9701 CHEMISTRY · TOPIC 14 · AS LEVEL

Alkanes and Alkenes

01 · ALKANES — STRUCTURE

C_nH_{2n+2}, all σ bonds, sp^3 carbon, tetrahedral at 109.5°. Free rotation about every C–C bond.

Non-polar, so only London forces: boiling point rises with chain length and falls with branching, and they are insoluble in water.

02 · WHY ALKANES ARE UNREACTIVE

C–C and C–H bonds are strong and almost non-polar, so there is no δ+ carbon for a nucleophile to attack and no electron-rich site for an electrophile. Only radicals and combustion get past that.

03 · COMBUSTION

Complete: $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$.
Incomplete: limited oxygen gives CO (toxic, binds haemoglobin) and carbon soot.

Other pollutants: NO_x from the high engine temperature, SO_2 from sulfur impurities, and unburnt hydrocarbons — all removed or reduced by a catalytic converter.

04 · FREE-RADICAL SUBSTITUTION

$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$, UV light

Initiation $Cl_2 \rightarrow 2Cl\bullet$ (homolysis by UV)
Propagation $Cl\bullet + CH_4 \rightarrow \bullet CH_3 + HCl$
$\bullet CH_3 + Cl_2 \rightarrow CH_3Cl + Cl\bullet$
Termination $Cl\bullet + \bullet CH_3 \rightarrow CH_3Cl$
$2\bullet CH_3 \rightarrow C_2H_6$

Poor for synthesis: further substitution gives CH_2Cl_2, $CHCl_3$ and CCl_4, and termination gives a mixture.

05 · CRACKING

Long alkanes are broken into shorter, more useful ones plus an alkene.

Catalytic — zeolite, ~450 °C, moderate pressure; gives branched alkanes and arenes for fuels.
Thermal — higher temperature and pressure; gives more alkenes for polymers.

06 · ALKENES — STRUCTURE

C_nH_{2n}. The C=C is one σ plus one π bond; each carbon is sp^2, trigonal planar at 120°.

The π electrons sit above and below the plane, exposed and easily attacked — so alkenes react with **electrophiles**. The π bond also blocks rotation, giving cis–trans isomerism.

07 · ADDITION REACTIONS OF ALKENES

Reagent	Conditions	Product
H_2	Ni, 150 °C	alkane
Br_2	room temp	dibromoalkane
HBr	room temp	bromoalkane
steam	H_3PO_4, 300 °C, 60 atm	alcohol
cold dilute $KMnO_4$	—	diol

Test for a C=C: bromine water is decolourised from orange to colourless at room temperature.

08 · ELECTROPHILIC ADDITION MECHANISM

1 The π electrons attack the δ+ end of HBr (or induce a dipole in Br_2).
2 The H–Br bond breaks heterolytically, giving Br^- and a **carbocation**.
3 Br^- attacks the carbocation to give the product.

Curly arrow 1 from the C=C to the H; arrow 2 from the H–Br bond to Br; arrow 3 from the lone pair on Br^- to the positive carbon.

09 · MARKOVNIKOV'S RULE

The hydrogen adds to the carbon that already carries **more** hydrogens, because that route goes through the more stable carbocation.

Stability order **tertiary > secondary > primary**: alkyl groups are electron-releasing and spread the positive charge. So propene + HBr gives mainly 2-bromopropane.

10 · OXIDATION OF ALKENES

Cold dilute acidified $KMnO_4$ → diol; purple decolourises.

Hot concentrated acidified $KMnO_4$ → the C=C is cleaved. A terminal $=CH_2$ gives CO_2; $=CHR$ gives a carboxylic acid; $=CR_2$ gives a ketone — which lets you deduce where the double bond was.

11 · WORKED EXAMPLE — LOCATE THE C=C

An alkene C_5H_{10} gives propanone and ethanoic acid on vigorous oxidation. Identify it.

Propanone ← $(CH_3)_2C=$
Ethanoic acid ← $=CHCH_3$
Join the fragments: **$(CH_3)_2C=CHCH_3$**, 2-methylbut-2-ene.

12 · ADDITION POLYMERISATION

$n\,CH_2=CH_2 \rightarrow -(CH_2–CH_2)_n-$. Draw the repeat unit in brackets with bonds through them and n outside.

Poly(alkenes) are inert and non-biodegradable, so disposal means landfill, incineration with energy recovery, or recycling. PVC releases HCl on burning.

13 · WORKED EXAMPLE — MARKOVNIKOV

Predict the major product of but-1-ene + HBr.

H can add to C1 or C2.
Adding to C1 gives a **secondary** carbocation on C2.
Adding to C2 gives a primary carbocation on C1.

The secondary cation is the more stable, so the major product is **2-bromobutane**; 1-bromobutane forms in small amounts.

14 · ALKANES AGAINST ALKENES

	Alkane	Alkene
bonding	all σ	σ + π
attacked by	radicals	electrophiles
typical reaction	substitution	addition
Br_2(aq)	no change	decolourised
$KMnO_4$	no change	decolourised

MARKS LOST HERE

— Leaving out a termination step, or writing initiation without UV.

— Forgetting the induced dipole when Br_2 attacks a C=C.

— Predicting the minor product by ignoring carbocation stability.

— Drawing a polymer repeat unit still containing a double bond.

9701 CHEMISTRY · TOPIC 28 · A LEVEL

Arenes — Benzene Chemistry

15 · STRUCTURE OF BENZENE

C_6H_6, planar, regular hexagon, all bond angles 120°, every carbon sp^2. Each carbon's remaining p orbital overlaps sideways into a **delocalised π system** above and below the ring.

Evidence: all six C–C bonds are the same length, between a single and a double bond; and the enthalpy of hydrogenation is about 150 kJ mol^{-1} less exothermic than three times that of cyclohexene, so benzene is more stable than the Kekulé structure predicts.

16 · WHY SUBSTITUTION, NOT ADDITION

Addition would destroy the delocalised system and its extra stability. Substitution keeps the ring intact, so benzene undergoes **electrophilic substitution** — and it needs stronger conditions than an alkene because the π electrons are spread out and less available.

17 · THE FOUR SUBSTITUTIONS

Reaction	Reagents	Electrophile
nitration	conc. HNO_3 / conc. H_2SO_4, 55 °C	NO_2^+
halogenation	Cl_2 or Br_2 with $AlCl_3$ / $FeBr_3$	Cl^+ or Br^+
Friedel–Crafts alkylation	RCl / $AlCl_3$	R^+
Friedel–Crafts acylation	RCOCl / $AlCl_3$	RCO^+

$AlCl_3$ is a **halogen carrier** — it polarises the reagent to generate the electrophile and is regenerated at the end.

18 · THE MECHANISM IN THREE STEPS

1 · Generate the electrophile
$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$

2 · Attack — two π electrons from the ring form a bond to the electrophile, giving an unstable intermediate with a broken delocalised system and a positive charge.

3 · Restore aromaticity — H^+ is lost from that carbon and the ring's delocalisation is re-formed.

19 · SIDE-CHAIN REACTIONS

UV light favours free-radical substitution in the side chain: methylbenzene + Cl_2 → chloromethylbenzene.

$AlCl_3$ and no light favours substitution in the ring instead. The condition decides the site.

Hot alkaline $KMnO_4$ oxidises any alkyl side chain all the way to –COOH: methylbenzene → benzoic acid.

20 · DIRECTING EFFECTS

Group	Effect	Directs to
–OH, $–NH_2$, $–CH_3$	activating	2- and 4-
$–NO_2$, –COOH, –CHO	deactivating	3-

Electron-releasing groups push charge into the ring, making it more reactive than benzene; electron-withdrawing groups do the reverse. Phenol reacts with bromine water alone, without a catalyst.

21 · WORKED EXAMPLE — PLAN A SYNTHESIS

Make 3-nitrobenzoic acid from methylbenzene.

Nitrate first and you get the 2- and 4- isomers, since $–CH_3$ directs there.

So **oxidise first**:
1 · hot alkaline $KMnO_4$, then H^+ → benzoic acid
2 · conc. HNO_3 / conc. H_2SO_4, 55 °C → the –COOH group directs to the 3- position.

22 · COMPARING BENZENE WITH ALKENES

	Benzene	Alkene
π electrons	delocalised	localised
Br_2(aq)	no reaction	decolourised
typical reaction	substitution	addition

This test distinguishes them in seconds and is the standard exam question.

23 · EQUATIONS TO KNOW

$C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$
$C_6H_6 + Br_2 \rightarrow C_6H_5Br + HBr$
$C_6H_6 + CH_3Cl \rightarrow C_6H_5CH_3 + HCl$
$C_6H_6 + CH_3COCl \rightarrow C_6H_5COCH_3 + HCl$

$C_6H_5CH_3 + 3[O] \rightarrow C_6H_5COOH + H_2O$
$C_6H_5NO_2 + 6[H] \rightarrow C_6H_5NH_2 + 2H_2O$

24 · BENZENE, METHYLBENZENE, PHENOL

Reactivity to electrophiles rises in the order **benzene < methylbenzene < phenol**.

$–CH_3$ releases electrons inductively; –OH donates a whole lone pair into the delocalised system. The more electron-rich the ring, the more readily it attracts an electrophile — which is why phenol needs only bromine water while benzene needs a halogen carrier.

25 · WORKED EXAMPLE — IDENTIFY THE PRODUCT

Methylbenzene is refluxed with Cl_2 in the presence of $AlCl_3$, then the product is treated with hot alkaline $KMnO_4$.

$AlCl_3$, no UV → ring substitution, and $–CH_3$ directs to 2- and 4- → 4-chloromethylbenzene
Hot alkaline $KMnO_4$ → the side chain is oxidised → **4-chlorobenzoic acid**

26 · WHY THE CONDITIONS MATTER

Nitration above about 60 °C gives dinitro products; below 50 °C the reaction is impractically slow. The quoted 55 °C is the working compromise.

Friedel–Crafts must be run in dry conditions, since $AlCl_3$ is hydrolysed by water and the catalyst is destroyed.

MARKS LOST HERE

— Drawing benzene with three localised double bonds when asked about delocalisation.

— Omitting the step that regenerates the aromatic ring by losing H^+.

— Saying benzene decolourises bromine water.

— Nitrating before oxidising when the directing effects demand the reverse.