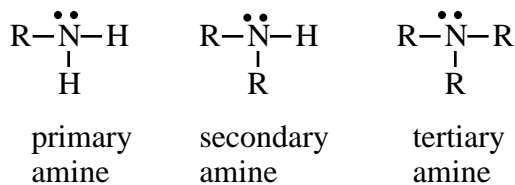


# Chem 4563 Organic Qualitative Analysis

## Amines - Functional Group Tests

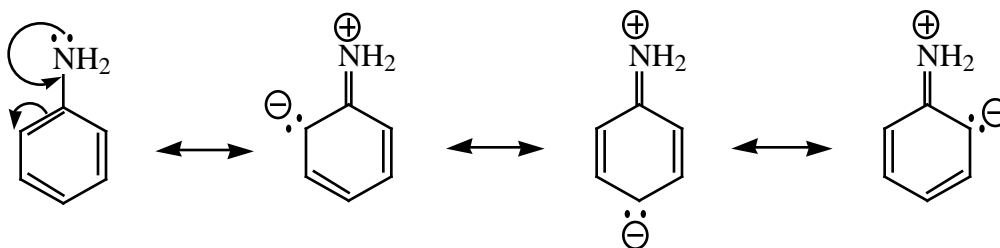
### 1. Introduction

Amines are organic derivatives of ammonia ( $\text{NH}_3$ ) in which one or more of the hydrogens has been replaced by a carbon group, either aliphatic or aromatic. There are three different types of amines:  $1^\circ$  amines which have one carbon group,  $2^\circ$  amines which have two and  $3^\circ$  which have three.

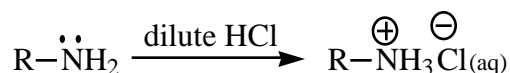


Amines have an unshared pair of electrons on nitrogen and, therefore, act as bases, nucleophiles, and compounds that may be oxidized. As Lewis bases, they form salts with acids and form coordination complexes with metal cations. As nucleophiles they displace halogen from alkyl halides and acyl halides to give more highly alkylated amines and amides, respectively. They may be oxidized by a variety of oxidizing agents including oxygen, permanganate ion, hydrogen peroxide and nitrous acid.

The basicity of an amine is influenced by the number and types of carbon groups attached to the nitrogen atom. Aliphatic amines are stronger bases than ammonia because the alkyl groups are electron donors relative to hydrogen. Aromatic amines are weaker bases than ammonia because delocalization of the unshared electron pair on the nitrogen into the ring lowers the electron density on the nitrogen



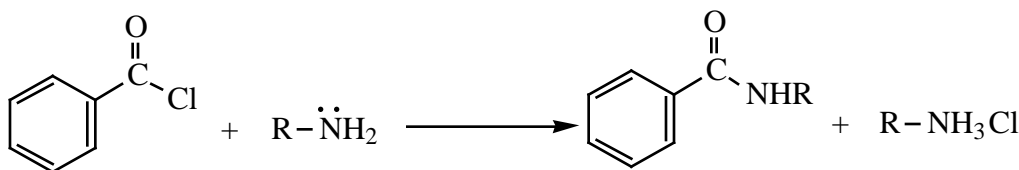
Amines up to approximately five carbon atoms are soluble in water and belong to solubility class  $\text{S}_\text{B}$ . Higher molecular weight amines are insoluble in water, but will dissolve in dilute aqueous hydrochloric acid through the formation of salts forming solubility class B. This provides a convenient method for separating such amines from water insoluble neutral and acid compounds.



Some diaryl- and triarylamines are not basic due to the extensive delocalization of the nitrogen lone-pair into the aromatic rings.

### 2. Acid Chloride Test

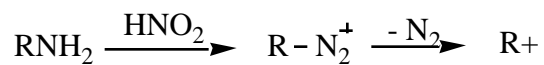
Amines react as nucleophiles toward acyl(acid) chlorides to give amides. This reaction can be used to indicate the possibility of an amine functional group. The suspected amine is added to benzoyl chloride, as the reaction occurs heat is released, and the test tube gets warm.



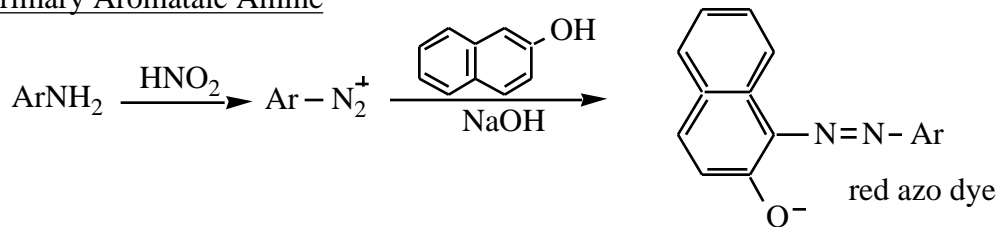
During the course of this reaction  $\text{HCl}$ , a gas, is formed, but no bubbling of gas is observed because the  $\text{HCl}$  reacts with unreacted amine forming the hydrochloride salt.



Primary Aliphatic Amine

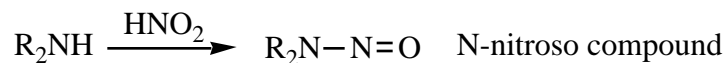


Primary Aromatic Amine



Secondary amines (both aliphatic and aromatic) do not form diazonium salts upon treatment with nitrous acid. However, they do form N-nitroso compounds, which will then precipitate out of solution as yellow oils or solids.

Secondary Aliphatic Amine



The greatest utility of the nitrous acid test is the demonstration of primary aliphatic and aromatic amines.