

Electron-pair sharing reactions

Reactivity 3.4 · SL and AHL

Why does bromoethane react with alkali?

In this unit a whole electron pair moves.

- Bromoethane + warm NaOH(aq) gives ethanol; ethane does nothing.
- The difference is one polar bond.
- This unit: nucleophiles → substitution → electrophiles → addition.

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^+

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 $\text{C}^{\delta+}$.

From the C–Br bond to Br.

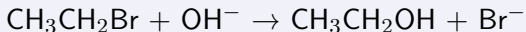
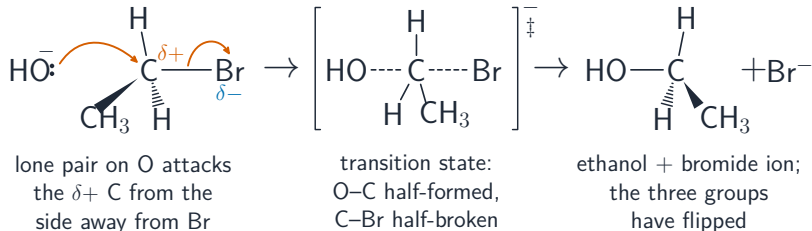
Loses the mark

Arrow starting at a $+$ charge.

Arrow from an atom with no lone pair.

Nucleophilic substitution

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



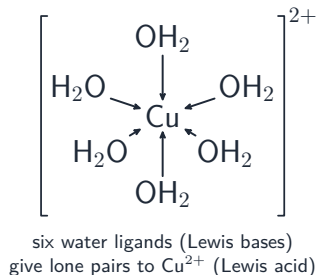
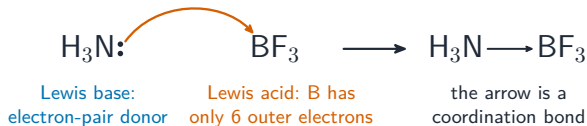
Three additions to alkenes

Reagent	Conditions	Product from ethene
Br ₂	room temperature	1,2-dibromoethane
HBr	room temperature	bromoethane
H ₂ O (steam)	H ₃ PO ₄ , about 300 °C	ethanol

Use the evidence

Bromine water turns from orange to colourless with an alkene.

AHL: Lewis acids and bases



Nucleophiles are Lewis bases; electrophiles are Lewis acids.

AHL: S_N1 or S_N2 ? S_N2 (primary)

One step, attack from the back.

rate = $k[RX][OH^-]$; inversion.

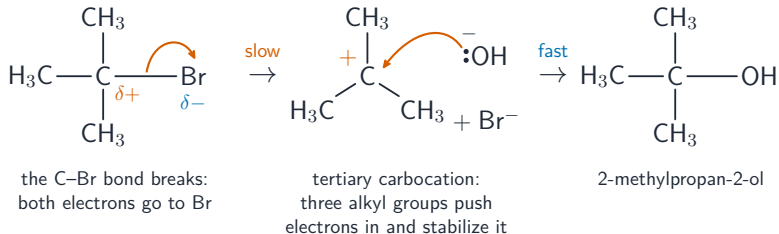
 S_N1 (tertiary)

Slow ionization, then fast attack.

rate = $k[RX]$; planar **carbocation**.

AHL: The S_N1 mechanism

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



Three alkyl groups stabilize the **tertiary carbocation**.

AHL: Solvent and leaving group

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

Use the evidence

The weakest bond breaks most easily.

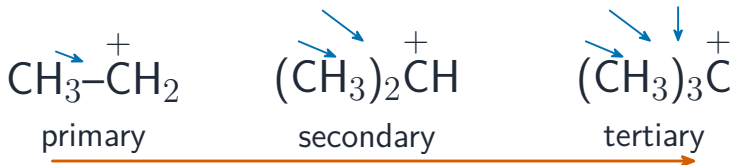
AHL: Bromine adds to ethene

- 1 **Attack.** C=C electrons to $\text{Br}^{\delta+}$; Br-Br pair to the far Br.
- 2 **Intermediate.** A **carbocation** and Br^- form.
- 3 **Finish.** Br^- lone pair attacks C^+ .

Decision

1,2-dibromoethane

AHL: Markovnikov's rule

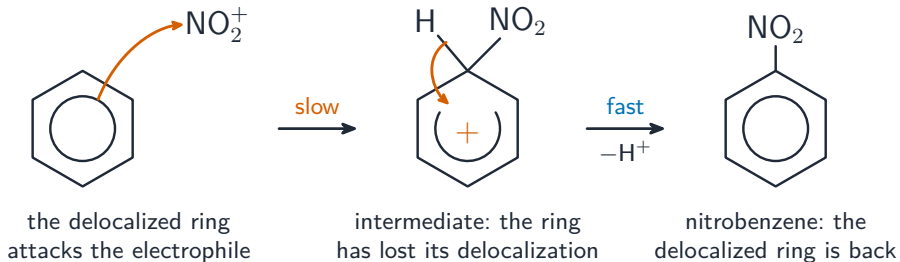


more alkyl groups push more electrons in $\Rightarrow$ more stable

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

The more stable **carbocation** forms faster.

AHL: Nitration of benzene



H_2SO_4 is a catalyst; HSO_4^- takes the H^+ back.

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 $\text{S}_{\text{N}}1$.