3.3.6 Organic Analysis

Mass Spectrometry
When organic molecules are passed through mass spectrometer, it detects both the whole molecules + fragments of the molecule.

Mass spectrum of butane

C_4H_{10} = 58

peak w/ highest mass/charge ratio is usually due to the original molecule that hasn't fragmented (called the molecular)

As the charge on molecular ion is +1, the mass/charge ratio is equal to Mr

Molecular ion: the molecule w/ one e^- knocked off. It's both an ion & free radical
$M \rightarrow [M]^+ + e^-$

High resolution mass spectrometry
- can be used to determine the Mr of a compound from the accurate mass of the molecular ion
- it can measure the mass to 5dp so can distinguish between compounds that appear to have similar Mr (to whole number)
- Accurate masses of atoms:
  - H: 1.0078
  - C: 12.0000
  - O: 15.9949
  - N: 14.0031

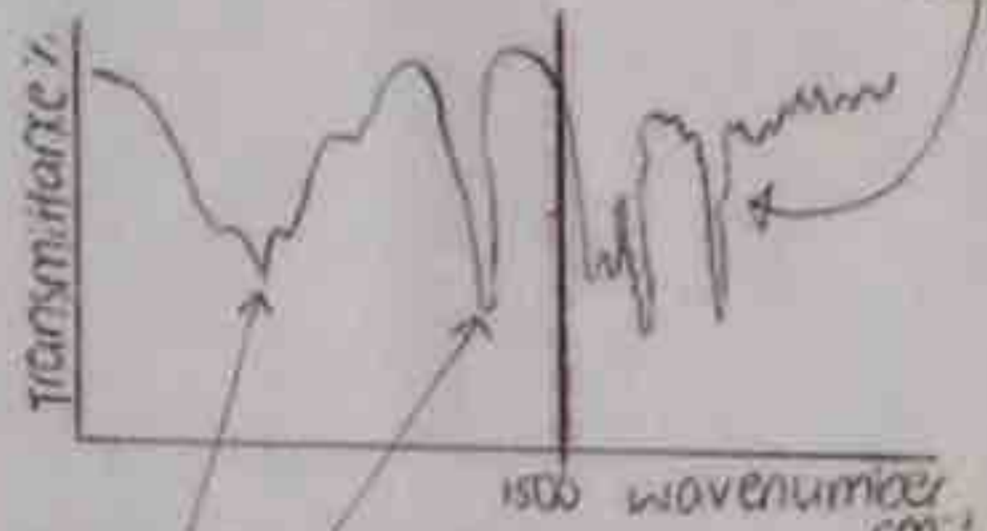
→ Example: the following Mr's are all roughly 60, but a more precise Mr can give the molecular formula:
- Mr = 60.02112 = $C_2H_4O_2$
- Mr = 60.05751 molecular formula = C_3H_8O
- Mr = 60.03235 = CH_4N_2O

Example: a compound has accurate Mr of 46.0417. It is thought to be either CH_3CH_2OH or $H_2NCH_2NH_2$. Calc. Mr of each compound to 4dp to work out which one it is

$CH_3CH_2OH = (12.0000 \times 2) + 15.9949 + (1.0078 \times 6) = 46.0417$

$H_2NCH_2NH_2 = 12.0000 + (14.0031 \times 2) + (1.0078 \times 6) = 46.0530$

Infrared Spectrometry
- bonds in a molecule absorb infrared radiation at characteristic wavenumbers/frequencies
- enables scientists to identify groups of atoms in a molecule & the environment surrounding them. eg analysis of an infrared spectrum may indicate presence of C=O bond & will also indicate if it's part of a -CHO group in an aldehyde or part of a -COOH group in a CA.



peaks due to energy absorption from a particular frequency of infrared radiation which excites bonds in the molecules to a higher state of vibration (either stretching or bending)

below 1500 cm^{-1} - fingerprinting
- fingerprint region: complex & caused by complicated vibrations of the whole molecule
- → unique for every compound
- use IR table to deduce presence/absence of bonds

always quote wave no. range from data sheet

eg. C=O: 1680-1750 cm^{-1}
O-H (acid): 2500-3000 cm^{-1} → O-H absorptions tend to be broad

- A computer can compare IR spectra against a database of pure compounds to identify the compound.
- NOTE: extra peaks can indicate that the compound is not pure
- The absorption of IR radiation in this type of spectrometry is the same absorption that bonds in CO_2, methane and water vapour absorb (in the atmosphere), maybe causing global warming

Testing for functional groups (test tube reactions):
- alkene: add Bromine water, orange colour decolourises
- aldehyde: add Fehling's solution, +ve result: blue solution to red PPT
- aldehyde: Tollen's reagent, +ve result: silver mirror PPT forms
- carboxylic acid: add Na_2CO_3 or $NaHCO_3$, +ve: effervescence due to CO_2 production
- 1° and 2° alcohol and aldehyde: add acidified potassium dichromate (VI), +ve result: orange to green colour
- chloroalkanes: warm w/ silver nitrate (AgNO3): slow formation of AgCl white precipitate

3.3.5 Alcohols
- relatively low volatility & high bpts due to ability to form H bonds between alcohol molecules

Example: propane-1,2,3-triol: H_2C-OH, HC-OH, H_2C-OH

1° alcohol: R-CH₂-OH; 2°: R_2CH-OH; 3°: R_3C-OH

Formation of ethanol
1) Fermentation

$C_6H_{12}O_6 \rightarrow 2CH_3CH_2OH + 2CO_2$

conditions: yeast, anaerobic conditions, temp 30-40°C b/c of enzymes, in a neutral aqueous solution
- presence of air would result in extra reactions eg oxidation of ethanol to ethanoic acid. optimum enzyme temp: 35°C. If too low: reaction slow, if too high enzymes denature
- +ves of fermentation: sugar: renewable resource; production uses low level tech/cheap equipment; uses gentler temps & atmospheric pressures
- -ves: batch process: slow & gives high production costs; ethanol made is not pure & needs purifying by fractional distillation; depletes land used for growing crops (= higher food costs)

heating under reflux prevents reagents from escaping, allows the reaction to run to completion

ethanol as a biofuel
- biofuel: any fuel made from living organisms or their waste, i.e. made from crops
- ethanol produced via fermentation & then fractional distillation = biofuel
- classed as carbon-neutral - no net annual emissions of CO_2 into atmosphere
- the idea: CO_2 given off when biofuel is burnt would have been extracted from air by photosynthesis when plant grew ∴ no net emissions. H/e, this doesn't take into account any energy needed to irrigate plants, fractionally distil ethanol from reaction mixture or process the fuel. If the energy for this process comes from fossil fuels, then the ethanol produced is not carbon neutral

Removal of CO_2 by photosynthesis

$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$

production of CO_2 by fermentation & combustion

$C_6H_{12}O_6 \rightarrow 2CH_3CH_2OH + 2CO_2$

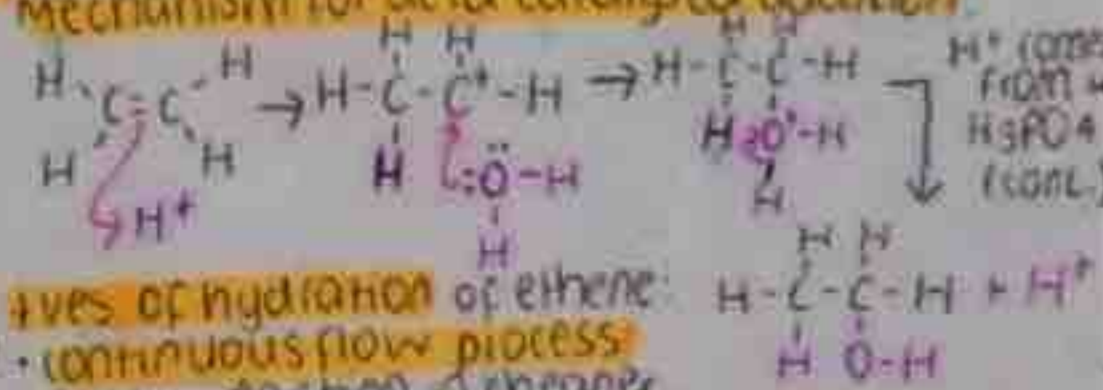
$2CH_3CH_2OH + 6O_2 \rightarrow 4CO_2 + 6H_2O$

Overall, for every 6 molecules of CO_2 absorbed, 6 CO_2 molecules are released so no net emissions of CO_2 into atmosphere

2) Hydration of ethene
- Reagent: ethene (from cracking of fractions from distilled crude oil)
- Type of reaction: hydration/addition (addition of water to a molecule)
- conditions:
  - high temp 300°C
  - high pressure 70atm
  - strong acidic catalyst of conc. H_3PO_4 absorbed on a solid silica surface

$CH_2{=}CH_{2(g)} + H_2O_{(g)} \rightarrow CH_3CH_2OH_{(l)}$ (hydration of ethene)

Mechanism for acid catalysed addition



- +ves of hydration of ethene: continuous flow process; faster reaction so cheaper manpower; faster reaction; purer product
- -ves: high tech equipment needed (expensive initial costs); ethene: non renewable resource (will become more expensive when raw materials run out); high energy costs for pumping to produce high pressures; uses high temps: lots of energy input

Oxidising alcohols
Potassium dichromate (VI): oxidising agent ($K_2Cr_2O_7$)

Primary alcohols
- Partial oxidation: 1° alcohol → aldehyde
- Reagent: acidified $K_2Cr_2O_7$ (w/ H_2SO_4)
- conditions: limit amount of $K_2Cr_2O_7$, warm gently + distil off aldehyde as it forms to prevent CA from forming

$CH_3CH_2CH_2OH + [O] \rightarrow CH_3CH_2CHO + H_2O$ (propan-1-ol → propanal)

Observation: orange dichromate (VI) ion ($Cr_2O_7^{2-}$) is reduced to green Cr^{3+} ion.

- Full oxidation of 1° alcohols: 1° alcohol → carboxylic acid
- Reagent: acidified $K_2Cr_2O_7$
- conditions: excess of $K_2Cr_2O_7$, heat under reflux, distil off product after reaction has finished

$CH_3CH_2CH_2OH + 2[O] \rightarrow CH_3CH_2COOH + H_2O$

Never seal end of condenser b/c gas buildup of high pressure could cause explosion of apparatus

Anti-bumping granules added to RBF in distillation/reflux to prevent vigorous uneven boiling by making small bubbles form instead of large bubbles

Secondary alcohols
- 2° alcohol → ketone
- Reagent: acidified $K_2Cr_2O_7$
- conditions: heat under reflux
- No further oxidation of ketones

$CH_3CH(OH)CH_3 + [O] \rightarrow CH_3COCH_3 + H_2O$ (propanone)

observation when 1° & 2° alcohols are oxidised by $K_2Cr_2O_7$: orange $Cr_2O_7^{2-}$ ion reduces to green Cr^{3+} ion

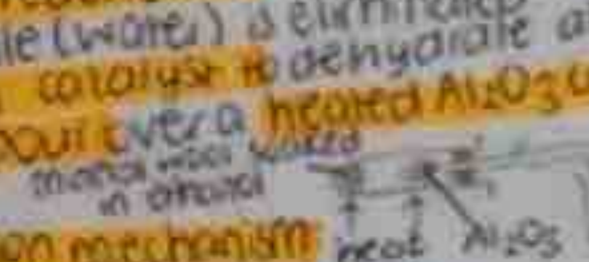
- 3° alcohols can't be oxidised by $K_2Cr_2O_7$ b/c there's no H atom bonded to C atom with OH group

Testing for aldehydes & ketones
1) Tollen's reagent (ammoniacal silver nitrate)
- aldehydes: silver mirror PPT forms on inside of test tube b/c CA formed & silver(I) ions are reduced to silver atoms
- ketones: no visible change.

2) Fehling's solution: contains blue Cu^{2+} ions
- aldehydes: blue Cu^{2+} ions change to orange-red PPT of Cu_2O b/c aldehydes oxidised by Fehling's solution & Cu^{2+} ions reduced to Cu_2O
- ketones: no visible change, solution remains blue as ketones do not react

3) Test presence of CA by adding $NaHCO_3$, if effervescence due to CO_2 production then CA

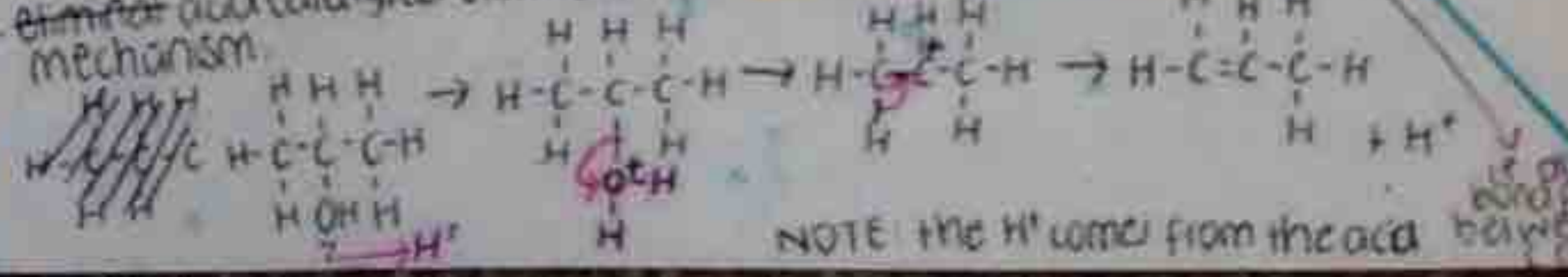
Elimination/dehydration reaction
chemical reaction where a small molecule (water) is eliminated
1) using conc. H_2SO_4 as a catalyst to dehydrate alcohols
2) or passing alcohol vapour over a heated Al_2O_3 catalyst at 600°C



Acid catalysed elimination mechanism
- alcohol → alkene
- Reagent: conc H_2SO_4 or conc. H_3PO_4
- Role of reagent: dehydrating agent/catalyst
- acid catalysed elimination mechanism

acid regenerated

in the elimination of unsymmetrical 1°/3° alcohols a mixture of isomeric products is formed



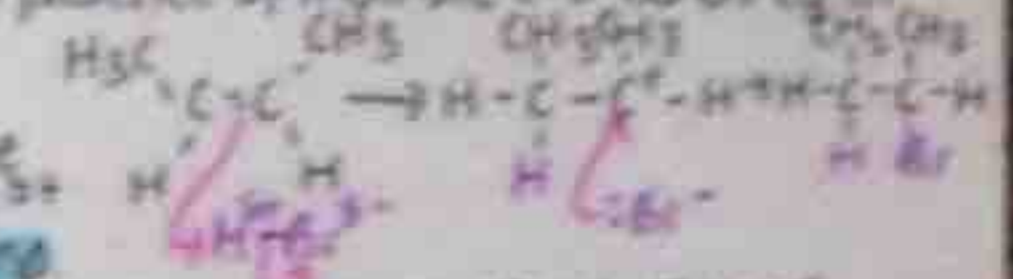
3.3.4 Alkenes
unsat HC (C_nH_{2n})
- planar arrangement of bonds around >C=C< w/ bond angle of 120°C
- C=C double covalent bond consists of one sigma (σ) bond & one pi (π) bond

- π bonds exposed & have high e^- density so make C=C bond vulnerable to attack by species which like e's - electrophiles
- electrophile - electron pair acceptor
- C=C bonds: areas of high e^- density
  - polar molecules such as H-Br = electrophile b/c δ+ end attracted to high e^- density
  - non-polar molecules eg Br-Br b/c high e^- density region between C=C bond repels e's pair in Br-Br bond → this induces dipole & Br_2 becomes polar & electrophilic ($Br^{\delta+}$)
  - heterolytic fission b/c covalent bond breaks + both e's in bond move to one atom, forming 2 oppositely charged ions ie $Br^{\delta+}$ & $Br^{\delta-}$

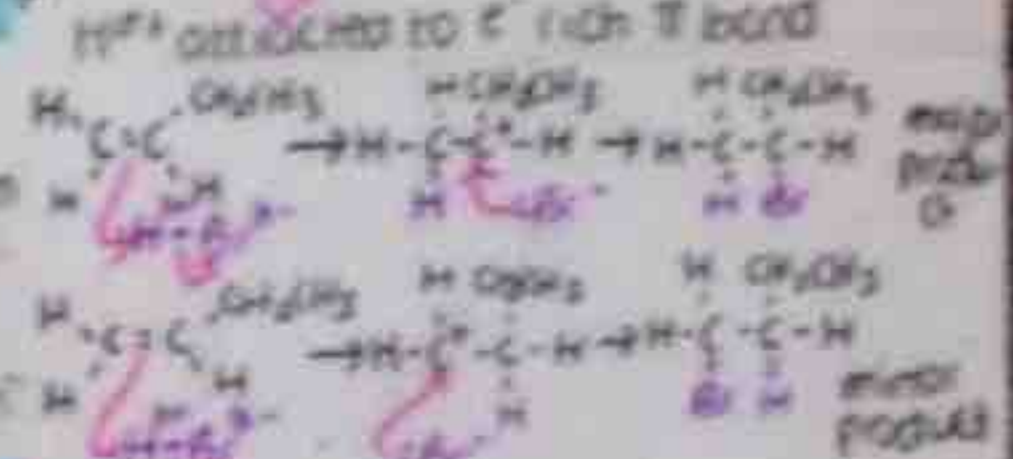
Reaction of alkenes w/ bromine
- alkene → dihalogenoalkane
- reagent: bromine
- conditions: room temp (not in UV light)
- Mechanism: electrophilic addition
- electrophile: $Br^{\delta+}$

- Br_2 used to test for presence of alkenes/C=C bond. Br_2 added to water & reacts w/ alkenes to form a colourless product (orange → colourless)
- use quantitatively to show presence of multiple C=C bonds eg in polyunsat. oils

Reaction of alkenes w/ HBr
- alkene → HA
- reagent: HBr
- conditions: room temp
- Mechanism: electrophilic addition
- electrophile: $H^{\delta+}$



- If unsymmetrical, HBr electrophilic addition can lead to 2 isomeric products
- both products is formed but approx. 90% 2-bromo... major product → due to relative stability of different carbocations formed



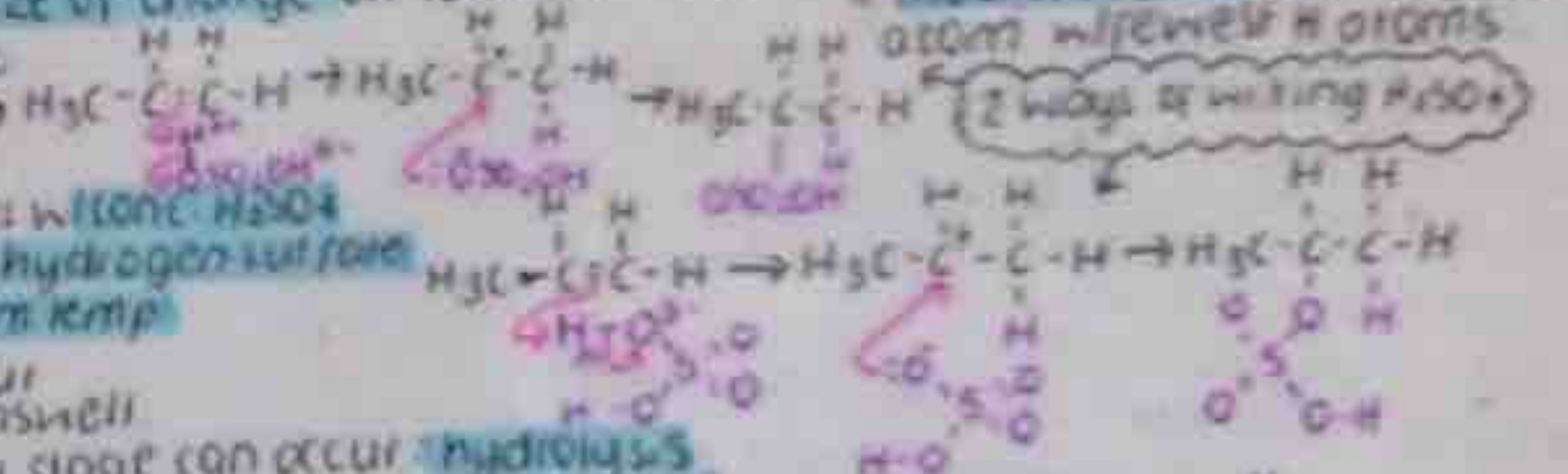
tertiary secondary primary

$R_3C^+ > R_2CH^+ > RCH_2^+$

> means "more stable than"

- Tertiary most stable due e⁻ releasing alkyl groups which have a donating effect + decrease size of charge on ion which stabilises
- if both carbocations secondary, then equally stable so 50/50 split
- Markownikov's rule: when HBr (or any HX) is added to an alkene, H atom adds to C atom w/ most H atoms & Br adds to C atom w/ fewest H atoms

Reaction of alkenes w/ conc. H_2SO_4
- alkene → alkylhydrogen sulfate
- conditions: room temp, but will occur below it as well



Another stage can occur: hydrolysis
- alkylhydrogen sulfate → alcohol
- reagent: water
- conditions: warm mixture
- overall role of H_2SO_4: catalyst b/c regenerated

$H_3C-CH(OSO_3H)-CH_3 + H_2O \rightarrow H_3C-CH(OH)-CH_3 + H_2SO_4$

Addition polymers
- formed from alkenes via addition polymerisation

$n\ CH_2{=}CH_2 \rightarrow [-CH_2-CH_2-]_n$

monomer ethene → polymer (polyethene)

- polymer: long chain of repeating monomer units joined together
- HDPE: less flexible, stiffer, crates; LDPE: more flexible: plastic bags
- strong covalent bonds between C-C & C-H → unreactive; weak vdW forces between molecules but long chains so often v strong vdW forces = more energy required to overcome them: high mpts/bpts
- chain length variable, most polymers contain chains of a variety of diff lengths so vdW forces are of variable strengths so these polymers tend to melt gradually over a range of temps rather than sharply at a fixed temp → eg HDPE (strong vdW)
- polymers w/ few branches: compact + chains pack together efficiently: strong
- highly branched polymers can't pack together as well = weaker vdW so these polymers tend to be softer/weaker → pure form: uPVC (unplasticised)
- PVC (polychloroethene): uses: rigid plastic used for door frames, window frames, drainpipes → eg phthalates when plasticiser added: more flexible; uses: electrical wire insulation, wellies, raincoats