Notes for Exam Preparation: Carbonyl Compounds

1. Introduction to Carbonyl Compounds

1.1 Structure and Properties

- Functional group: C=O (carbonyl group)
- Contains sp² hybridized carbon
- Planar geometry around carbonyl carbon
- Bond angle approximately 120°

1.2 Types of Carbonyl Compounds

- 1. Aldehydes: R-CHO
- 2. Ketones: R-CO-R'

Structure comparison:

Aldehyde: O=CH-R

Ketone: O=C(R)-R'

2. The Homologous Series

2.1 Aldehydes

- General formula: CnH2n+1CHO
- Examples:
 - Methanal (HCHO)
 - Ethanal (CH3CHO)
 - Propanal (CH3CH2CHO)

2.2 Ketones

- General formula: CnH2n+1COCnH2n+1
- Examples:
 - Propanone (CH3COCH3)
 - Butanone (CH3COC2H5)
 - Pentan-2-one (CH3COC3H7)

3. Nomenclature

3.1 Aldehydes

- Replace -e of alkane with -al
- Examples:
 - CH3CHO: ethanal
 - CH3CH2CHO: propanal
 - CH3CH2CH2CHO: butanal

3.2 Ketones

- Replace -e of alkane with -one
- Position number indicates carbonyl group
- Examples:
 - CH3COCH3: propanone
 - CH3COC2H5: butan-2-one
 - CH3CH2COCH3: pentan-2-one

4. Preparation Methods

4.1 Oxidation of Primary Alcohols (Aldehydes)

 $\mathsf{RCH2OH} + [\mathsf{O}] \rightarrow \mathsf{RCHO} + \mathsf{H2O}$

Conditions:

- K2Cr2O7/H⁺
- Distill product immediately
- Heat under reflux

4.2 Oxidation of Secondary Alcohols (Ketones)

 $\mathsf{R2CHOH} + [\mathsf{O}] \to \mathsf{R2CO} + \mathsf{H2O}$

Conditions:

- K2Cr2O7/H⁺
- Heat under reflux

5. Reduction Reactions

5.1 Using NaBH4

 $\mathsf{RCHO} + \mathsf{NaBH4} + \mathsf{H}^{\scriptscriptstyle +} \to \mathsf{RCH2OH}$

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\mathsf{R2CO} + \mathsf{NaBH4} + \mathsf{H}^{\scriptscriptstyle +} \to \mathsf{R2CHOH}
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Conditions:

- Room temperature
- Methanol/ethanol solvent
- Add water to hydrolyze

5.2 Using LiAIH4

 $\mathsf{RCHO} + \mathsf{LiAIH4} \to \mathsf{RCH2OH}$

 $\mathsf{R2CO}+\mathsf{LiAIH4}\to\mathsf{R2CHOH}$

Conditions:

- Dry ether solvent
- Room temperature

6. Nucleophilic Addition Reactions

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6.1 Addition of HCN

 $RCHO + HCN \rightarrow RCH(OH)CN$

 $\text{R2CO} + \text{HCN} \rightarrow \text{R2C(OH)CN}$

Conditions:

- KCN + HCI
- Room temperature
- pH control (4-7)

6.2 Mechanism Steps

- 1. Nucleophilic attack by CN⁻
- 2. Protonation of intermediate
- 3. Formation of cyanohydrin

7. Testing Methods

7.1 Carbonyl Group Test (2,4-DNPH)

Reagent: 2,4-dinitrophenylhydrazine

Result: Orange/yellow precipitate

Mechanism:

- Condensation reaction
- Forms hydrazone derivative

7.2 Tollens' Test (Aldehydes)

Reagent: [Ag(NH3)2]⁺ + OH⁻

Result: Silver mirror

Reaction:

 $\mathsf{RCHO} + 2[\mathsf{Ag}(\mathsf{NH3})2]^{\scriptscriptstyle +} + 2\mathsf{OH}^{\scriptscriptstyle -} \rightarrow \mathsf{RCOOH} + 2\mathsf{Ag} + 4\mathsf{NH3} + \mathsf{H2O}$

7.3 Fehling's Test (Aldehydes)

Reagent: Cu²⁺ in alkaline tartrate solution

Result: Red Cu2O precipitate

Reaction:

 $\mathsf{RCHO} + 2\mathsf{Cu}^{2*} + 4\mathsf{OH}^{-} \rightarrow \mathsf{RCOOH} + \mathsf{Cu2O} + 2\mathsf{H2O}$

8. Tri-iodomethane Formation

8.1 lodoform Test

 $RCH(OH)CH3 + 3I2 + 3OH^{-} \rightarrow CHI3 + RCOO^{-} + 3H2O$

Conditions:

- NaOH/I2
- Room temperature
- Yellow precipitate (CHI3)

8.2 Testing CH3CH(OH)- Group

- Positive with:
 - CH3CH(OH)R compounds
 - CH3COR compounds
- Yellow precipitate
- Characteristic smell

9. Practical Examples

Example 1: Oxidation of Propan-1-ol

$\text{CH3CH2CH2OH} \rightarrow \text{CH3CH2CHO}$

Procedure:

- 1. Add K2Cr2O7/H2SO4
- 2. Heat under reflux
- 3. Distill product
- 4. Test distillate with 2,4-DNPH

Example 2: Distinguishing Tests

Given unknown A and B:

- 1. 2,4-DNPH test (both positive)
- 2. Tollens' test:
 - A: Silver mirror
 - B: No change
- 3. Conclusion:
 - A: Aldehyde
 - B: Ketone

1. Fundamental Concepts

What is IR Spectroscopy?

- A technique used to identify functional groups in organic molecules
- Based on molecular vibrations caused by absorption of infrared radiation
- Different bonds absorb IR radiation at specific frequencies (wavenumbers)

How it Works

- 1. IR radiation is passed through a sample
- 2. Molecules absorb specific frequencies that match their vibration modes
- 3. Transmitted radiation is measured
- 4. Results are plotted as % transmission vs wavenumber (cm⁻¹)

2. Types of Molecular Vibrations

Stretching Vibrations

- Symmetric stretching: Bonds stretch in and out simultaneously
- Asymmetric stretching: One bond stretches while another contracts
- Generally occur at higher wavenumbers (1500-4000 cm⁻¹)

Bending Vibrations

- Scissoring: Bonds move towards and away from each other
- Rocking: Bonds move in the same direction
- **Wagging**: Bonds move out of plane
- Twisting: Bonds rotate
- Generally occur at lower wavenumbers (600-1500 cm⁻¹)

3. Key Absorption Ranges

O-H Bonds

- Alcohols: 3200-3600 cm⁻¹ (strong, broad)
- Carboxylic acids: 2500-3300 cm⁻¹ (very broad)
- Example: Ethanol shows broad peak at ~3300 cm⁻¹

N-H Bonds

- **Primary amines**: 3300-3500 cm⁻¹ (medium, two peaks)
- Secondary amines: 3300-3500 cm⁻¹ (medium, one peak)
- Example: Methylamine shows two peaks at ~3400 cm⁻¹

C-H Bonds

- Alkanes: 2850-3000 cm⁻¹ (strong)
- Alkenes: 3010-3100 cm⁻¹ (medium)
- Aromatic: 3000-3100 cm⁻¹ (medium)
- Example: Propane shows strong peaks at ~2900 cm⁻¹

C=O Bonds (Carbonyl)

- Aldehydes: 1700-1740 cm⁻¹ (strong)
- Ketones: 1705-1725 cm⁻¹ (strong)
- Carboxylic acids: 1700-1725 cm⁻¹ (strong)
- Esters: 1735-1750 cm⁻¹ (strong)
- Example: Acetone shows strong peak at ~1715 cm⁻¹

C=C Bonds

- Alkenes: 1620-1680 cm⁻¹ (medium)
- Aromatic: 1450-1600 cm⁻¹ (multiple peaks)
- Example: Ethene shows peak at ~1650 cm⁻¹

C≡N Bonds

• Nitriles: 2200-2260 cm⁻¹ (medium)

• Example: Acetonitrile shows peak at ~2230 cm⁻¹

4. Practical Examples and Analysis

Example 1: Ethanol (CH₃CH₂OH)

Key peaks:

- 1. 3300-3400 cm⁻¹: broad O-H stretch
- 2. 2850-3000 cm⁻¹: C-H stretches
- 3. 1050-1150 cm⁻¹: C-O stretch

Example 2: Acetone (CH₃COCH₃)

Key peaks:

- 1. 1715 cm⁻¹: strong C=O stretch
- 2. 2850-3000 cm⁻¹: C-H stretches

5. Exam Techniques and Tips

Spectrum Analysis Steps

- 1. Look for obvious functional groups first (O-H, C=O)
- 2. Check the fingerprint region (below 1500 cm⁻¹) for pattern matching
- 3. Cross-reference with other data (e.g., molecular formula)

Common Exam Questions

- 1. Identifying functional groups from spectra
- 2. Matching spectra to given structures
- 3. Drawing structures based on spectral data
- 4. Explaining the presence/absence of specific peaks

Remember

- Peak intensity is described as strong (s), medium (m), or weak (w)
- Broad peaks typically indicate hydrogen bonding
- Multiple peaks close together often indicate aromatic compounds
- The fingerprint region (<1500 cm⁻¹) is unique to each molecule

6. Practice Problems

- Basic Analysis Question: A compound shows a strong peak at 1715 cm⁻¹ and no broad peak above 3000 cm⁻¹. What functional group is present? Answer: Ketone group (C=O), absence of O-H suggests it's not a carboxylic acid
- 2. Complex Analysis Question: A compound shows:
 - Broad peak at 3300 cm⁻¹
 - Strong peak at 1720 cm⁻¹
 - C-H stretches at 2900 cm⁻¹ What functional groups are present? Answer: Carboxylic acid group (O-H broad + C=O at 1720 cm⁻¹)