Addition
Substitution
Elimination

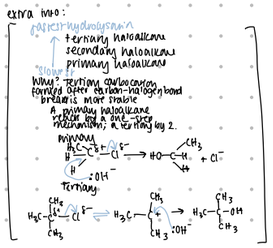
Mechanism — equation
Synthetic route
Reversible

✕ Do. mechanisms

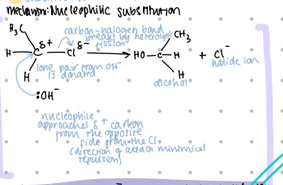
Haloalkanes
−F, −Cl, −Br, −I

extra info:
- primary haloalkane
- secondary haloalkane
- tertiary haloalkane

Why? Tertiary carbocation formed after carbon–halogen bond breaks is most stable
A secondary haloalkane reacting via a one-step mechanism; a tertiary by 2.



substitution reaction
mechanism: nucleophilic substitution



haloalkane + OH^- ⟶ alcohol + halide ion

Hydrolysis
Hydrolysis: a chemical reaction in which water or an aqueous solution of a hydroxide that causes one compound to split into 2 products

the halogen atom is replaced by an –OH group

Rate of hydrolysis depends on the strength of the carbon–halogen bond:
- C–F — strongest — unreactive
- C–Cl
- C–Br
- C–I — weakest — fastest reaction

Hydrolysis of haloalkanes more reactive than chloroalkanes as less energy required to break C–X bond
decreasing bond enthalpy

substitution reaction
Alcohols react with hydrogen halides

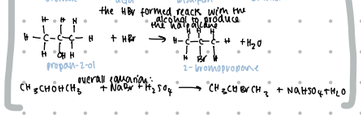
A alcohol is heated under reflux with sulfuric acid & a sodium halide: the hydrogen halide is formed in situ

① sodium halide + sulfuric acid → sodium bisulfate + hydrogen halide
$NaX_{(aq)} + H_2SO_{4(aq)} \rightarrow NaHSO_{4(aq)} + HX_{(g)}$

② alcohol + hydrogen halide → haloalkane + water

overall: alcohol + sodium halide + sulfuric acid → haloalkane + sodium + water bisulfate

e.g.
$NaBr_{(s)} + H_2SO_{4(aq)} \rightarrow NaHSO_{4(aq)} + HBr_{(aq)}$
sodium bromide · sulfuric acid · sodium bisulfate · hydrogen bromide



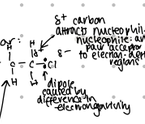
$CH_3CH(OH)CH_3 + NaBr + H_2SO_4 \rightarrow CH_3CH(Br)CH_3 + NaHSO_4 + H_2O$

substitution reaction
NaOH (aq)
Reaction is very slow at room temp so the mixture is heated under reflux for a good yield of alcohol

haloalkane + NaOH(aq) → alcohol + NaX(aq)

– OH replaces the halide

Hydrolysis
can be classified as primary, secondary or tertiary just like alcohols



polar: C–Cl

only Cl & Br reactive enough
F – too reactive
I – not reactive enough

Halogen/UV light (sunlight)
e.g. $CH_{4(g)}$ + Br_2 (l) —UV→ $CH_3Br_{(g)} + HBr_{(g)}$
bromomethane

alkane + halogen —UV→ haloalkane + hydrogen halide
Cl or Br
high-energy UV radiation provides the activation energy

radical substitution reaction
mechanism: radical substitution

① Initiation
reaction is caused when the covalent bond in Br_2 is broken by homolytic fission
$Br–Br \xrightarrow{UV} Br\cdot + Br\cdot$
bromine radicals

② Propagation
2 propagation steps; a chain reaction
bromine radical · methyl radical
$CH_4 + Br\cdot \rightarrow \cdot CH_3 + HBr$
methane · A Bromine radical reacts with a C–H bond in methane · hydrogen bromide
methyl radical · bromine molecule
$\cdot CH_3 + Br_2 \rightarrow CH_3Br + Br\cdot$
organic product – bromomethane · new bromine radical
diffrent bromine radicals

③ Termination
2 radicals collide → molecule with all electrons paired
all possible
$\cdot Br + \cdot Br \rightarrow Br_2$
$\cdot CH_3 + \cdot CH_3 \rightarrow C_2H_6$
$\cdot CH_3 + \cdot Br \rightarrow CH_3Br$

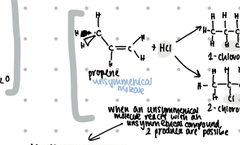
Limitations of radical substitution in organic synthesis:
- Further substitution
  e.g. CH_4 reactions could be multiple times (more substituted)
- Substitution at different positions

Addition reaction
Alkenes with gaseous hydrogen halides, room temp

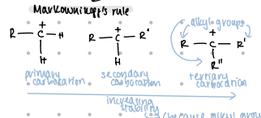
- 1 alkene molecule e.g. ethene, gaseous and dry
- 1 HX molecule, gaseous and dry
- Neither dissolved in solvent

Alkenes also react with conc. HCl or HBr after fractions of hydrogen halides in water

alkene + hydrogen halide —RTP→ haloalkane



When an unsymmetrical alkene reacts with an unsymmetrical reagent, 2 products are possible

Markovnikoff's rule


addition of a hydrogen halide to an unsymmetrical alkene results in the major product via the more stable carbocation

∴ 2-chloropropane is the major product

Addition reaction
Rapid addition reaction

case of bromine can be used to test for unsaturation

(i.e. a C=C bond preserves orange bromine water decolourises)

Chlorine or bromine at room temp

alkene + Cl_2/Br_2 —RTP→ chloro/bromo alkane

all C=C bonds undergo "addition" reactions; added across the double bond

Addition reaction
Hydrogenation with a nickel catalyst, 423 K

alkene + H_2 —Ni, 423K→ respective alkane

Alkene heated with hydrogen in presence of finely divided nickel catalyst at 423 K

all C=C bonds undergo to form

Alkanes
C_nH_{2n+2}
aliphatic alkanes

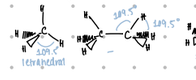
bonding in alkanes:
- only carbon & hydrogen atoms joined by σ-bonds
- 2 electrons "shared" between atoms (single covalent)

C – C (single covalent)

σ-bonds are all axes around which atoms can rotate freely

result of the overlap of 2 orbitals, one from each bonding atom

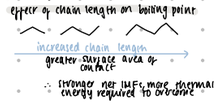
Shapes of alkanes



gas	CH_4 — C_4H_{10}	lowest
petrol	C_5H_{12} — C_9H_{20}	boiling points
kerosene	$C_{10}H_{22}$ — $C_{16}H_{34}$	
diesel	$C_{17}H_{26}$ — $C_{20}H_{42}$	highest

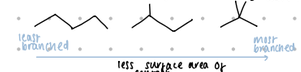
Separated using fractional distillation; relies on boiling points ~400°C

effect of chain length on boiling point



∴ stronger net IMFs; more thermal energy required to overcome

effect of branching on boiling point



∴ weaker net IMFs; less thermal energy required to overcome

Combustion
- Most oxygen — complete — alkane + plentiful oxygen —heat→ carbon dioxide + water (colourless, odourless gas)
- Incomplete
  - e.g. in a closed space, car engine, inadequately ventilated areas (toxic, colourless, odourless gas)
  - alkane + limited oxygen —heat→ carbon monoxide + water (colourless liquid)
  - alkane + even more limited oxygen —heat→ carbon + water (least oxygen; soot (black solid))

Reactivity
- C–C & C–H σ-bonds are strong
- C–C bonds non-polar
- exceptionally strong & C & H similar; C–H bond non-polar

∴ unreactive

Alkenes
C_nH_{2n}
unsaturated hydrocarbons

if ≥1 C=C → polyunsaturated

aliphatic alkenes with 1 C=C bond

Reactivity
- π-electrons are more exposed than σ-electrons
- readily undergo to electrons undergo addition reaction easily

∴ More reactive than alkanes

the nature of the C=C bond
- π-bond — locks the 2 carbon atoms in position, prevents rotation
- σ-bond
- 120° — trigonal planar — C atoms & all atoms in same plane, number can't be increased
- π-overlap: overlap above & below the plane of carbon atoms

a π-bond is not as strong as the σ-bond, since there is some repulsion

Stereoisomerism
same structural formula, different arrangement of atoms in space

E/Z isomerism → cis–trans isomerism
occurs in compounds with a C=C bond

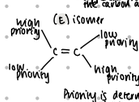
special case of E/Z isomerism: one of the attached groups on each carbon atom is the same

molecule must have
- a C=C bond
- different group attached to the carbon atoms of the C=C bond

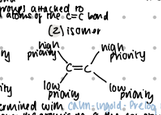
CIS = Z
trans = E

e.g. trans-but-2-ene

(E) isomer



(Z) isomer



Priority is determined with atom: unpaired electrons nomenclature
? The higher the atomic no. of the 1st atom, the higher the priority
• Isotopes ✓ equal

Addition reaction
Alkenes irregularly take part in addition reactions to form saturated compounds (high C=C electron density attracts electrophiles)

Mechanism: Electrophilic addition
e.g. but-2-ene & HBr

electrophile: an electron pair acceptor attracted to regions of electron density (electron-abundant regions)

can also happen with an unlisted halide e.g. in bromine Br_2, the TL-electron induce polarisation in Br_2 & the mechanism occurs.

Addition reaction
Hydration with steam

in the presence of a phosphoric acid (conc. sulfuric acid) catalyst

alkene + steam —H_3PO_4→ alcohol

e.g. ethene + $H_2O_{(g)}$ → propan-1-ol + propan-2-ol

mixture of products

Alcohols
–OH functional group (hydroxyl)

Physical properties
- less volatile than alkanes & higher melting point
- more soluble

Why?
The –OH bond makes the molecule polar → greater van der Waals forces (stronger) → enables formation of hydrogen bonds with water

chain length increases → solubility decreases (the "hydrocarbon" part has less effect on the overall molecule)

In liquid state, intermolecular forces in addition to bonds hold the alcohol molecules together. overcoming these requires more energy than overcoming temporary dipole–induced dipole interactions

chain length increases → intermolecular forces increase → boiling points closer to respective alkanes

- Methanol: chemical feedstock, fuel (petrol additive)
- Ethanol: drinks & fuel; solvent & feedstock

Combustion
complete combustion of ethanol:
$C_2H_5OH_{(l)} + 3O_{2(g)} \xrightarrow{\text{heat}} 2CO_{2(g)} + 3H_2O_{(l)}$
ΔH = the increasingly less exothermic

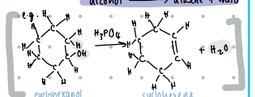
as carbon chain increases, less oxygen is required per mole of alcohol

alcohol + plentiful oxygen —heat→ carbon dioxide + water

Elimination reaction
Dehydration of alcohols in the presence of an acid catalyst

e.g. H_3PO_4 conc. (l)

alcohol —H_3PO_4→ alkene + water



dehydration: water removed from a molecule in which the original molecule is regenerated from that starting material

Addition reaction
Hydration with steam

in the presence of a phosphoric acid (conc. sulfuric acid) catalyst

alkene + steam —H_3PO_4→ alcohol

e.g. ethene + $H_2O_{(g)}$ → propan-1-ol + propan-2-ol

mixture of products

Polymerisation in Alkenes
Polymers – large molecules formed from thousands of monomers joined in repeat units

monomers —high temp., high pressure→ polymer

Sustainability
Environmental concerns

Solutions (biomaterials)

Biodegradable polymers
- Made of starch or cellulose
- Broken down by microorganisms into water, CO_2 & biological components
- Compostable polymers: completely biodegraded into water, CO_2 & biomass (called PLA)

Photodegradable polymers
- contain bonds weakened by light → faster degradation

Unsaturated alkene molecules undergo addition polymerisation to produce long saturated chains

Industrial polymerisation happens at high temp & pressure using catalysts
- Addition polymers have high Mrs
- Symmetric polymers are named after the monomer that reacts, prefixed by "poly"

e.g. ethene → poly(ethene)
used in bags, boxes, toys etc

monomer → repeat unit

large no. of repeats

e.g.
- poly(chloroethene) / PVC / poly(vinyl chloride) — used in pipes, insulation, flooring, bottles
- poly(propene) — ropes, guttering, ropes
- poly(styrene) / poly(phenylethene) — packaging material, food trays, foam — thermal insulating properties
- poly(tetrafluoroethene) / PTFE (teflon) — non-stick coatings, clothing, wires, cable insulation

Issues: Non-Biodegradable
- lack of reactivity means disposal is challenging
- kill marine life

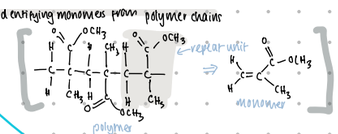
Recycling
- Reduces landfill waste
- conserves finite fossil fuels
- cons: Polymers must be sorted (produces impurities if mixed) & cleaned, time / resources

PVC recycling
- When burnt, hazardous: releases hydrogen chloride (corrosive gas) & toxic dioxins

Using waste polymers as fuel
- Burnt to release energy
- Unlike fossil fuels, they are derived from recyclable waste and are carbon neutral
- Can be incinerated to use as fuel

Feedstock recycling
- Chemicals of chemical processes that produce polymers, glass or oil from can undergo unsorted & unwashed polymers
- produce regenerate waste products from crude oil in refineries
- can be used as raw materials for new polymers

Identifying monomers from polymer chains



Alcohols
–OH functional group (hydroxyl)

Physical properties
- less volatile than alkanes & higher melting point
- more soluble

Why?
The –OH bond makes the molecule polar → greater van der Waals forces (stronger) → enables formation of hydrogen bonds with water

chain length increases → solubility decreases (the "hydrocarbon" part has less effect on the overall molecule)

In liquid state, intermolecular forces in addition to bonds hold the alcohol molecules together. overcoming these requires more energy than overcoming temporary dipole–induced dipole interactions

chain length increases → intermolecular forces increase → boiling points closer to respective alkanes

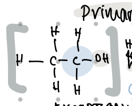
- Methanol: chemical feedstock, fuel (petrol additive)
- Ethanol: drinks & fuel; solvent & feedstock

Combustion
complete combustion of ethanol:
$C_2H_5OH_{(l)} + 3O_{2(g)} \xrightarrow{\text{heat}} 2CO_{2(g)} + 3H_2O_{(l)}$
ΔH = the increasingly less exothermic

as carbon chain increases, less oxygen is required per mole of alcohol

alcohol + plentiful oxygen —heat→ carbon dioxide + water

Primary

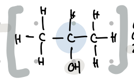


Hydroxyl group is attached to a carbon atom with 2 hydrogens & 1 alkyl group

C + 1 alkyl group

EXCEPTION: Methanol

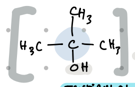
Secondary



Hydroxyl group is attached to a carbon atom with 1 hydrogen & 2 alkyl groups

2 alkyl groups

Tertiary



Hydroxyl group is attached to no hydrogens & 3 alkyl groups

3 alkyl groups

Tertiary alcohols cannot be oxidised (not enough bonds!)

acidified dichromate stays orange

Oxidation

oxidising mixture:

Acidified Potassium dichromate (VI)

$K_2Cr_2O_7 / H_2SO_4$ (↑ dilute sulfuric acid)

If oxidised: orange to green colour change of solution (reduction)

orange: $Cr_2O_7^{2-}$ dichromate (VI) ions

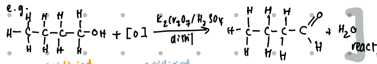
green: Cr^{3+} chromium (III) ions

1st reaction – gentle heating

primary alcohol + [O] $\xrightarrow[\text{distil}]{K_2Cr_2O_7/H_2SO_4}$ aldehyde + water

(oxidising agent)

e.g.

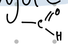


acidified dichromate (orange) – acidified potassium dichromate (VI) – acidified dichromate (green)

butan-1-ol → butanal

distillation of the aldehyde from the reaction mixture as it forms to prevent further reaction

Aldehyde



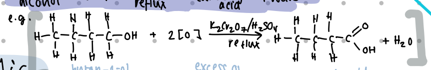
2nd reaction (if left to continue)

strong heating; excess of [O] to ensure all of the alcohol is oxidised

reflux ensures any aldehyde also undergoes oxidation to become a carboxylic acid

primary alcohol + 2[O] $\xrightarrow[\text{reflux}]{K_2Cr_2O_7/H_2SO_4}$ carboxylic acid + water

e.g.

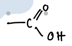


butan-1-ol → butanoic acid

excess of acidified potassium dichromate (VI) ← ensures all of solution is oxidised

Carboxylic acid

weak acids



Alcohol $\xrightarrow[\text{distil}]{\text{oxidation}}$ Aldehyde $\xrightarrow{\text{oxidation}}$ Carboxylic acid

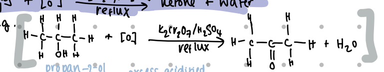
Alcohol → Carboxylic acid: reflux (double oxidation)

Secondary alcohols

reflux ensures the reaction goes to completion

secondary alcohol + [O] $\xrightarrow[\text{reflux}]{K_2Cr_2O_7/H_2SO_4}$ ketone + water

e.g.

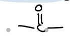
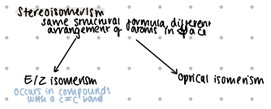


propan-2-ol → propanone

excess acidified potassium dichromate (VI) ← ensures all of solution is oxidised

Ketone

(it is not possible to further oxidise)



isomerism mindmap