Electron-pair sharing reactions

Reactivity 3.4 · SL

Why does bromoethane react with alkali?

> In this unit a whole electron pair moves.

- Warm aqueous hydroxide can substitute Br in bromoethane to form ethanol.
- Ethane shows little reaction with the same reagent under ordinary conditions.
- Trace electron pairs, bonds, charges and conditions.

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

Nucleophiles seek $\delta+$; electrophiles seek electron density.

Check: which is the nucleophile?

Your turn

Which species is a nucleophile?

A. NO_2^+
B. H^+
C. NH_3
D. CH_3^+

A neutral molecule can donate or accept a pair

Species	Site	Role in this example
NH_3	N lone pair	**nucleophile**
H_2O	O lone pair	nucleophile
H^+	accepting proton	**electrophile**
Br_2 near C=C	induced $Br\delta^+$	electrophile

Heterolytic and homolytic fission

heterolytic fission



both electrons go to Br: a cation and an anion form

homolytic fission



one electron to each atom: two radicals form

A **curly arrow** moves a pair; a fishhook moves one electron.

Rules for curly arrows

Correct

From the O lone pair of OH^- to $C^{\delta+}$.

From the C–Br bond to Br.

Incorrect

Arrow beginning at $C\delta^+$ or another electron-poor positive centre.

Arrow with no electron source shown.

Formal heterolysis is not proof of a free intermediate

Formal equation

$CH_3Br \rightarrow CH_3^+ + Br^-$ allocates both C–Br electrons to Br.

It illustrates charge and pair accounting.

Pathway limit

It does not prove that free CH_3^+ readily forms in water.

Primary substitution can form and break bonds together.

Nucleophilic substitution

1. **Given.** Bromoethane and warm aqueous hydroxide.
2. **Replace.** O donates a lone pair to the C bonded to Br; the C–Br pair goes to Br.
3. **Equation.** $CH_3CH_2Br + OH^- \rightarrow CH_3CH_2OH + Br^-$.

Decision

Common content: electron-pair changes and net equation; detailed mechanisms at Higher Level.

One ammonia makes a bond; another accepts a proton

1. **Equation.** $CH_3CH_2Br + 2NH_3 \rightarrow CH_3CH_2NH_2 + NH_4^+ + Br^-$.
2. **Donate.** One N lone pair makes the organic C–N bond.
3. **Transfer.** A second NH_3 accepts H^+; there are 11 H atoms on each side.

Decision

Neutral products require proton accounting as well as bond formation.

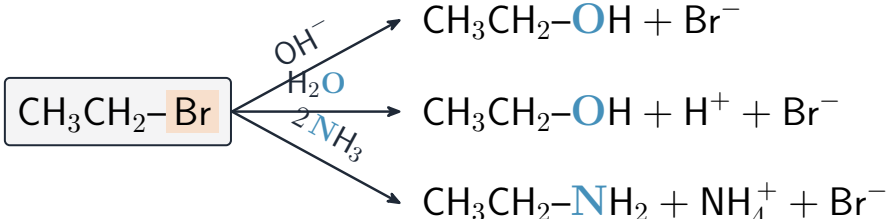
Substitution amount and isolated yield

1. **Given.** 0.0200 mol 1-bromopropane; excess OH^-; invented yield 68.0%.
2. **Ratio.** $RBr + OH^- \rightarrow ROH + Br^-$: maximum alcohol $= 0.0200$ mol.
3. **Yield.** Actual amount $= 0.0200 \times 0.680 = 0.0136$ mol.

Decision

Carbon atoms stay in each molecule; three carbons do not triple the mole ratio.

Three nucleophiles, one substrate



the donor atom replaces Br; the carbon skeleton is unchanged

The donor atom replaces the bromine

Three additions to alkenes

Reagent	Conditions	Product from ethene
Br_2	room temperature	1,2-dibromoethane
HBr	room temperature	bromoethane
H_2O (steam)	H_3PO_4, about 300 °C	ethanol

Use the evidence

Suitable dark comparison: cyclohexene consumes bromine; cyclohexane shows no rapid change. Decolourization alone does not identify ethene.

Map the atoms across the double bond

Halogen or hydrogen halide

Br_2: add Br to each double-bond carbon.

HBr: add H and Br to opposite double-bond carbons.

Hydration

Add H and OH across C=C.

Water is consumed overall; the acid catalyst is regenerated.

Invented single-addition amount calculation

1. **Given.** 0.0120 mol but-2-ene; Br_2 molar mass 159.8 g/mol.
2. **Ratio.** One C=C consumes one Br_2: required amount = 0.0120 mol.
3. **Mass.** $m = nM = 0.0120 \times 159.8 = 1.9176$ g ≈ 1.92 g.

Decision

Name the product from its connectivity: $CH_3CHBrCHBrCH_3$.

Choose a route and name each reaction

1. **Add.** $CH_2{=}CH_2 + HBr \rightarrow CH_3CH_2Br$ under usual ionic addition conditions.
2. **Substitute.** $CH_3CH_2Br + OH^- \rightarrow CH_3CH_2OH + Br^-$ with warm aqueous OH^-.
3. **Check.** Two carbon atoms remain in every organic molecule.

Decision

Related compounds can be connected through different reaction patterns.

Functional groups, oxidation and polymerization

Oxidation

A **functional group** controls characteristic reactions; an alcohol contains OH.

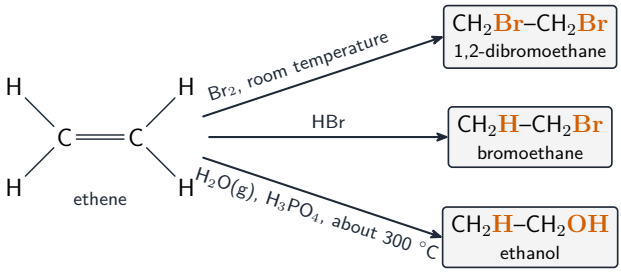
$CH_3CH_2OH + 2[O] \rightarrow CH_3COOH + H_2O$. Excess acidified dichromate under reflux makes a carboxylic acid.

Addition polymerization

Ethene monomers join as $–CH_2–CH_2–$ units; C=C bonds become C–C links.

Suitable initiator, temperature and pressure; no small molecule is lost. Each repeat unit retains two carbons.

Three additions to ethene



C=C becomes C–C; one added atom or group on each carbon

Steam with H_3PO_4 at about 300 °C: ethanol

Exam tips

> Say "colourless", not "clear", for bromine water.

- Every **curly arrow** starts at electrons.
- Show the lone pair and the $\delta+/\delta-$ on C–X.

Check yourself

Try these

Write the reaction of 1-bromopropane with OH^-; name the nucleophile and leaving group.

Write equations for propene with bromine and with steam.

Describe a test to tell cyclohexene from cyclohexane.