Electron-pair sharing reactions

Reactivity 3.4 · SL and AHL

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.

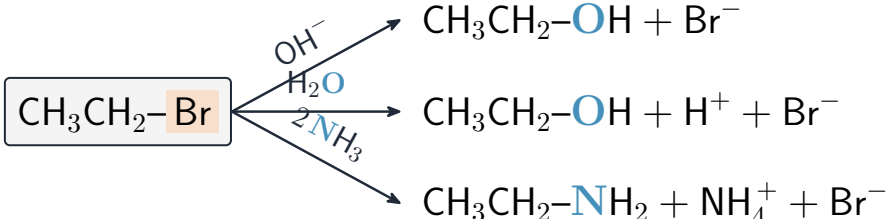
Substitution amount and isolated yield

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.

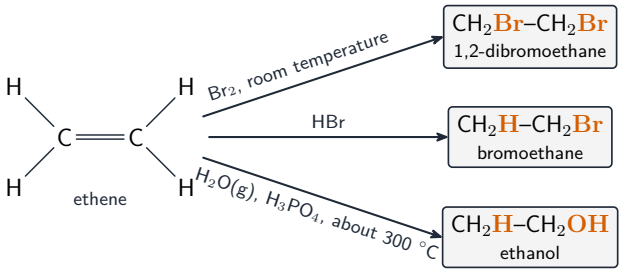
$CH_3CH_2OH + 2[O] \rightarrow CH_3COOH + H_2O$. Excess acidified dichromate under reflux makes a carboxylic acid.

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.

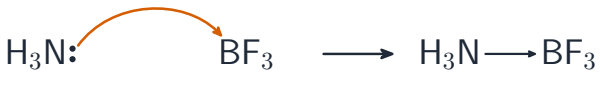
Three additions to ethene



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

Steam with H_3PO_4 at about 300 °C: ethanol

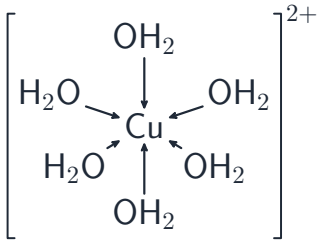
AHL: Lewis acids and bases



Lewis base: electron-pair donor

Lewis acid: B has only 6 outer electrons

the arrow is a coordination bond



six water ligands (Lewis bases) give lone pairs to Cu^{2+} (Lewis acid)

> Nucleophiles are Lewis bases; electrophiles are Lewis acids.

AHL: Lewis roles and the wider definition

$NH_3 + H^+$

N lone pair $\rightarrow$ H^+ gives $NH_4{}^+$.

NH_3 is both a **Lewis base** and a proton-accepting Brønsted–Lowry base.

$NH_3 + BF_3$

N lone pair $\rightarrow$ B gives the adduct.

BF_3 accepts a pair without donating a proton.

AHL: Complex charge and coordination number

1. **Given.** $[Fe(CN)_6]^{4-}$ and $[Co(NH_3)_5Cl]^{2+}$; monodentate ligands.
2. **Iron.** $x + 6(-1) = -4$ gives Fe $+2$; six donor atoms.
3. **Cobalt.** $x + 5(0) - 1 = +2$ gives Co $+3$; six donor atoms.

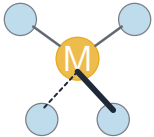
Decision

Complex charge, metal oxidation state and **coordination number** are different counts.

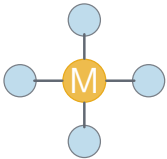
Ligands as Lewis bases



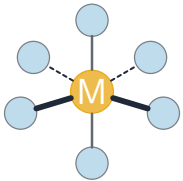
linear
CN 2



tetrahedral
CN 4



square planar
CN 4



octahedral
CN 6

Each **ligand** donates a lone pair

AHL: S_N1 or S_N2?

S_N2 (primary)

One step, attack from the back.

rate $= k[\mathrm{RX}][\mathrm{OH}^-]$; inversion.

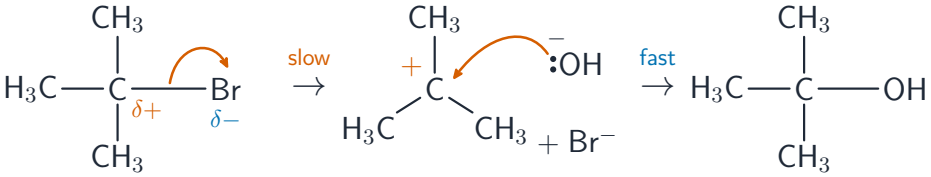
S_N1 (tertiary)

Slow ionization, then fast attack.

rate $= k[\mathrm{RX}]$; planar **carbocation**.

AHL: The S_N1 mechanism

S_N1 (tertiary, e.g. 2-bromo-2-methylpropane): two steps



the C–Br bond breaks: both electrons go to Br

tertiary carbocation: three alkyl groups push electrons in and stabilize it

2-methylpropan-2-ol

Slow ionization, then fast **nucleophile** attack.

AHL: Compare leaving groups under matched conditions

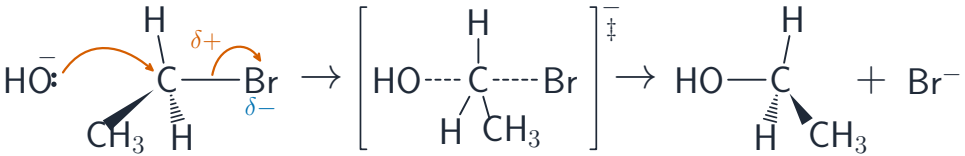
Bond	Bond enthalpy / kJ mol^{-1}	Rate
C–Cl	324	slowest
C–Br	285	middle
C–I	228	fastest

Use the evidence

Iodoalkanes commonly substitute faster: weaker C–I and a better **leaving group**. Polarity alone predicts the wrong trend.

AHL: One transition state or a real intermediate?

S_N2 (primary, e.g. bromoethane): one step



lone pair on O attacks the $\delta+$ C from the side away from Br

transition state: O–C partly formed, C–Br partly broken

ethanol + bromide ion; the three groups have flipped

SN2 has one peak; SN1 has two peaks and a **carbocation** valley.

AHL: Invented kinetic data test the model

1. **Given.** [RBr] 0.020 mol/dm^3; [OH$^-$] 0.100 mol/dm^3; rate 4.0 $\times$ 10^{-5} mol/(dm^3 s).
2. **Model.** Doubling either alone doubles rate: r = k[RBr][OH$^-$].
3. **Calculate.** k = r/([RBr][OH$^-$]) = 0.020 dm^3/(mol s).
4. **Predict.** Doubling both gives fourfold rate = 1.6 $\times$ 10^{-4} mol/(dm^3 s).

Decision

Kinetic order is not copied from overall stoichiometry.

AHL: Inversion is spatial, not a compound identity

Correct description

The reacting carbon undergoes inversion.

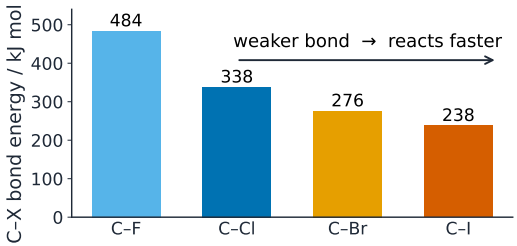
Chiral 2-bromobutane can give butan-2-ol with inverted arrangement.

Incorrect description

The alcohol is not the other enantiomer of the starting **halogenoalkane**.

Different compositions cannot form an enantiomeric pair.

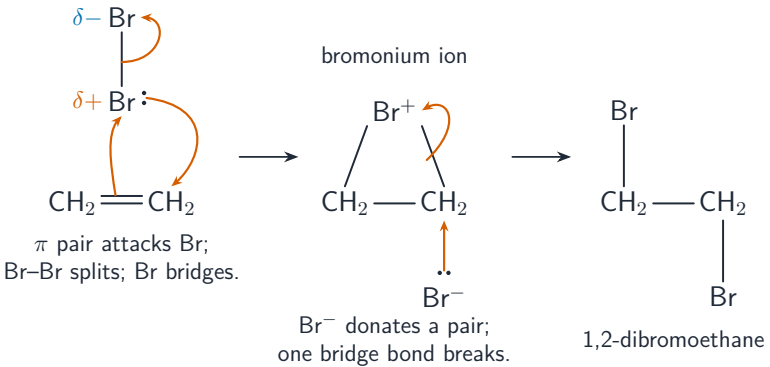
Bond strength and reactivity



rate: RI > RBr > RCl (weaker C–X ⇒ faster)

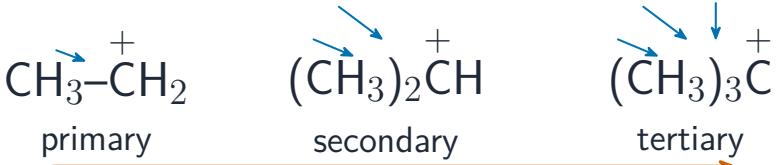
So iodoalkanes react fastest

AHL: Bromine addition uses a bridged intermediate



A bromonium bridge forms, then Br^- opens it to give the dibromide.

AHL: Markovnikov's rule



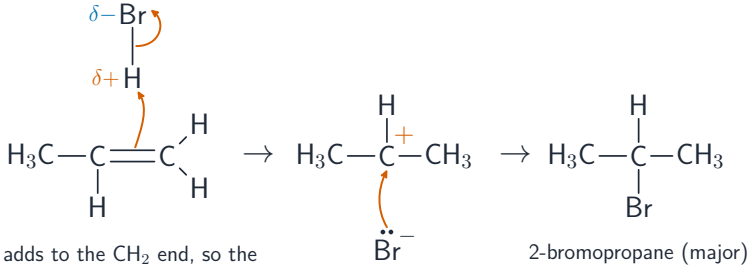
more alkyl groups push more electrons in $\Rightarrow$ more stable

Markovnikov: HBr adds so the *more stable* carbocation forms

> Under usual ionic addition, the route through the more stable **carbocation** predominates.

AHL: HBr addition uses a carbocation

Hydrogen bromide + propene



$H^{\delta+}$ adds to the CH_2 end, so the positive charge lands on the middle C

secondary carbocation: two alkyl groups stabilize it

2-bromopropane (major)

HBr + propene: mainly 2-bromopropane under usual ionic addition.

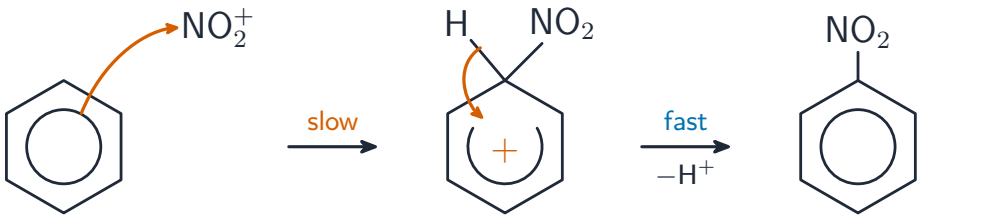
AHL: Hydration includes proton transfer

1. **Protonate.** Ethene π pair $\rightarrow$ H^+ gives $CH_3CH_2{}^+$.
2. **Attack.** H_2O O pair $\rightarrow$ carbon gives $CH_3CH_2OH_2{}^+$.
3. **Restore.** A base removes H^+; the O–H pair returns to O, giving ethanol.

Decision

The oxonium intermediate has three oxygen bonds and positive charge.

AHL: Nitration of benzene



the delocalized ring attacks the electrophile

intermediate: the ring has lost its delocalization

nitrobenzene: the delocalized ring is back

Substitution restores the aromatic system; addition would not restore it.

AHL: Ring attack, then aromaticity restored

1. **Attack.** Ring π pair $\rightarrow E^+$: a C–E bond forms and aromatic delocalization is interrupted.
2. **Lose H^+.** A base removes H^+ while the C–H pair returns into the ring.
3. **Product.** C_6H_5E regains aromaticity; the change is substitution, not addition.

Decision

The intermediate temporarily loses aromaticity; the final ring restores it.

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.
- AHL. **Primary** S_N2, **tertiary** S_N1.
- AHL. Draw the nitration intermediate with a horseshoe and $+$.

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.

AHL. Explain why 2-bromo-2-methylpropane reacts by S_N1.