Chemistry 1B – CHEM1102

Lecture 11 – Amines

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1. What are amines?
2. What’s special about Nitrogen?
3. What kind of Chemistry do amines do?
4. Where do I find some?
Structure of Amines

**Amines** contain $\geq 1$ organic groups bonded to **nitrogen**

General formulae: $\text{RNH}_2$, $\text{R}_2\text{NH}$, $\text{R}_3\text{N}$

Organic derivatives of ammonia ($\text{NH}_3$)

Can be **aliphatic** or **aromatic**

- **Ethylamine**
- **Aminobenzene**

C.f. **Ethanol**
C.f. **Phenol**
Key is Nitrogen

Nitrogen: $1s^2\ 2s^2\ 2p^3$

- has 7 electrons:
  - ⇒ 5 in valence shell
  - ⇒ needs 3 more for full shell (8)
  - ⇒ forms 3 covalent bonds AND has 1 lone pair
Amine Nomenclature

- Amines are classified as primary, secondary or tertiary.

Primary amine (eg ethylamine)

Secondary amine (eg diethylamine)

Tertiary amine (eg triethylamine)

Quaternary ammonium salt

c.f. alcohols

Primary

tertiary
Amine Nomenclature II

• IUPAC ending for amines is ... –yl amine
  
  \[
  \text{Methylamine} \quad \text{Ethylamine} \quad \text{Propylamine}
  \]

  \[
  \text{Diethylamine} \quad \text{Triethylamine}
  \]

• Two non-systematic ones to watch out for ...

  \[
  \text{Pyridine} \quad \text{Aniline}
  \]
1. Amines are **basic** – react with acids
2. Amines are **nucleophilic** – react with electrophiles
Amines are bases (like their ‘parent compound’ ammonia, NH₃)

- the amino group (R-NH₂) is a proton acceptor (base) …
- the protonated amino group (RNH₃⁺) is a proton donor (acid)

\[
R-NH_2 + H_2O \rightleftharpoons R-NH_3^+ + OH^-
\]

- Amines react with acids to yield ammonium salts

\[
H_3C-NH_2 + HCl \rightarrow H_3C-NH_3^+Cl^- \quad \text{salt}
\]
\[
H_3C-NH_2 + CH_3CO_2H \rightarrow H_3C-NH_3CH_3CO_2^- \quad \text{salt}
\]
Measure of Basicity

\[ \text{pK}_{\text{aH}} \] is a useful way to describe basicity = \[ pK_a \] of conjugate acid

i.e. high value means the conjugate acid is not acidic
Which means the base is strong
High \[ \text{pK}_{\text{aH}} \] = strong base

Groups attached to N govern basicity:

- \( \text{NH}_3 \)  \( \text{MeNH}_2 \)
  - Electron-donating alkyl groups enhance basicity

- \( \text{Cl}_3\text{C} \equiv \text{NH}_2 \)  \( \text{Cl}_3\text{C} \equiv \text{NH}_2 \)
  - Electron-withdrawing groups decrease basicity
  - ...but effect drops off with increased distance
Measure of Basicity II

Lone pair tied up in ring

Lone pair tied up in carbonyl

Protonates on oxygen to preserve conjugation

Amidines can protonate on nitrogen and still maintain conjugation
Amines are nucleophiles
• consider their reaction with alkyl halides ...

\[
\begin{align*}
R' \text{NH}_2 & \quad \text{H} \quad \text{Cl} & & \rightarrow \quad \text{H} \quad \text{H} \quad \text{N} \quad \text{CH}_3 & \quad \text{Cl}^-
\end{align*}
\]

• 2° amine goes to 3° amine goes to 4° salt:

Note that amines are stable compounds, hence good leaving groups:

\[
\begin{align*}
\text{Base} & \quad \text{H} \quad \text{N} \quad \text{Cl} & & \rightarrow \quad \text{Base-H} & \quad \text{NH}_3
\end{align*}
\]
Amines are Widespread

Amines can be easily extracted from plants using dilute acid, among the earliest organic compounds studied.

Several important neurotransmitters and hormones are amines:

- **Adrenaline**
  
- **Serotonin**
  
- **Acetylcholine**
Amines are Widespread

- Many stimulants also include amine functionality ... ... coincidence?

Cocaine

Nicotine

MDMA (‘E’)
Nature manufactures these alkaloids

Complex natural amines ("alkaloids") made by biochemical pathways

\[
\begin{align*}
\text{ornithine} & \quad \text{putrescine} \\
\text{Naturally-occurring, non-proteinaceous amino acid}
\end{align*}
\]

Isotopic labelling of an organism’s food can reveal biochemical pathways

\[
\begin{align*}
\text{hygrine}
\end{align*}
\]
Amines Summary

You should now be able to:

• Recognise and name amines
• Understand the chemistry of an amine’s lone pair
• Draw mechanisms for amines acting as bases and nucleophiles

Next Lecture: The 3rd Dimension