Amines and Related Nitrogen Compounds

Chapter Summary

**Amines** are organic derivatives of ammonia. They may be **primary**, **secondary**, or **tertiary**, depending on whether one, two, or three organic groups are attached to the nitrogen. The nitrogen is $sp^3$-hybridized and pyramidal, nearly tetrahedral.

The **amino group** is $-\text{NH}_2$. Amines are named according to the Chemical Abstracts (CA) system by adding the suffix -**amine** to the names of the alkyl groups attached to the nitrogen. Amines can also be named using the IUPAC system in which the amino group is named as a substituent. Aromatic amines are named as derivatives of aniline or of the aromatic ring system.

Primary and secondary amines form intermolecular $\text{N}--\text{H}--\text{N}$ bonds. Their boiling points are higher than those of alkanes but lower than those of alcohols with comparable molecular weights. Lower members of the series are water-soluble because of $\text{N}--\text{H}--\text{O}$ bonding.

Amines can be prepared by $S_N2$ alkylation of ammonia or $1^\circ$ and $2^\circ$ amines. Aromatic amines are made by reduction of the corresponding nitro compounds. Amides, nitriles, and imines can also be reduced to amines.

Amines are weak bases. Alkylamines and ammonia are of comparable basicity, but aromatic amines are much weaker as a result of delocalization of the unshared electron pair on nitrogen to the **ortho** and **para** carbons of the aromatic ring. **Amides** are much weaker bases than amines because of delocalization of the unshared electron pair on nitrogen to the adjacent carbonyl oxygen. Amides are stronger Brønsted acids than amines because of the partial positive charge on the amide nitrogen and resonance in the **amidate anion**.

Amines react with strong acids to form **amine salts**. The $pK_a$s of amine salts are related to the base strength of the corresponding amines. Alkylammonium salts have $pK_a$s of 9–10 while arylammonium salts have $pK_a$s of 4–5. The fact that these salts are usually water-soluble can be exploited in separating amines from neutral or acidic contaminants. Chiral amines can be used to resolve enantiomeric acids, through the formation of diastereomeric salts.

Primary and secondary amines react with acid derivatives to form **amides**. Amides made commercially this way include **acetanilide** and **$N,N$-diethyl-$m$-toluamide** (the insect repellent Off).

Tertiary amines react with alkyl halides to form **quaternary ammonium salts**. An example of this type of salt with important biological properties is **choline** (2-hydroxyethyltrimethylammonium ion).
Primary aromatic amines react with nitrous acid to give aryldiazonium ions, $\text{ArN}_2^+$, which are useful intermediates in synthesis of aromatic compounds. The process by which they are formed is called diazotization. The nitrogen in these ions can readily be replaced by various nucleophiles (OH, Cl, Br, I, CN). Diazonium ions couple with reactive aromatics, such as amines or phenols, to form azo compounds, which are useful as dyes.

**Reaction Summary**

**Alkylation of Ammonia and Amines**

$$\text{R–X} + 2 \text{NH}_3 \rightarrow \text{RNH}_2 + \text{NH}_4^+ \text{X}^-$$

**Reduction Routes to Amines**

- NO$_2$H$_2$, Ni catalyst or SnCl$_2$, HCl
- RCO$\equiv$N R$'$$''$ LiAlH$_4$ → RCH$_2$NR$'$ R$''$
- RCO$\equiv$N LiAlH$_4$ → RCH$_2$NH$_2$
- RCO$\equiv$R$'$ NaBH$_3$CN → NR$''$ R$'$

**Amine Basicity**

$$\text{RNH}_2 + \text{HCl} \rightarrow \text{RNH}_3^+ \text{Cl}^-$$