

1) Guide to Rxns

- Electrophilic ____
 - C is e^- rich which needs presence of C=C π bond (alkenes, arenes)
- Nucleophilic ____
 - C is e^- poor which means C is δ^+ (halogenoalkane, carbonyl)
- ____ addition
 - π bond is broken
- ____ substitution
 - σ bond is broken

2) Hybridisation

- describe sp^3 , sp^2 , sp hybridisation*
 - sp^3 hybridization involves one s and three p orbitals, resulting in four sp^3 hybrid orbitals and a tetrahedral geometry
 - sp^2 hybridization uses one s and two p orbitals, creating three sp^2 hybrid orbitals and a trigonal planar geometry.
 - sp hybridization combines one s and one p orbital to form two sp hybrid orbitals, leading to a linear geometry
- explain the shapes of, and bond angles in, the ethane, ethene, benzene, and ethyne molecules in relation to σ and π carbon-carbon bonds*
 - VSEPR:
 - To minimise electron repulsion, electron pairs arrange themselves as far apart as possible
 - lone pair lone pair repulsion > bond pair lone pair repulsion > bond pair bond pair repulsion

3) Isomerism

- describe constitutional (structural) isomerism*
 - Same molecular formula, different structural formula where atoms are connected differently
- describe conditions for cis-trans isomerism in alkenes,*
 - Restricted rotation around C=C bond and each C has 2 different groups attached to it
- explain what is meant by a chiral centre*
 - C atom bonded to 4 unique groups

4) Explaining Rxn Products

- Explaining production of racemic mixture*
 - Electrophile / Nucleophile can attack trigonal planar C / carbocation from either side of the plane with equal probability $\rightarrow$ both enantiomers are formed in equal concentrations $\rightarrow$ equal but opposite rotation of plane-polarised light results in net zero optical activity
- Theoretical ratio of mono-substituted products*
 - Assumes each H has equal chance of being substituted by X
- Why is XXX the major product?*
 - more ED alkyl groups $\rightarrow$ e^- deficiency on carbocation / alkyl radical is reduced more $\rightarrow$ more stable carbocation / alkyl radical is formed preferentially

d) *Difference in rate of formation of AgX ppt.*

- Stronger bond strength → more time taken to form free halide ions → more time taken to observe ppt.

5) Explaining why Rxn occurs

a) *Why alkanes are generally unreactive*

- the C–H bonds are non-polar (C and H have similar electronegativities)
- C–C and C–H bonds are rather strong

b) *Why alkenes can react with electrophiles*

- The electrons are found in the regions above and below the plane of the molecule. Being less tightly bound to the carbon nuclei, the presence of electrons causes a region of relatively high electron density at C=C, thus alkene is more likely to react with electrophiles such as HBr and Br₂ molecules.

c) *Why alkenes can react with Br₂ but not benzene*

- benzene has resonance → π electrons less available for rxn in benzene compared to π electrons in alkene → stronger electrophile like Br⁺ is needed

d) *Why benzene prefers substitution than addition (and even so requires stronger electrophiles)*

- Benzene consists of delocalised π electrons above and below the plane. Less susceptible to attack by electrophiles Requires a stronger electrophile (eg. Br⁺ instead of polarised Br₂) to react.
- The ring of delocalised π electrons gives benzene additional aromatic stability. Addition Reaction that destroys the aromatic ring requires an additional input of energy and is thus unfavourable. Undergoes substitution reaction to preserve aromatic stability.

e) *Why is C=O susceptible to nucleophilic attack?*

- O is highly electronegative which makes C atom highly e⁻ deficient

f) *Factors affecting Rate of Nucleophilic Addition*

- Steric factor
 - Greater number of alkyl groups → more steric hindrance → hinders approach of attacking nucleophile → rate decreases
- Electronic factor
 - More e⁻ donating alkyl groups → reduce partial positive charge on C to a greater extent → C is less e⁻ deficient → rate decreases

g) *Activating vs deactivating groups in benzene*

- Activating → EDG → increase e⁻ density in benzene ring → more susceptible to electrophilic substitution
- Deactivating → EWG → decrease e⁻ density in benzene ring → less susceptible to electrophilic substitution

h) *explain the differences in reactivity between carbonyl compounds and alkenes towards nucleophilic reagents, such as lithium aluminium hydride and hydrogen cyanide*

- The carbonyl carbon carries a partial positive charge as it is directly bonded to the electronegative O atom. This makes the carbonyl carbon susceptible to nucleophilic attack.
- Carbon in alkene does not carry partial positive charge

i) *explain ease of hydrolysis of acyl chlorides, alkyl chlorides and aryl chlorides*

- Aryl Chlorides hardest to hydrolyse: P orbital of X overlapping with π electron cloud of benzene ring → Partial double bond character of C-X bond + High electron density of

aromatic ring repels approaching nucleophile [same answer for Why cannot break C-Cl/C-OH bond in benzene ring]

- Acyl chlorides undergo hydrolysis most readily: The presence of an additional highly electronegative O atom attached to the carboxyl C atom makes it highly electron-deficient, hence most susceptible to nucleophilic attack.

6) Explaining Relative Acidity & Basicity

a) Explaining Relative Acidity

- Presence of EDG / EWG / benzene ring / O-C=O
 - EDG → intensifies negative charge on alkoxide ion → alkoxide ion less stable → dissociates less readily into H^+ → less acidic (to the extent alcohols are neutral)
 - EWG → disperses negative charge on ion → ion more stable → dissociates more readily into H^+ → more acidic
 - Smaller Distance of EWG to COOH also disperses negative charge to a greater extent
 - Benzene ring → negative charge dispersed into benzene ring as a result of resonance → ion more stable → dissociates more readily into H^+ → more acidic
 - EDG on benzene ring disperses negative charge less whereas EWG on benzene ring disperses negative charge more
 - O-C=O → negative charge dispersed significantly over 2 highly electronegative O atoms as a result of resonance → ion most stable → dissociates most readily into H^+ → most acidic

b) Explaining Relative Basicity

- Presence of EDG / EWG / benzene ring / C=O
 - EDG → increase e^- density on N atom → lone pair of e^- on N is more available to accept H^+ → more basic
 - EWG → decrease e^- density on N atom → lone pair of e^- on N is less available to accept H^+ → less basic
 - Benzene ring → decrease e^- density on N atom due to delocalisation of lone pair e^- of N → lone pair of e^- on N is less available to accept H^+ → less basic
 - C=O → significant delocalisation of lone pair e^- of N → lone pair of e^- on N is not available to accept H^+ → not basic

7) Miscellaneous

a) Why $LiAlH_4$ is the most powerful reducing agent?

- Larger electronegativity difference between H and Al (more polarised) → H is more e^- rich

b) Characteristics of CFCs

- Inert, non-flammable, odourless
- Can be liquefied under pressure and vaporise readily when pressure is released

c) How is ozone layer destroyed?

- CFCs release Cl radicals which react with O_3 to form O_2