9701 CHEMISTRY · TOPICS 15 & 29 · AS + A LEVEL

Halogen Compounds

01 · WHY THEY REACT

The halogen is more electronegative than carbon, so the C–X bond is polar with a **δ+ carbon** — the site every nucleophile attacks.

Rate of hydrolysis is decided by **bond enthalpy, not polarity**: C–I is weakest so iodoalkanes react fastest; C–F is strongest and barely reacts at all.

02 · NUCLEOPHILIC SUBSTITUTION

Reagent	Conditions	Product
NaOH(aq)	warm, aqueous	alcohol
KCN in ethanol	reflux	nitrile (chain +1 C)
excess NH_3 in ethanol	heat, sealed tube	amine
H_2O	slow, warm	alcohol

The cyanide route is the standard way to **lengthen a carbon chain**; the nitrile can then be hydrolysed to an acid or reduced to an amine.

03 · S_N2 MECHANISM

Primary halogenoalkanes. One step.

The nucleophile attacks the δ+ carbon from the side opposite the halogen while the C–X bond breaks. The transition state has five groups round the carbon.

rate = k[RX][Nu^-] — second order overall.
The configuration is inverted.

04 · S_N1 MECHANISM

Tertiary halogenoalkanes. Two steps.

Slow C–X breaks heterolytically → a tertiary carbocation, stabilised by three electron-releasing alkyl groups.
Fast the nucleophile attacks the carbocation.

rate = k[RX] — first order; the nucleophile is absent from the rate equation.
Attack from either face gives a racemic mixture.

05 · CHOOSING BETWEEN THEM

Primary → S_N2 (little steric hindrance, no stable carbocation available). **Tertiary → S_N1** (crowded carbon, but a very stable carbocation). **Secondary** goes by both.

The kinetics tell you which: if the nucleophile appears in the rate equation it is S_N2.

06 · ELIMINATION

Hot ethanolic KOH gives an alkene: OH^- acts as a base, removing H from the carbon next to the C–X, and HX is lost.

The competition is set by the conditions: **aqueous NaOH → substitution**, **ethanolic KOH, hot → elimination**. Tertiary halogenoalkanes eliminate most readily, and unsymmetrical ones can give more than one alkene.

07 · COMPARING HYDROLYSIS RATES

Warm 1-chloro-, 1-bromo- and 1-iodobutane with aqueous $AgNO_3$ in ethanol.

RI → yellow precipitate first
RBr → cream precipitate next
RCl → white precipitate slowest

Ethanol is the common solvent; the silver halide precipitates as soon as the halide ion is released.

08 · EQUATIONS TO KNOW

$CH_3CH_2Br + OH^- \rightarrow CH_3CH_2OH + Br^-$
$CH_3CH_2Br + CN^- \rightarrow CH_3CH_2CN + Br^-$
$CH_3CH_2Br + 2NH_3 \rightarrow CH_3CH_2NH_2 + NH_4Br$
$CH_3CH_2Br + KOH(ethanol) \rightarrow CH_2{=}CH_2 + KBr + H_2O$

09 · USES AND HAZARDS

Halogenoalkanes are versatile intermediates — the –X can be swapped for –OH, –CN, $–NH_2$ and more, which is why they sit at the centre of synthesis routes.

Also used as solvents, refrigerants, anaesthetics and in PTFE. **CFCs** are inert enough to reach the stratosphere, where UV homolysis releases Cl• radicals that catalyse ozone breakdown.

10 · OZONE DEPLETION

$CCl_2F_2 \rightarrow {\bullet}CClF_2 + Cl{\bullet}$ (UV)
$Cl{\bullet} + O_3 \rightarrow ClO{\bullet} + O_2$
$ClO{\bullet} + O \rightarrow Cl{\bullet} + O_2$
overall $O_3 + O \rightarrow 2O_2$

The Cl• is regenerated, so it acts as a catalyst and one radical destroys many ozone molecules.
Replacements: HFCs, which carry no chlorine.

11 · WORKED EXAMPLE — DEDUCE THE MECHANISM

2-bromo-2-methylpropane hydrolyses with rate = k[RBr]. What does that tell you?

The nucleophile is absent from the rate equation, so it takes part **after** the slow step.
Slow step = C–Br breaking → tertiary carbocation.
Mechanism is **S_N1**, and the product from an optically active substrate would be racemic.

12 · MAKING HALOGENOALKANES

From	Reagent
alkane	Cl_2 or Br_2 with UV
alkene	HBr, or Br_2
alcohol	PCl_5, or HCl / $ZnCl_2$

The alcohol route is the cleanest for synthesis; the UV route gives a mixture and is rarely useful.

13 · WORKED EXAMPLE — PREDICT THE PRODUCTS

2-bromobutane is treated with (a) NaOH(aq) and (b) KOH in hot ethanol.

(a) substitution → butan-2-ol

(b) elimination → but-1-ene and but-2-ene, since H can be removed from either neighbouring carbon; but-2-ene is the major product and shows cis–trans isomerism.

CONDITIONS DECIDE THE PRODUCT

NaOH(aq), warm → alcohol (substitution)
KOH in ethanol, hot → alkene (elimination)
KCN in ethanol, reflux → nitrile
Excess NH_3, sealed tube → primary amine

MARKS LOST HERE

— Explaining reactivity by bond polarity; it is **bond enthalpy** that decides the rate.

— Giving aqueous conditions for elimination or ethanolic for substitution.

— Drawing S_N2 in two steps or S_N1 in one.

— Forgetting excess ammonia, without which further substitution gives secondary and tertiary amines.