9701 CHEMISTRY · TOPICS 16 & 30 · AS + A LEVEL

Alcohols and Phenol

01 · PHYSICAL PROPERTIES

The –OH group **hydrogen bonds**, so alcohols boil far higher than alkanes of similar M_r and the short-chain ones mix with water in all proportions.

Solubility falls as the non-polar chain lengthens: the hydrocarbon part cannot hydrogen bond to water.

02 · MAKING ALCOHOLS

Hydration of an alkene — steam, H_3PO_4, 300 °C, 60 atm. Fast, pure product, continuous, but needs crude oil and high energy.

Fermentation — glucose with yeast, 35 °C, no air: $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$. Renewable and low-energy, but slow, batch, and gives dilute impure ethanol needing distillation.

03 · OXIDATION — THE KEY REACTION

Alcohol	Conditions	Product
primary	distil off	aldehyde
primary	reflux, excess	carboxylic acid
secondary	reflux	ketone
tertiary	—	no reaction

Reagent: acidified $K_2Cr_2O_7$, **orange → green**. A tertiary alcohol has no H on the carbon bearing the –OH, so it cannot be oxidised without breaking a C–C bond.

04 · OTHER REACTIONS OF ALCOHOLS

Reagent	Product
Na	alkoxide + H_2 (steady fizzing)
conc. H_2SO_4, 170 °C	alkene (dehydration)
PCl_5 or HCl / $ZnCl_2$	halogenoalkane
carboxylic acid + H_2SO_4	ester (reflux)
combustion	$CO_2 + H_2O$

05 · THE TRI-IODOMETHANE TEST

Warm with I_2 and NaOH(aq). A **pale yellow precipitate of CHI_3** with an antiseptic smell is positive.

Positive for a $CH_3CH(OH)$– group or a CH_3CO– group: ethanol, propan-2-ol, ethanal and all methyl ketones. Propan-1-ol and propanal give nothing.

06 · DISTINGUISHING 1°, 2° AND 3°

Warm each with acidified $K_2Cr_2O_7$.

Orange stays orange → tertiary
Turns green → primary or secondary

Then distil the product and test with Fehling's or Tollens':
Positive → aldehyde → the alcohol was primary
Negative → ketone → it was secondary

07 · PHENOL — STRUCTURE A2

C_6H_5OH: the –OH is bonded straight to the ring. A lone pair on the oxygen overlaps with the delocalised π system, which has two consequences.

1 The O–H bond weakens and the phenoxide ion formed is stabilised by delocalisation, so phenol is **acidic**. **2** The ring becomes electron-rich, so it is **more reactive** to electrophiles than benzene.

08 · ACIDITY COMPARED A2

carboxylic acid > phenol > water > alcohol

Phenol reacts with NaOH to give sodium phenoxide, but **not** with Na_2CO_3 — it is too weak to displace carbonic acid, so no fizzing. A carboxylic acid does fizz, which distinguishes the two.

09 · REACTIONS OF PHENOL A2

$C_6H_5OH + NaOH \rightarrow C_6H_5O^-Na^+ + H_2O$
$2C_6H_5OH + 2Na \rightarrow 2C_6H_5O^-Na^+ + H_2$

$C_6H_5OH + 3Br_2 \rightarrow C_6H_2Br_3OH + 3HBr$
— white precipitate with bromine **water**, no catalyst needed

Nitration with dilute HNO_3 at room temperature also works, where benzene needs concentrated acids at 55 °C.

10 · WORKED EXAMPLE — IDENTIFY THE ALCOHOL

$C_4H_{10}O$ turns dichromate green, gives a positive tri-iodomethane test and no silver mirror with Tollens'. Identify it.

Oxidised → not tertiary
Tri-iodomethane positive → has $CH_3CH(OH)$–
No aldehyde formed → secondary
→ **butan-2-ol**, oxidised to butanone.

11 · EQUATIONS TO KNOW

$C_2H_5OH + [O] \rightarrow CH_3CHO + H_2O$
$CH_3CHO + [O] \rightarrow CH_3COOH$
$2C_2H_5OH + 2Na \rightarrow 2C_2H_5ONa + H_2$
$C_2H_5OH \rightarrow C_2H_4 + H_2O$ (conc. H_2SO_4, 170 °C)
$C_2H_5OH + PCl_5 \rightarrow C_2H_5Cl + HCl + POCl_3$
$C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

12 · DISTINGUISHING THE HYDROXY COMPOUNDS

Test	Alcohol	Phenol	Acid
Na	fizz	fizz	fizz
NaOH	none	reacts	reacts
Na_2CO_3	none	none	**fizz**
Br_2(aq)	none	white ppt	none

Two tests separate all three: carbonate for the acid, bromine water for phenol.

13 · USES

Ethanol — solvent, disinfectant, and a fuel. As a biofuel from fermentation it is close to carbon neutral, since the CO_2 released was absorbed by the crop.

Ethane-1,2-diol — antifreeze and a monomer for polyesters. Phenol — antiseptics, resins and the starting point for aspirin and many dyes.

MARKS LOST HERE

— Giving reflux when the aldehyde is wanted; it must be **distilled off** as it forms.

— Saying a tertiary alcohol resists oxidation "because it is bulky" rather than having no H on the carbon bearing the –OH.

— Claiming phenol fizzes with sodium carbonate.

— Forgetting the colour change of the oxidising agent when asked for observations.