



Haloalkanes I

OCR A Chemistry A H432 | Specification-led student notes

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SPECIFICATION COVERAGE

OCR A REF	THIS PACK TEACHES	SECTIONS
4.2.2(b), (c)	Polar C–X bonds, nucleophiles and primary haloalkanes	1
4.2.2(a)(i), (c)	Hydrolysis with aqueous alkali and its mechanism	2–3
4.2.2(d)	C–X bond enthalpies and the hydrolysis rate trend	4
4.2.2(a)(ii), (d)	Hydrolysis in water, silver halides and comparing rates	5–6
4.2.2(a)–(d)	Original mixed practice and complete worked answers	7–8; answers

YOUR AIM Predict the alcohol formed by hydrolysis, draw a precise substitution mechanism and explain the results of a controlled hydrolysis-rate experiment.

LESSON BOUNDARY Builds on Introduction to Organic Chemistry II. This pack covers OCR 4.2.2(a)–(d). Ozone chemistry belongs to Haloalkanes II. Other substitution reagents and elimination are outside this lesson.

OCR A Chemistry A H432 | Specification version 3.1 (May 2026)

Two experiments, two different roles for the reagents

Aqueous hydroxide converts a haloalkane to an alcohol by nucleophilic substitution. In the silver nitrate experiment, water hydrolyses the haloalkane and silver ions reveal the halide ions released.

How to use these notes

Learn the definition, follow the worked mechanism, then attempt each TEST IT before checking the answers. Draw complete structures and charges. Explain a rate comparison by naming the C–X bonds involved.

The questions are original CrackingChem practice. The suggested marks are for self-checking.

1. The carbon–halogen bond is polar



SPEC 4.2.2(b), (c) Identify the electron-pair donor and the carbon attacked in a primary haloalkane.



CRACK IT The C–X bond is polar because the halogen is more electronegative than carbon. The carbon atom is $\delta+$ and can accept an electron pair from a nucleophile.

A haloalkane has a halogen atom bonded to a saturated carbon atom. X is shorthand for a halogen such as Cl, Br or I. Replacing X with OH produces an alcohol.



Br attracts the bonding pair more strongly than C.

The C-Br bond is polar.

DEFINITION TO LEARN

A nucleophile is an electron pair donor.

The hydroxide ion, OH^- , is a nucleophile because oxygen has a lone pair available to donate to an electron-deficient carbon. A nucleophile does not have to be negatively charged: water can also donate a lone pair.

Recognise a primary haloalkane

Count the carbon atoms directly attached to the carbon bearing X. A primary haloalkane has one; secondary has two and tertiary has three. Do not count all the carbons in the molecule.

HALOALKANE	CARBONS ATTACHED TO C–X CARBON	CLASS
$\text{CH}_3\text{CH}_2\text{Br}$	1	Primary
$\text{CH}_3\text{CHBrCH}_3$	2	Secondary
$(\text{CH}_3)_3\text{CBr}$	3	Tertiary



EXAM CHECK A branched molecule can still be primary. In $(\text{CH}_3)_2\text{CHCH}_2\text{Br}$, the carbon carrying Br is attached to only one other carbon. The mechanism required here is for primary haloalkanes.



TEST IT 1 (a) Name $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$. [1]
 (b) Explain why it is a primary haloalkane. [1]
 (c) State which atom in its C–Cl bond is $\delta+$ and which is $\delta-$. [1]
 (d) Define nucleophile. [1]

[4 marks]



✓ DONE WHEN You can locate the $\delta+$ carbon, identify a primary haloalkane and give the nucleophile definition precisely.

2. Hydrolysis replaces the halogen



SPEC 4.2.2(a)(i) Describe hydrolysis of haloalkanes with aqueous alkali.



CRACK IT Heat a haloalkane with aqueous sodium hydroxide or potassium hydroxide. The hydroxide ion substitutes for the halogen atom to form an alcohol.



R represents an alkyl group. OH^- forms a new C–O bond while the C–X bond breaks. Hydrolysis is the breaking of a bond using water or hydroxide ions; in this reaction the halogen is replaced by OH.

WHAT TO STATE	WHY IT MATTERS
Aqueous NaOH or aqueous KOH	Provides hydroxide ions as the nucleophile.
Heat under reflux	Speeds up reaction while vapour condenses and returns to the flask.
Alcohol + halide ion	The carbon skeleton stays the same; X is replaced by OH.

WORKED EXAMPLE | Hydrolysis of bromoethane

Bromoethane reacts with warm aqueous sodium hydroxide. Predict the organic product and write the ionic and full equations.

The two-carbon skeleton is unchanged, so the alcohol is ethanol.



Na^+ is a spectator ion. The ionic equation focuses on the species that change.



EXAM CHECK State aqueous hydroxide and heating. An equation must show the halide ion with its negative charge. OH^- is the reacting ion, not a hydroxyl radical, $\bullet\text{OH}$.



TEST IT 2 1-chloropropane is hydrolysed using potassium hydroxide.

- State the solvent and heating condition. [1]
- Name the organic product. [1]
- Write the ionic equation. [1]
- Write the full equation using KOH. [1]

[4 marks]



✓ **DONE WHEN** You can preserve the carbon skeleton, replace X with OH and balance atoms and charge in the equation.

3. Draw the substitution mechanism



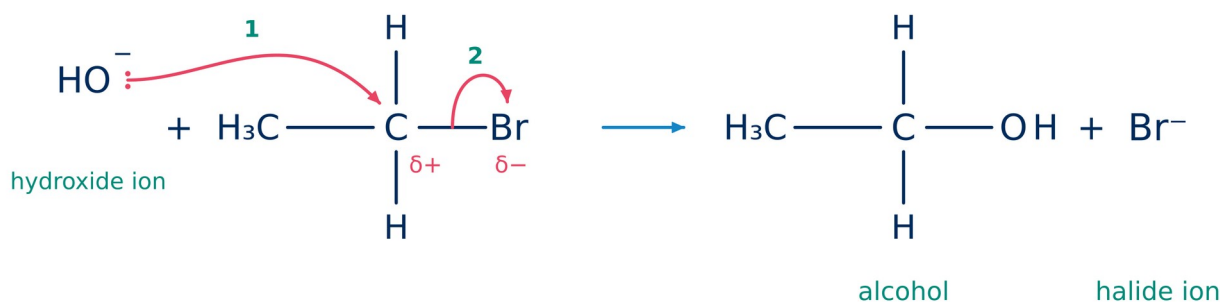
SPEC 4.2.2(b), (c) Draw the nucleophilic-substitution mechanism for a primary haloalkane with aqueous alkali.



CRACK IT A curly arrow represents the movement of an electron pair. Show both electron-pair movements: oxygen to carbon, and the C–X bond to X.

WORKED EXAMPLE | Bromoethane + hydroxide

The nucleophile is OH^- . Show the attacking oxygen lone pair, the C–Br dipole and both products.



- 1 A lone pair on oxygen is donated to the δ^+ carbon, forming a C–O bond.
- 2 The C–Br bonding pair moves to Br. The bond breaks heterolytically and Br^- forms.

For this primary-haloalkane mechanism, show both curly arrows on the reactants. Do not insert a carbocation. The alcohol is neutral and the halide ion carries the negative charge.



EXAM CHECK Start the first arrow between the two lone-pair dots, close to O. Start the second on the C–Br bond and point it towards Br. Use a full arrowhead for each electron pair. Keep δ^+ and δ^- beside their atoms.



TEST IT 3 Draw the nucleophilic-substitution mechanism for chloroethane reacting with OH^- . Include the attacking lone pair, both curly arrows, the C–Cl dipole and both products.

[4 marks]



✓ **DONE WHEN** Your arrow tails identify actual electron pairs; your products have the correct bonds, formulae and charges.

4. Bond enthalpy explains the rate



SPEC 4.2.2(d) Explain the hydrolysis-rate trend in terms of C–F, C–Cl, C–Br and C–I bond enthalpies.



CRACK IT Compare haloalkanes with the same carbon skeleton under the same conditions. The weaker C–X bond is easier to break, so hydrolysis is faster.

C–X BOND	RELATIVE BOND ENTHALPY	HYDROLYSIS
C–F	Highest; strongest bond	Slowest
C–Cl	Lower than C–F	Slower than C–Br
C–Br	Lower than C–Cl	Faster than C–Cl
C–I	Lowest; weakest bond	Fastest

Bond enthalpy: C–F > C–Cl > C–Br > C–I

Hydrolysis rate: R–I > R–Br > R–Cl > R–F

WORKED EXAMPLE | Comparing two primary haloalkanes

Why does 1-iodopropane hydrolyse faster than 1-chloropropane under the same conditions?

The C–I bond has a lower bond enthalpy than the C–Cl bond. Less energy is needed to break C–I, so it breaks more readily and 1-iodopropane hydrolyses faster.

The comparison names the bonds, compares their strength and links this directly to the rate.

Why polarity alone gives the wrong prediction

C–F is the most polar carbon–halogen bond, but it is also the strongest. Fluoroalkanes hydrolyse very slowly. For this series, the bond-enthalpy difference is the key explanation for the observed rate trend.



EXAM CHECK Do not write only “iodine is more reactive”. Compare the C–I and C–Cl bonds. These are covalent bonds within molecules, not intermolecular forces.



TEST IT 4 (a) Put 1-chlorobutane, 1-bromobutane and 1-iodobutane in order of increasing hydrolysis rate. [1]
 (b) Explain why 1-bromobutane hydrolyses faster than 1-chlorobutane. [2]
 (c) A student predicts that 1-fluorobutane is fastest because C–F is most polar. Explain why this prediction is wrong. [1]

[4 marks]



✓ **DONE WHEN** You can explain the rate trend using the strength of the C–X bond, including why C–F is the exception to a polarity-only prediction.

5. Compare hydrolysis rates experimentally



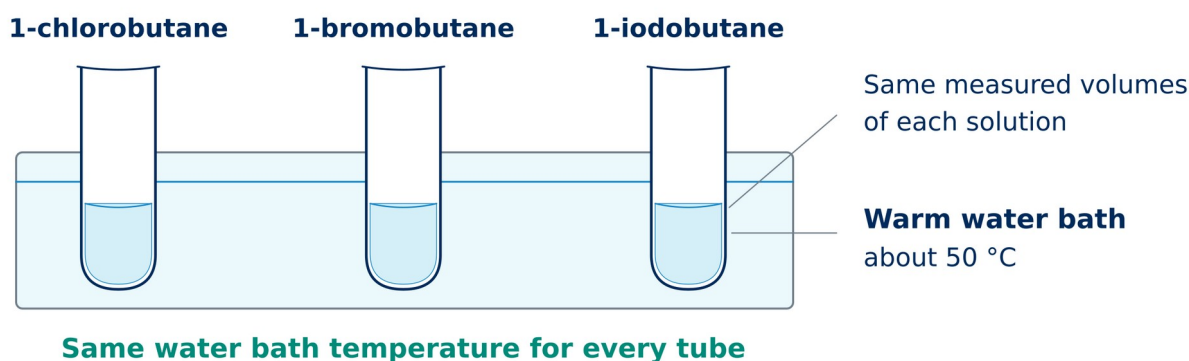
SPEC 4.2.2(a)(ii), (d) Use water, silver nitrate and ethanol to compare hydrolysis rates for different C–X bonds.



CRACK IT In this experiment water hydrolyses the haloalkane. Ag^+ then reacts with the halide ions released, forming a visible silver halide precipitate.



REAGENT	ROLE
Water	Hydrolyses the haloalkane; acts as the nucleophile.
Ethanol	Helps the haloalkane mix with the aqueous solution.
Aqueous silver nitrate	Provides Ag^+ to detect the halide ions released.



A controlled comparison

- 1 Label three tubes for 1-chlorobutane, 1-bromobutane and 1-iodobutane. Add equal measured volumes of equally concentrated ethanolic haloalkane solutions.
- 2 Warm these and the aqueous silver nitrate to the same temperature in a water bath, for example about 50 °C.
- 3 Add the same volume and concentration of silver nitrate solution to each sample. Mix and start timing each reaction as its reagents are combined.
- 4 Record the time to the first persistent cloudiness. Use the same observation criterion, repeat the tests and compare the results.



EXAM CHECK Keep the temperature, haloalkane concentration, reagent volumes and ethanol–water proportions constant. Ethanol is flammable: use a water bath, not a naked flame. Wear eye protection; silver nitrate can damage eyes and skin.



- TEST IT 5** (a) Explain why ethanol is included. [1]
 (b) State what Ag^+ ions reveal in this experiment. [1]
 (c) Give one variable to control and explain why controlling it makes the rate comparison valid. [2]

[4 marks]



✓ DONE WHEN You can distinguish the hydrolysis step from the precipitation step and describe a fair rate comparison.

6. Interpret the precipitate correctly



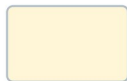
SPEC 4.2.2(a)(ii), (d) Use silver halide observations to compare the rate at which halide ions are released.



CRACK IT The colour identifies the halide ion. The time taken to form a precipitate gives evidence about the hydrolysis rate under controlled conditions.



AgCl white



AgBr cream



AgI yellow

HALIDE RELEASED	OBSERVATION	IONIC PRECIPITATION EQUATION
Cl^-	White precipitate	$\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$
Br^-	Cream precipitate	$\text{Ag}^+(\text{aq}) + \text{Br}^-(\text{aq}) \rightarrow \text{AgBr}(\text{s})$
I^-	Yellow precipitate	$\text{Ag}^+(\text{aq}) + \text{I}^-(\text{aq}) \rightarrow \text{AgI}(\text{s})$

Under comparable conditions, the iodoalkane gives a precipitate first, the bromoalkane next and the chloroalkane last. You are comparing haloalkane hydrolysis, not simply the speed of mixing free halide ions with silver nitrate.

WORKED EXAMPLE | Reading an observation

An unknown primary haloalkane gives a cream precipitate when warmed with aqueous silver nitrate and ethanol.

The precipitate is AgBr, so Br^- has been released. The unknown contains a C–Br bond.

If the cream precipitate appears sooner than the white precipitate from a matched chloroalkane, that supports faster hydrolysis of the bromoalkane. It does not tell you the exact carbon skeleton.



EXAM CHECK A shorter time means a faster hydrolysis reaction in this controlled test. It does not mean that more total halide ions will eventually form. Do not add aqueous NaOH to this rate-test mixture: it is a different experiment.



TEST IT 6 Under the same conditions, three matched primary haloalkanes give these results: A gives white cloudiness after 150 s; B gives yellow cloudiness after 12 s; C gives cream cloudiness after 48 s.

(a) Identify the halide ion released by A, B and C. [3]

(b) Write the ionic equation for the precipitate formed by C, including state symbols. [1]

(c) State which haloalkane hydrolyses fastest and explain why in terms of its C–X bond. [2]

[6 marks]



✓ **DONE WHEN** You can separate the evidence for halide identity from the evidence for hydrolysis rate.

7. Apply the mechanism to a new structure



SPEC 4.2.2(b), (c) Transfer the primary-haloalkane mechanism to a branched carbon skeleton.



CRACK IT The reacting centre is the carbon bonded to the halogen. Follow that carbon through the reaction and preserve the rest of the skeleton.



TEST IT 7 1-bromo-2-methylpropane, $(\text{CH}_3)_2\text{CHCH}_2\text{Br}$, reacts with aqueous hydroxide.

(a) Explain why it is a primary haloalkane. [1]

(b) Draw its nucleophilic-substitution mechanism. Include the relevant lone pair, dipole, both curly arrows and both products. [4]

[5 marks]

Check your own mechanism

Find the carbon that originally carried Br. It must still have four bonds in the alcohol. Trace each curly arrow back to a pair of electrons and check the total charge before and after the reaction.



✓ **DONE WHEN** You can apply the same electron-pair movements to an unfamiliar primary haloalkane without changing its carbon skeleton.

Answers and working

Use these answers after attempting the questions. Award a mark for each stated point up to the maximum shown.

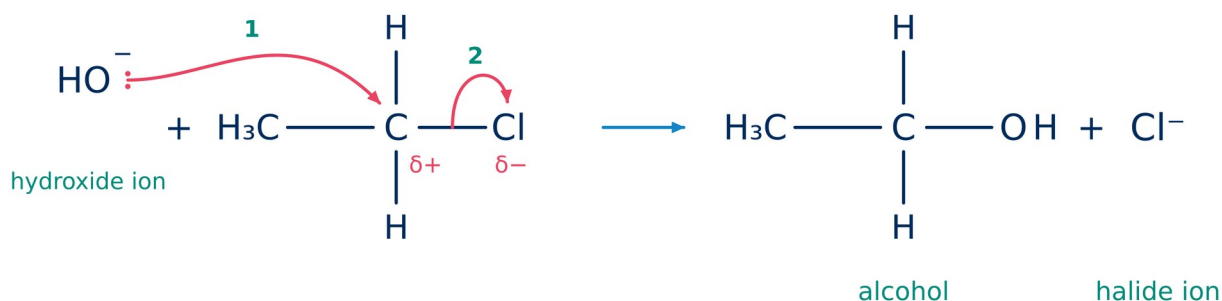
TEST IT 1 Polarity and nucleophiles [4 marks]

- (a) 1-chloropropane. [1]
- (b) The carbon bonded to Cl is attached to only one other carbon atom. [1]
- (c) C is $\delta+$ and Cl is $\delta-$. Both are needed. [1]
- (d) An electron pair donor. [1]

TEST IT 2 Hydrolysis with aqueous alkali [4 marks]

- (a) Aqueous KOH, heated under reflux. [1]
- (b) Propan-1-ol. [1]
- (c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} + \text{OH}^- \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{Cl}^-$ [1]
- (d) $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} + \text{KOH} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{KCl}$ [1]

TEST IT 3 Chloroethane mechanism [4 marks]



O lone-pair arrow to the reacting carbon [1]; C–Cl bond arrow to Cl [1]; $\text{C}\delta+ - \text{Cl}\delta-$ dipole [1]; ethanol and Cl^- as products [1]. The pair stays close to O, with the arrow starting between its dots.

TEST IT 4 Rate trend [4 marks]

- (a) 1-chlorobutane < 1-bromobutane < 1-iodobutane. [1]
- (b) C–Br has a lower bond enthalpy than C–Cl [1], so it is easier to break and hydrolysis is faster [1].
- (c) C–F is the strongest bond / has the highest bond enthalpy, so it is difficult to break despite its high polarity. [1]

Answers and working continued

TEST IT 5 Roles and controls [4 marks]

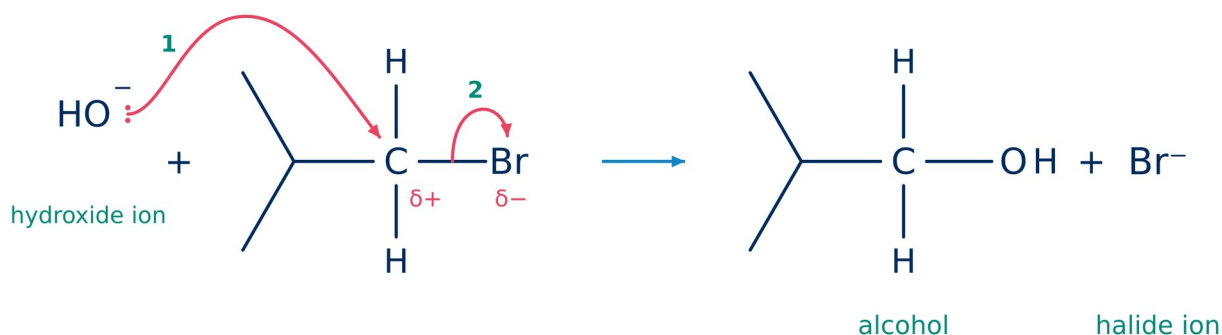
- (a) Ethanol helps the haloalkane mix with the aqueous solution. [1]
 (b) Ag^+ detects halide ions released by hydrolysis, by forming a silver halide precipitate. [1]
 (c) For example, keep temperature constant [1] because temperature changes the reaction rate, so any observed difference should be due to the different C–X bond [1].
 Also accept a named concentration, reagent volume or solvent proportion with a valid explanation of how it could otherwise affect the comparison.

TEST IT 6 Colour and time [6 marks]

- (a) A: Cl^- [1]; B: I^- [1]; C: Br^- [1].
 (b) $\text{Ag}^+(\text{aq}) + \text{Br}^-(\text{aq}) \rightarrow \text{AgBr}(\text{s})$. [1]
 (c) B hydrolyses fastest [1]. C–I has the lowest bond enthalpy of the three C–X bonds, so it is the easiest to break [1].

TEST IT 7 A branched primary haloalkane [5 marks]

- (a) The CH_2Br carbon is directly attached to only one other carbon atom, so the haloalkane is primary. [1]



- (b) O lone-pair arrow to the carbon bearing Br [1]; C–Br bond arrow to Br [1]; $\text{C}\delta^+ - \text{Br}\delta^-$ dipole [1]; $(\text{CH}_3)_2\text{CHCH}_2\text{OH}$ and Br^- as products [1]. The organic product is 2-methylpropan-1-ol.

CHECK THE PRODUCTS



The four-carbon skeleton is unchanged. The reacting CH_2 carbon has two C–H bonds, one C–C bond and one C–O bond in the product.

The total charge is -1 on each side of the equation.

Investigation answer and final recall

TEST IT 8 Investigation plan [8 marks]

- (a) Use equal measured volumes of the two equally concentrated haloalkane solutions. [1]
 Use the same measured volume and concentration of aqueous silver nitrate for each, keeping ethanol–water proportions the same. [1]
 Use a warm water bath and allow both sets of reagents to reach the same temperature before mixing. [1]
 Start timing each reaction when silver nitrate is added; mix consistently. [1]
 Measure the time to the same visible endpoint, such as first persistent cloudiness. [1]
 Repeat each experiment and compare consistent results or calculate a mean from repeat times. [1]
 (b) 1-iodopentane gives a yellow precipitate first [1]. Its C–I bond has a lower bond enthalpy than the C–Cl bond, so it breaks more readily and hydrolysis is faster [1].



EXAM CHECK Cloudiness is an observation; faster hydrolysis is the inference. A strong answer links the two and then explains the rate in terms of the relevant C–X bond.

The key distinctions to retain

IDEA	CORRECT STATEMENT
Nucleophile	An electron pair donor.
Aqueous alkali hydrolysis	OH^- attacks the δ^+ carbon; the products are an alcohol and X^- .
Primary mechanism	A lone pair forms C–O as the C–X pair moves to X.
Rate explanation	A lower C–X bond enthalpy means the bond is easier to break.
Silver nitrate experiment	Water hydrolyses; ethanol helps mixing; Ag^+ detects released X^- .

Specification and exam guidance

Aligned to OCR Chemistry A H432 specification version 3.1 (May 2026), 4.2.2(a)–(d). Curly-arrow conventions build on 4.1.1(h), (i). The mechanism checks also reflect the OCR H432/02 June 2018 examiner report, Q19. The worked examples and questions in this booklet are original CrackingChem material.

Specification: ocr.org.uk/Images/171720-specification-accredited-a-level-gce-chemistry-a-h432.pdf

Examiner report: ocr.org.uk/Images/537986-examiners-report-synthesis-and-analytical-techniques.pdf