Summary and Notes for Exam Preparation: Alcohol, ester and carboxylic acid

The Homologous Series of Alcohols

General Formula and Structure

- General formula: $C_nH_{2n+1}OH$
- Functional group: -OH (hydroxyl group)
- Example series:
    - CH_3OH (Methanol)
    - CH_3CH_2OH (Ethanol)
    - $CH_3CH_2CH_2OH$ (Propanol)
    - $CH_3CH_2CH_2CH_2OH$ (Butanol)

Key Characteristics

- Each member differs by CH_2
- Similar chemical properties due to -OH group
- Gradual change in physical properties:
    - Boiling point increases with chain length
    - Solubility decreases with chain length

Hydrogen Bonding in Alcohols

- Forms between O-H group and O of another molecule
- Results in:
    - Higher boiling points than equivalent alkanes
    - High solubility in water for lower members

2. Types of Alcohols

Primary Alcohols (1°)

- -OH attached to carbon with two hydrogens
- Structure: RCH_2OH
- Example: CH_3CH_2OH (ethanol)
- Oxidizes to aldehydes, then carboxylic acids

Secondary Alcohols (2°)

- -OH attached to carbon with one hydrogen
- Structure: R2CHOH
- Example: CH3CH(OH)CH3 (propan-2-ol)
- Oxidizes to ketones only

Tertiary Alcohols (3°)

- -OH attached to carbon with no hydrogens
- Structure: R3COH
- Example: (CH3)3COH (2-methylpropan-2-ol)
- Does not undergo oxidation

3. Reactions of Alcohols

3.1 Combustion

C2H5OH + 3O2 → 2CO2 + 3H2O

Biofuels

- Ethanol as renewable fuel
- Advantages:
  - Renewable
  - Carbon neutral
  - High octane number
- Disadvantages:
  - Lower energy density
  - Competes with food production
  - Requires land use

3.2 Substitution to Form Halogenoalkanes

Method 1: Using Hydrogen Halides

CH3CH2OH + HBr → CH3CH2Br + H2O

- Conditions: concentrated HBr/HCl, heat
- Mechanism: Nucleophilic substitution

Method 2: Using Phosphorus Halides

3CH3CH2OH + PCl3 → 3CH3CH2Cl + H3PO3

- More vigorous reaction
- Better yields

Practical Example - Bromoethane Production

Key Points:

- NaBr + H2SO4 generates HBr in situ
- Distillation separates product
- White NaBr crystals visible

3.3 Reaction with Group 1 Metals

$2CH_3CH_2OH + 2Na \rightarrow 2CH_3CH_2ONa + H_2$

- Vigorous reaction
- Produces metal alkoxide and hydrogen
- Test: Pop with lighted splint

3.4 Esterification

$CH_3CH_2OH + CH_3COOH \rightleftharpoons CH_3COOCH_2CH_3 + H_2O$

- Reversible reaction
- Requires H2SO4 catalyst
- Heat under reflux
- Products: Pleasant-smelling esters

3.5 Hydrolysis of Esters

$CH_3COOCH_2CH_3 + H_2O \rightleftharpoons CH_3COOH + CH_3CH_2OH$

- Reverse of esterification
- Conditions: H+/OH- catalyst, heat
- Applications: Soap making

3.6 Dehydration

$CH_3CH_2OH \rightarrow CH_2=CH_2 + H_2O$

- Conditions: conc. H2SO4, 170°C
- Forms alkenes
- Important industrial process

3.7 Oxidation

Primary Alcohols

1. $RCH_2OH \rightarrow RCHO \rightarrow RCOOH$

- First forms aldehyde
- Then carboxylic acid

- Uses K2Cr2O7/H+

Secondary Alcohols

2. `R2CHOH → R2C=O`

- Forms ketone only
- Uses K2Cr2O7/H+

Tertiary Alcohols

- No oxidation occurs
- Used as distinguishing test

4. Distinguishing Tests

Primary vs Secondary vs Tertiary

1. Oxidation with K2Cr2O7/H+
    - Primary: Orange to green, forms aldehyde/acid
    - Secondary: Orange to green, forms ketone
    - Tertiary: No color change
2. Lucas Test (ZnCl2/conc. HCl)
    - Primary: Slow clouding
    - Secondary: Moderate clouding
    - Tertiary: Immediate clouding

Example Problems

1. **Oxidation Products** Question: Predict the products when propan-1-ol is oxidized with K2Cr2O7/H+

3. `Step 1: CH3CH2CH2OH → CH3CH2CHO (propanal)`

   `Step 2: CH3CH2CHO → CH3CH2COOH (propanoic acid)`

2. **Esterification** Question: What ester is formed from ethanol and propanoic acid?

4. `CH3CH2OH + CH3CH2COOH → CH3CH2COOCH2CH3 + H2O`

   `(ethyl propanoate)`

Exam Tips

1. Always show complete structural formulas in answers
2. Remember oxidation conditions and products
3. Know practical tests for different alcohols
4. Practice writing balanced equations
5. Understand mechanisms of substitution
6. Remember conditions for each reaction type
7. Be able to identify primary/secondary/tertiary alcohols from structures
8. Know the applications of each reaction type

Introduction to Carboxylic Acids

1.1 Structure and Properties

- Functional group: -COOH (carboxyl group)
- General formula: R-COOH
- Contains two key parts:
    - Carbonyl group (C=O)
    - Hydroxyl group (-OH)

1.2 Physical Properties

Boiling Points

- Higher than corresponding alcohols
- Forms dimers in non-polar solvents

Solubility

- Lower members (C1-C4) highly soluble in water
- Solubility decreases with chain length
- Due to:
    - Polar -COOH group (hydrophilic)
    - Non-polar hydrocarbon chain (hydrophobic)

1.3 Nomenclature

Examples:

- HCOOH: Methanoic acid
- CH_3 COOH: Ethanoic acid
- CH_3 CH_2 COOH: Propanoic acid

2. Reactions that Form Carboxylic Acids

2.1 Oxidation of Primary Alcohols

$RCH_2OH + [O] \rightarrow RCHO + [O] \rightarrow RCOOH$

Conditions:

- Oxidizing agent: $K_2Cr_2O_7/H^+$
- Heat under reflux
- Example: $CH_3CH_2OH \rightarrow CH_3COOH$

2.2 Oxidation of Aldehydes

$RCHO + [O] \rightarrow RCOOH$

Conditions:

- Oxidizing agent: $K_2Cr_2O_7/H^+$ or Tollen's reagent
- Heat under reflux

2.3 Hydrolysis of Nitriles

$RCN + 2H_2O \rightarrow RCOOH + NH_3$

Conditions:

- H^+ or OH^-
- Heat under reflux
- Example: $CH_3CN + 2H_2O \rightarrow CH_3COOH + NH_3$

2.4 Hydrolysis of Esters

$RCOOR' + H_2O \rightleftharpoons RCOOH + R'OH$

Conditions:

- H^+ or OH^- catalyst
- Heat under reflux

3. Reactions as Acids

3.1 Acid Dissociation

$RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+$

- Weak acids (partial dissociation)
- Ka typically 10^{-4} to 10^{-5}

3.2 Reaction with Metals

$2CH_3COOH + Mg \rightarrow (CH_3COO)_2Mg + H_2$

- More reactive metals give vigorous reaction
- Less reactive metals react slowly/not at all
- Test for H_2 : "pop" with lighted splint

3.3 Reaction with Metal Carbonates

$2CH_3COOH + Na_2CO_3 \rightarrow 2CH_3COONa + H_2O + CO_2$

- Effervescence observed
- Test for CO_2 : turns limewater milky

3.4 Reaction with Metal Oxides

$2CH_3COOH + MgO \rightarrow (CH_3COO)_2Mg + H_2O$

- Forms salt and water

3.5 Reaction with Alkalis

$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

- Neutralization reaction
- Forms salt and water
- Used in titrations

4. Reduction of Carboxylic Acids

4.1 Using $LiAlH_4$

$RCOOH + LiAlH_4 \rightarrow RCH_2OH$

Conditions:

- Dry ether solvent
- Room temperature
- Forms primary alcohol
- Example: $CH_3COOH \rightarrow CH_3CH_2OH$

4.2 Using $NaBH_4$

- Does NOT reduce carboxylic acids
- Important distinction from $LiAlH_4$

5. Practical Examples and Applications

5.1 Titration of Carboxylic Acid with Base

Procedure:

1. Fill burette with NaOH solution
2. Pipette acid into conical flask
3. Add indicator
4. Titrate until pink color persists

5.2 Preparation of Ethanoic Acid

Starting material: Ethanol

Oxidizing agent: $K_2Cr_2O_7/H^+$

Equipment:

- Round-bottomed flask

- Reflux condenser

Water bath

6. Example Problems and Solutions

Problem 1: Acid-Base Calculations

Calculate the pH of 0.1M ethanoic acid ($K_a = 1.8 \times 10^{-5}$)

Solution:

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$K_a = [H^+][CH_3COO^-]/[CH_3COOH]$

$1.8 \times 10^{-5} = [H^+]^2/0.1$

$[H^+] = \sqrt{(1.8 \times 10^{-5} \times 0.1)}$

$[H^+] = 1.34 \times 10^{-3}$

$pH = -\log[H^+] = 2.87$

Problem 2: Neutralization Calculations

25.0 cm^3 of ethanoic acid reacts with 20.0 cm^3 of 0.1M NaOH. Calculate the concentration of the acid.

Solution:

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nNaOH = 20.0 × 0.1/1000 = 0.002 mol

Since 1:1 ratio, nAcid = 0.002 mol

[Acid] = 0.002 × 1000/25.0 = 0.08M
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7. Exam Tips

Writing

1. Always show balanced equations
2. Include state symbols where required
3. Draw full structural formulas when asked

Calculations

1. Show all working
2. Include units
3. Give answers to appropriate significant figures

Practical

1. Know tests for products
2. Understand safety precautions
3. Be able to explain choice of apparatus

Common Mistakes to Avoid

1. Forgetting state symbols
2. Incomplete equations
3. Wrong oxidation products
4. Confusion between reduction reagents

8. Key Definitions

1. **Carboxylic acid**: Organic compound containing -COOH group
2. **Dissociation**: Process of acid releasing H^+ in solution
3. **Neutralization**: Reaction between acid and base to form salt and water
4. **Reduction**: Process involving addition of hydrogen or removal of oxygen

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