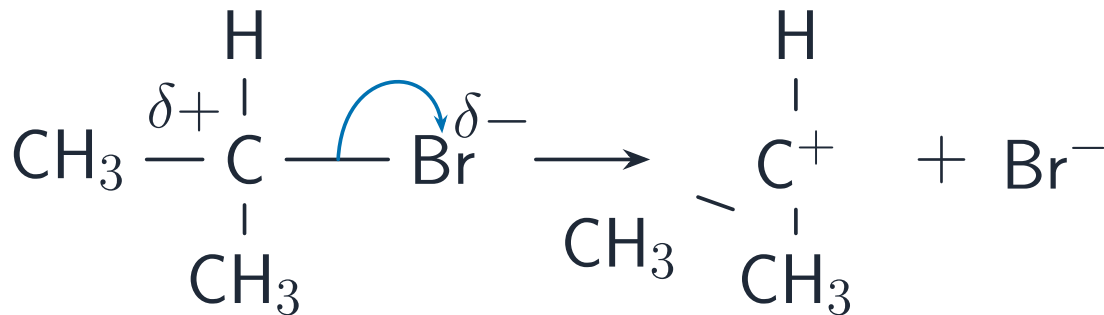
9701/24 N25 Q3(b)(ii)

The paper states that 2-bromopropane reacts with $(\text{CH}_3)_2\text{CHO}^-$ by an S_N1 mechanism. Sketch the two stages, including dipoles, charges, a lone pair and curly arrows.

- 1 Break C–Br heterolytically and show the intermediate.
- 2 Show the oxygen lone pair forming the new C–O bond.

Use the mechanism stated in this question; do not infer it solely from the word secondary.

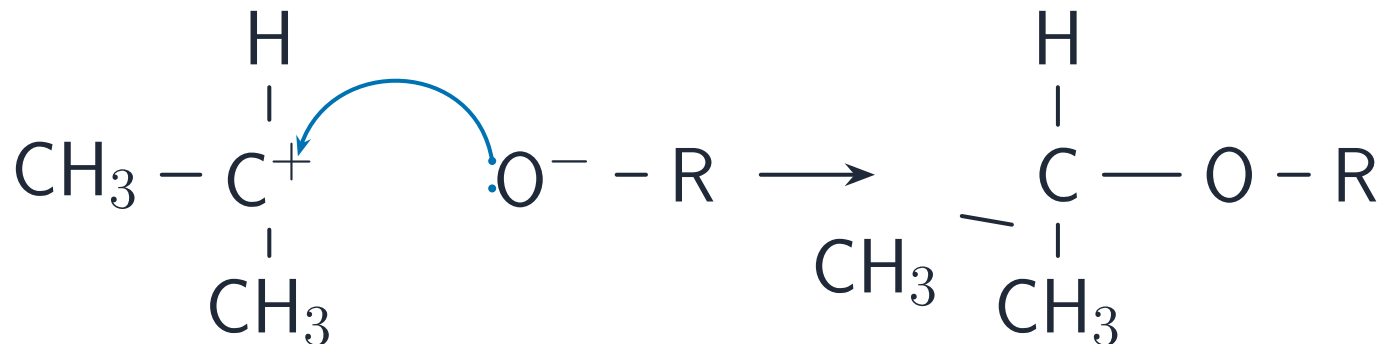
SN1 stage one: the bond pair leaves



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

Both C–Br electrons go to Br: bromide and a carbocation form. Start the full curly arrow on the bond.

SN1 stage two: donate an oxygen lone pair



An oxygen lone pair forms the C–O bond. Here $\text{R} = \text{CH}(\text{CH}_3)_2$.

Start the full curly arrow at the oxygen lone pair and end it at C^+ . The new bond uses that pair.

Compare the worksheet substitution mechanisms

Worksheet case	Description	Intermediate
2-bromo-2-methylpropane	S_N1 , two stages	tertiary carbocation
1-bromobutane	S_N2 , one stage	no carbocation

Explain, rather than name only

Three alkyl groups help stabilise the tertiary carbocation by their electron-releasing effect. A primary carbocation is much less stable. In the worksheet's primary case, attack and leaving-group departure occur together.

For S_N2 , show lone-pair-to-carbon and bond-to-Br arrows in the same stage.

Use equations to identify radical chain stages

Stage	Methane + chlorine under UV light
Initiation	$\text{Cl}_2 \longrightarrow 2\text{Cl}\cdot$
Propagation	$\text{Cl}\cdot + \text{CH}_4 \longrightarrow \text{HCl} + \cdot\text{CH}_3$
Propagation	$\cdot\text{CH}_3 + \text{Cl}_2 \longrightarrow \text{CH}_3\text{Cl} + \text{Cl}\cdot$
Termination	$\cdot\text{CH}_3 + \text{Cl}\cdot \longrightarrow \text{CH}_3\text{Cl}$

Initiation makes radicals; each propagation step consumes and regenerates one; termination consumes two without regenerating a radical.

Exercises 2.1·3.1

2.1 Define a **nucleophile**.

[1]

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

[1]

3.1 Heterolytic fission of a covalent bond produces:

[1]

☐

A two free radicals

B two ions

C two atoms

D a double bond

Exercises 2.1·3.1

2.1 Define a **nucleophile**.

[1]

2.1

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

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

[1]

2.2

- homolytic fission

3.1 Heterolytic fission of a covalent bond produces:

[1]

☐

A two free radicals

B two ions

C two atoms

D a double bond

3.1 B

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

Exercise 3.2

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

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☐

A addition

B substitution

C elimination

D hydrolysis

3.2 C

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

Exercise 3.3

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

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

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

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

Exercise 3.4

3.4 Explain why a $\text{C}=\text{C}$ double bond is attacked by electrophiles.

[2]

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3.4

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

Exercise 3.5 (a)

3.5 2-bromo-2-methylpropane, $(\text{CH}_3)_3\text{CBr}$, reacts with warm aqueous sodium hydroxide.

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

Exercise 3.5 (a)

3.5 2-bromo-2-methylpropane, $(\text{CH}_3)_3\text{CBr}$, reacts with warm aqueous sodium hydroxide.

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(a)

- Nucleophilic substitution; by the S_N1 mechanism

Exercise 3.5 (b)

3.5 2-bromo-2-methylpropane, $(\text{CH}_3)_3\text{CBr}$, reacts with warm aqueous sodium hydroxide.

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

Exercise 3.5 (b)

3.5 2-bromo-2-methylpropane, $(\text{CH}_3)_3\text{CBr}$, reacts with warm aqueous sodium hydroxide.

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

(b)

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

Exercise 3.5 (c)

3.5 2-bromo-2-methylpropane, $(\text{CH}_3)_3\text{CBr}$, reacts with warm aqueous sodium hydroxide.

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

Exercise 3.5 (c)

3.5 2-bromo-2-methylpropane, $(\text{CH}_3)_3\text{CBr}$, reacts with warm aqueous sodium hydroxide.

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

(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, $(\text{CH}_3)_3\text{C}^+$

Exercise 3.5 (d)

3.5 2-bromo-2-methylpropane, $(\text{CH}_3)_3\text{CBr}$, reacts with warm aqueous sodium hydroxide.

(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]

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(d)

- $\text{S}_{\text{N}}2$. 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