Organic chemistry

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Questions regarding free radical substitution

Why does it occur at high temperature?

- Sufficient energy for the X2 molecule to undergo homolytic fission to form free radicals

Why is an atom like oxygen described as a free radical

- Write configuration of atom and identify unpaired electrons
- Identify the orbital the unpaired electrons is in

Concept: radicals have unpaired electrons

What is a free radical?

- An atom with an unpaired electron

Explaining basicity of a compound

Factor	Explanation
Delocalisation of electrons due to continuous overlapping of at least 3 adjacent p orbitals (usually amide)	Delocalisation of lone pair of electrons to adjacent p orbitals due to presence of highly electronegative atoms , not available to accept H+/**donate lone pair of electrons to**

Factor	Explanation
	accept H+ (only for Lewis bases or when in gaseous state due to absence of H+) , compound neutral (amide)
Delocalisation of lone pair of electrons into benzene ring	Less significant than delocalisation of p orbitals, decreased electron density, less likely for lone pair of electrons available to donate to accept H+ and donate pair of electrons in gaseous state or Lewis bases
Presence of electron donating groups/ electron withdrawing	EDGs intensify the electron density on atom causing the atom to be electron rich, lone pair of electrons more likely to donate to accept H+ EWG decreases electron density on atom, more likely to accept H+

Questions regarding major products formed in mechanisms

Mechanism	Explanation
Free-radical substitution	Expected product: count the number of hydrogen atoms actual product: Compounds that form tertiary radical will be formed in a greater proportion than expected as it is more stable due to the 3 electron donating groups, reducing electron defiency in order to stabalise the carbon radical for the intermediate of the compound followed by secondary and followed by primary (you can draw the radical intermediate) Answering structure: 1. State if it’s primary, secondary or

Mechanism	Explanation
	tertiary radical 2. State how many alkyl groups are there 3. More Electron donating alkyl groups help to reduce electron defiency making radical more stable
Electrophilic addition/ SN2 Nu sub	During the electrophilic addition/Nu sun mechanism, tertiary carbocation is the most stable as it consists of 3 electron donating alkyl groups to reduce electron deficiency of carbocation, stabalising it, followed by secondary carbocation and primary carbocation (you can draw the carbocation intermediates)

Question regarding Nucleophillic substitutions

Why certain molecules undergo SN1 rather than SN2

- Conditions that favour SN1
  - Stable carbocation either by tertiary or resonance stabalised
  - High steric hindrance due to bulky hydrocarbon groups attached to nucleophile, unable to do rear side attack

Why certain compound unable to go through SN1 mechanism

- Will form carbocation that is not connected to any electron donating alkyl group but instead a EWG, intensifying positive charge on C making it unstable

Which mechanism produces single enantiomer or racemic mixture

- Sn2 mechanism occurs via rear side attack where nucleophile attack electron deficient carbon from opposite side of leaving group, producing a single enantiomer with an inverse stereochemistry
- SN1 can attack on both sides of the plane of the electron deficient carbon in a 50:50 ratio, forming equal concentrations of each enantiomer producing a racemic mixture

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Explaining acidity of a compound

Factor	Explanation
Presence of electron withdrawing groups/ electron donating groups	Disperses negative charge of conjugate base, stabalise to a greater extent, dissociate into conjugate base and H+ more readily, more acidic EDG intensify negative charge on conjugate base, decrease stability and hence less likely to dissociate into H+ ,Miles's acidic
Delocalisation into benzene ring	Negative charge disperse, more stable , more acidic

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Questions regarding electrophilic substitution

Why is Iodobenzene made in preference to chlorobenzene during reaction?

Approach: explain in terms of electronegativity of the atoms, which atoms forms a more stronger electrophile

- Cl more electronegative than iodine
- ICl reacts with AlCl3 to form Iodine electrophile that reacts with electrons rich benzene to produce iodobenzene

Roles of the Lewis acid catalyst

- Act as a Lewis acid acceptor when reacting with reactants
- Acts as a catalyst as it is regenerated at the end of the reaction

Why are products that have certain position of substituents Less likely to be formed?

- see if the group already there is 2,4 or 3,6 directing, Hence it will form a less stable intermediate and hence the formation of that product is unfavourable
- If there is an alkyl group, it can cause steric hindrance while electrophile is attacking at that position

How Reactivity of benzene is affected certain substitutients on benzene ring with electrophile

- Presence of EDG, increase electron density of pi electron cloud of benzene ring, more susceptible to electrophillic substitution as compared to benzene as it is able to attract the electrophile more
- Presence of EWG decreases electron density of pi electron cloud making it less susceptible to electrophillic substitution

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Acidic hydrolysis of nitrile group

$HOCH_2CN + H^+ + 2H_2O \longrightarrow HOCH_2COOH + NH_4^+$

Note: It is easier to balance using ionic equation as the SO_4^{2-} ion is a spectator ion in the Acid hydrolysis

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Identifying major species in pH solutions

- Apply rule
  - pH<pKa, species protonated
    - Reasoning: at low pH, no need to give up H+, can keep H+
    - **Take note that NH3+ is the default not NH2**

- pH>pKa , species deprotonated
  - At high pH, less H, need to give it up

Why is LiAlH4 a stronger reducing agent than NaBH4

- LiA*l*H4 is a stronger reducing agent than NaBH4 as the A*l*−H bond is longer and weaker than B−H bond

Why does LiAlH4 not react with alkenes

- it uses H- nucleophile for reduction and is usually attracted to partial charge of carbon like in carboxylic acid
- However it is repelled by electron rich C=C in alkenes and hence reduction does not occur

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Reactivity with cold water

Why does chlorobenzene not react with cold water

- C atom of of C-Cl is electron rich due to delocalisation pi electrons of benzene, repealing Nucleophillic H2O
- Partial double bond character C-Cl bond due to overlapping of the p orbital of cl with the pi electron cloud of benzene ring, much larger amount of energy is required to break the C-Cl bond

Note: benzene ring is electron rich due to delocalisation and also has partial double bond character

Why does ethanoyl chloride react with cold water?

- Presence of highly electronegative O atom and Cl atom attached to the carboxyl C atom makes the C atom highly electron deficient hence react rapidly with cold water

Note: Need to know the concept that highly electron rich species repel nucelophiles (Arene and alkenes) and highly electron deficient attract Nucleophille (carbonyl)

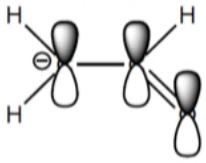
- Chloroethane does not react with water due to no electronegativite differences?

Why does benzene only undergo substitution reactions but not addition reactions

- The ring of delocalised pi electrons gives benzene additional aromatic stability.
- Addition reactions destroy the aromaticity amd hence it is no favourable
- Hence it undergoes substitution reactions to preserve aromaticity

Suggest how delocalisation of electrons occur with a diagram

- Continous side way overlap of p orbitals on 3 connected atoms allows pi electrons to delocalisation across these 3 atoms



- for diagram just show p orbitals

How to know which resonance structure is most closely resembles structure of actual ion

- See where the lone pair electron lies
- If it lies on a more electronegative atom, delocalised electrons have a greater tendency to be found there as it most likely for the atom to hold a negative charge

Distinguishing test for halogenoalkane

- heat holgenoalkane with NaOH

- Cool and followed by excess HNO_3
- Add $AgNO_3$

Questions Regarding Rate of reaction of an organic compound

Explaining rate of hydrolysis of a compound

Factor	Explanation
Presence of highly electronegative atom in a carbonyl	Presence of highly electronegative atom attached to carbon makes the C atom highly electron deficient, most susceptible to Nucleophillic attack by H_2O
Benzene ring	electron rich benzene caused by the delocalised pi electrons of benzene will repel the electron rich nucleophile of H_2O also, strong partial double bond character due to delocalisation of pi electrons across the overlapping p orbitals makes it harder to break

Note: In hydrolysis, H_2O acts as a Nucleophillic

Explain why chlorination of phenol occurs more readily than chlorobenzene

- In phenol, the delocalisation of the lone pair of electrons on oxygen into the benzene ring **increases** the electron density in the ring significantly. This makes phenol **more susceptible** than methylbenzene towards electrophilic attack.
- Even though methyl group of methylbenzene is also electron donating, it is only weakly activating whereas −OH of phenol is strongly activating.

Why does phenol not react directly with carboxylic acid

- Phenol is a weaker Nucleophile compared to OH- and lone pair of electrons on O atom on phenol is delocalisation into benzene ring making it less available for attack on electron deficient C on carboxyl group

Explain what is meant by homolytic fission

- even breaking of a covalent bond where one electron from the bond goes to each of the atom, forming radical

Why is KCN in slightly acidic conditions is preferred method for forming hydroxynitriles form carbonyl compounds

In slightly acidic conditions, a mixture of CN^- and HCN is obtained.

$$HCN \rightleftharpoons H^+ + CN^-$$

There would still be high concentration of CN^- to react with the carbonyl compound in the rate determining step of nucleophilic addition mechanism. [if solution is very acidic, $[CN^-]$ will be very low]

HCN would take part in step 2 of the reaction mechanism to produce the hydroxynitrile. [if solution is not acidic, there will be no HCN for step 2]

Why does the carbon atom of cyanide ion donates the pair of electrons but not the nitrogen atom

- C atom is less electronegative
- C more likely to donate its lone pair of electron

What is meant by zwitterion

- both positive and negative charges and net charge is zero