Summary and Notes for Exam Preparation: Halogenoalkanes

1. Introduction to Halogenoalkanes

Structure and Classification

- General formula: R-X (X = F, Cl, Br, I)
- Classification:
  - Primary (1°): RCH_2X
  - Secondary (2°): R_2CHX
  - Tertiary (3°): R_3CX

Physical Properties

1. **Boiling Points**
   - Increase down group: RF < RCl < RBr < RI
   - Due to increasing van der Waals forces
2. **Solubility**
   - Insoluble in water
   - Soluble in organic solvents
   - Higher density than water

Example: Comparing Boiling Points CH_3CH_2F (BP: -38°C) CH_3CH_2Cl (BP: 12°C) CH_3CH_2Br (BP: 38°C) CH_3CH_2I (BP: 72°C)

2. Reactivity Trends

Order of Reactivity

C-F < C-Cl < C-Br < C-I

Factors Affecting Reactivity

1. **Bond Strength**
   - C-F: 485 kJ/mol
   - C-Cl: 340 kJ/mol
   - C-Br: 280 kJ/mol
   - C-I: 228 kJ/mol
2. **Bond Polarity**
   - Decreases down group
   - F most electronegative
   - I least electronegative

Example Calculation: Calculate the relative rate of hydrolysis: CH_3 Br vs CH_3 I

- Rate ratio ≈ 1:4 (due to C-I being weaker)

3. Nucleophilic Substitution Reactions

General Mechanism

R-X + Nu^- → R-Nu + X^-

Common Nucleophiles

1. OH^- (hydroxide ions)
2. CN^- (cyanide ions)
3. NH_3 (ammonia)
4. ROH (alcohols)

4. SN2 Mechanism (Primary Halogenoalkanes)

Characteristics

- Single step mechanism
- Backside attack
- Inversion of stereochemistry

Step-by-Step Process

1. Nucleophile approaches from behind
2. Transition state forms
3. Leaving group departs
4. Product forms with inverted configuration

Example: CH_3 CH_2 Br + OH^- → CH_3 CH_2 OH + Br^-

5. SN1 Mechanism (Tertiary Halogenoalkanes)

Characteristics

- Two-step mechanism
- Carbocation intermediate
- Racemic mixture forms

Steps

1. **Slow step (rate-determining)**
    - C-X bond breaks
    - Carbocation forms
2. **Fast step**
    - Nucleophile attacks carbocation
    - Product forms

Example: $(CH_3)_3CBr \rightarrow (CH_3)_3C^+ + Br^-$ $(CH_3)_3C^+ + OH^- \rightarrow (CH_3)_3COH$

6. Substitution with Aqueous Alkali

Reaction Conditions

- Temperature: 50-60°C
- Solvent: Water/ethanol mixture
- Base: NaOH or KOH

Products

$R\text{-}X + OH^- \rightarrow R\text{-}OH + X^-$

Example: $CH_3CH_2Br + OH^- \rightarrow CH_3CH_2OH + Br^-$

7. Substitution with Cyanide Ions

Conditions

- Solvent: Ethanol
- Temperature: 60-80°C
- Source: KCN or NaCN

Products

$R\text{-}X + CN^- \rightarrow R\text{-}CN + X^-$

Important: Forms nitriles (extension of carbon chain)

8. Substitution with Ammonia

Conditions

- Solvent: Ethanol
- Temperature: 50-60°C
- Pressure: Sealed container

Products

$R\text{-}X + NH_3 \rightarrow R\text{-}NH_2 + HX$

9. Elimination Reactions

E2 Mechanism (Primary/Secondary)

- Single step
- Base removes β-hydrogen
- Alkene forms

Example

$CH_3\ CH_2\ CH_2\ Br + OH^- \rightarrow CH_3\ CH{=}CH_2 + H_2\ O + Br^-$

E1 Mechanism (Tertiary)

- Two-step process
- Carbocation intermediate
- More common in tertiary halogenoalkanes

10. Industrial Uses

1. Fluoropolymers

- Non-stick coatings (PTFE)
- Properties:
    - Chemical inertness
    - Heat resistance
    - Low friction

2. Anaesthetics

- Halothane ($CF_3\ CHClBr$)
- Properties:
    - Non-flammable
    - Controlled volatility
    - Chemical stability

3. CFC Substitutes

1. **HFCs (Hydrofluorocarbons)**

    - Zero ODP (Ozone Depletion Potential)
    - High GWP (Global Warming Potential)
2. **HFEs (Hydrofluoroethers)**
    - Low GWP
    - Used as solvents
    - Industrial cleaning

Practice Questions

1. Explain why tertiary halogenoalkanes undergo SN1 reactions.
2. Compare the reactivity of different halogenoalkanes.
3. Draw the mechanism for: a) SN2 reaction of CH_3 Br with OH^- b) E2 elimination of CH_3 CH_2 Br

Exam Tips

1. **Mechanisms**
    - Show all curly arrows
    - Include partial charges
    - Show transition states
2. **Reactions**
    - Learn conditions
    - Know nucleophiles
    - Remember products
3. **Environmental Chemistry**
    - ODP vs GWP
    - Alternatives to CFCs
    - Environmental impact

Key Definitions

1. Nucleophile: Electron-pair donor
2. Leaving group: Group that departs with electron pair
3. Carbocation: Carbon with positive charge
4. Elimination: Formation of double bond

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