9. AMINES

(Amines, Diazonium Salts, Cyanides and Isocyanides)

($R–NH_2$) ($Ar–N_2^+ Cl^-$) (R–CN) (R–NC)

STUDY NOTES

1. Amines, Diazonium Salts, Cyanides and Isocyanides:

i) Common name : • Amines, Diazonium Salts, Cyanides and Isocyanides

ii) IUPAC name : • Amines, Diazonium Salts, Nitrile and Carbylamine

iii) General Formula : • Primary Amines: R-NH_2 (or) C_nH_{2n+1} –NH_2

• Diazonium Salts: **$Ar–N_2^+ Cl^-$**

• Cyanides: R–CN (or) R–C ≡ N

• Isocyanides: R–NC (or) R–N ≡ C

iv) Amine Ex : • CH_3NH_2 (Methanamine-), $C_2H_5NH_2$(Ethanamine)

v) Diazonium Salts Ex : • $C_6H_5N_2^+ Cl^-$ (Benzenediazoniumchloride)

vi) CyanidesEx : • CH_3CN (Ethanenitrile), C_2H_5CN(Propanenitrile)

vii) IsocyanidesEx : • CH_3NC (Methylisocyanide), C_2H_5NC(Ethylisocyanide)
Methylcarbylamine(Isocyanomethane),
Ethylcarbyl amine (Isocyanoethane)
C_6H_5NC(Phenylisocyanide; Isocyanobenzene)

I) AMINES

2. 1. Classification of Amines:

Based on number of alkyl/aryl groups attached to nitrogen

Primary (1°) →$R–NH_3$

Secondary (2°)→R_2NH

Tertiary (3°)→ R_3N

Based on nature of groups:

• Aliphatic amines (alkyl amines) **• Aromatic amines (arylamines)**

2.2. Structure of Amines:

Amines are derivatives of ammonia (NH_3)

Nitrogen is **sp^3 hybridised**

Shape: trigonal pyramidal

Lone pair present → basic nature

3. Nomenclature:

Common Names:

Named as alkyl + amine

Ex: CH_3NH_2 → methylamine

IUPAC Naming: Replace "-e" of alkane with **-amine**

Ex: CH_3NH_2→ methanamine

4. Preparation of Amines:

i) Reduction of Nitro Compounds: Nitro → amine (using H, /Pd or Fe/HCl)

ii) Ammonolysis of Alkyl Halides: Alkyl halide + NH_3 → amine

iii)Reduction of Nitriles: Nitrile→ primary amine

iv)Reduction of Amides: Amide → amine

v) Gabriel Phthalimide Synthesis: Gives **only primary amines**

vi) Hoffmann Bromamide Degradation: Amide→ amine (one carbon less)

5. Physical Properties of Amines:

Lower amines → gases, higher → liquids/solids

Show **hydrogen bonding**

Boiling point: 1° > 2° > 3° amines

Solubility: lower amines soluble in water

6. Chemical Reactions of Amines:

(i) Basicity of Amines:

(a) Alkanamines vs Ammonia

Alkyl groups donate electrons (+I effect)→ increase basicity

Order in aqueous solution: 2° > 1° > 3° > NH_3 (Methyl substituted Amines)

Reason: Balance of **+I effect + solvation**

(b) Arylamines vs Ammonia

Less basic than ammonia

Lone pair delocalised in benzene ring (resonance)

(ii) Alkylation:

Amines + alkyl halides → higher amines

(iii) Acylation:

Formation of amides (important for identification)

(iv) Carbylamine Reaction:

Only **primary amines** give isocyanides (foul smell test)

(v) Reaction with Nitrous Acid (HNO_2):

- **1° aliphatic amine** → alcohol + N_2 gas
- **1° aromatic amine**→ diazonium salt
- **2° amine**→ nitroso compounds
- **3° amine** → no reaction

(vi) Reaction with Arylsulphonyl Chloride (Hinsberg Test):

Used to distinguish **1°, 2°, 3° amines**

(vii) Electrophilic Substitution (Aromatic Amines): $-NH_2$ is **activating group**

(a) Bromination: Gives tribromoaniline

(b) Nitration: Gives nitro derivatives

(c) Sulphonation: Forms sulphonated products

II) DIAZONIUM SALTS

7.1 Preparation of Diazonium Salts:

From **primary aromatic amines**

Reaction with nitrous acid at **273–278 K**

7.2 Physical Properties of Diazonium Salts :

• Stable only at **low temperature**

• Explosive when dry

7.3 Chemical Reactions of Diazonium Salts :

a) Reactions involving displacement of nitrogen:

Nitrogen gas is replaced by other groups:

Cl, Br → Sandmeyer reaction

F→ Balz–Schiemann reaction

OH → phenol

H → benzene

b) Reactions involving retention of diazo group:

Coupling Reactions

Reaction with phenols/anilines

Forms **azo compounds (–N=N–)**

7.4 Importance of Diazonium Salts:

Preparation of Phenols, Aryl halides, Dyes (azo dyes)

Important intermediates in **organic synthesis**

III) CYANIDES

8.1 Preparation of Cyanides:

From Alkylhalides & Ethanolic KCN

$$CH_3CH_2Cl \xrightarrow[KCN]{\text{Ethanolic}} CH_3 - CH_2 - CN\,(\text{Major})$$

8.2 From Amides with $C_6H_5SO_2Cl$

$$CH_3CONH_2 + C_6H_5SO_2Cl \xrightarrow[70^oC]{\text{Pyridine}} CH_3 - CN + C_6H_5SO_3H + HCl$$

IV) ISOCYANIDES

9.1 Preparation of Isocyanides:

From Alkylhalides with ethanolic AgCN

$$CH_3CH_2Cl \xrightarrow[AgCN]{\text{Ethanolic}} CH_3 - CH_2 - NC\,(\text{Major})$$

9.2 From 1° amine with $CHCl_3$ & Alk.KOH

$$\underset{1^o\,\text{Amines}}{R.NH_2} + \underset{\text{Chloroform}}{CHCl_3} + 3KOH \xrightarrow{\text{heat}} \underset{\substack{\text{Alkyl Isocyanide}\\(\text{foul smell})}}{R.NC} + 3KCl + 3H_2O$$

10. Daily life uses:

- **Aniline ($C_6H_5NH_2$)**-Used in dyes, rubber, pharmaceuticals
- **Amines (general)** -Used in medicines, drugs, agrochemicals
- Azo dyes (colour festival) derived from amines- Used for textile coloring

Quick Revision Points

- Amine →–NH_2, Types → 1°, 2°, 3°
- Nature→ Basic (lone pair)
- Basicity → 2° > 1° > 3°
- Aniline → Less basic (resonance)
- Reactions → Alkylation, Acylation
- Tests → Hinsberg, Carbylamine
- Diazonium →Very important
- Amines are **basic due to lone pair on nitrogen**
- **Primary amines → carbylamine test positive**
- Arylamines are **less basic (resonance effect)**
- Diazonium salts are **highly reactive intermediates**
- Used in **dye industry and aromatic substitutions**
- **Methyl substituted Amines (Order of basic strength in aqueous solution):**

2° > 1° > 3° > NH_3 $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

- **Ethyl substituted Amines:** 2°>3°>1°>NH_3 $(C_2H_5)_2NH > (C_2H_5)_3N > (C_2H_5)NH_2 > NH_3$