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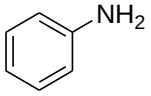
Experiment 13 – Properties of Amines and Amides

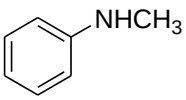
Discussion

Amines and amides are two classes of organic compounds that contain nitrogen. Amines behave as organic bases and may be considered derivatives of ammonia. Amides are compounds that have a carbonyl group connected to a nitrogen atom and are neutral. In this experiment, you will learn about the physical and chemical properties of some members of the amine and amide families.

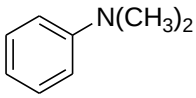
If the hydrogens of ammonia are replaced by alkyl or aryl groups, amines result. Depending on the number of carbon atoms bonded directly to nitrogen, amines are classified as either primary (one carbon atom) secondary (two carbon atoms), or tertiary (three carbon atoms). Consider the following examples:



Aniline
(1° amine)



N-Methylaniline
(2° amine)



N,N-Dimethylaniline
(3° amine)

There are a number of similarities between ammonia and amines that carry beyond the structure such as odor. The smell of amines resembles that of ammonia but is not as sharp. However, amines can be quite pungent. Anyone handling or working with raw fish knows how strong the amine odor can be: raw fish contains low molecular weight amines such as dimethylamine and trimethylamine. Other amines associated with decaying flesh have names suggestive of their odors: consider putrescine and cadaverine shown below.

$NH_2CHCH_2CH_2CH_2NH_2$
Putrescine

$NH_2CHCH_2CH_2CH_2CH_2NH_2$
Cadaverine

The solubility of low molecular weight amines in water is high. In general, if the total number of carbons attached to nitrogen is four or less, the amine is water soluble; amines with a carbon content greater than four are water insoluble. However, all amines are soluble in organic solvents such as diethyl ether or dichloromethane.

Because amines are organic bases, water solutions show weakly basic properties. If the basicity of aliphatic amines and aromatic amines is compared to that of ammonia, aliphatic amines are stronger than ammonia, while aromatic amines are weaker. Amines characteristically react with acids to form ammonium salts; the nonbonded electron pair on nitrogen bonds the hydrogen ion:

$$RNH_2 + HCl \rightarrow RNH_3^+Cl^-$$

Amine Ammonium Salt

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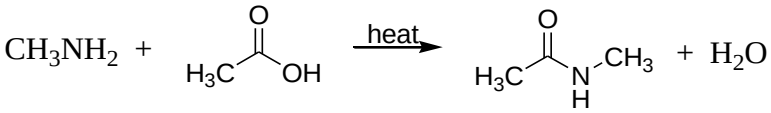
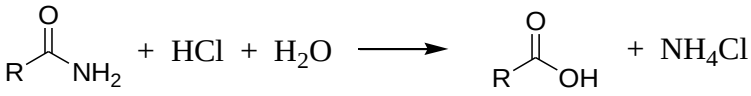
If an amine is insoluble, reaction with an acid produces a water-soluble salt. Because ammonium salts are water soluble, many drugs containing amines are prepared as ammonium salts. After working with fish in the kitchen, a convenient way to rid one's hands of fish odor is to rub a freshly cut lemon over the hands. The citric acid found in the lemon reacts with the amines found on the fish; a salt forms that can be easily rinsed away with water.

Amides are carboxylic acid derivatives. The amide group is recognized by the nitrogen connected to the carbonyl group. Amides are neutral compounds. Under suitable conditions, amide formation can take place between an amine and a carboxylic acid. Along with ammonia, primary and secondary amines yield amides with carboxylic acids. For example:



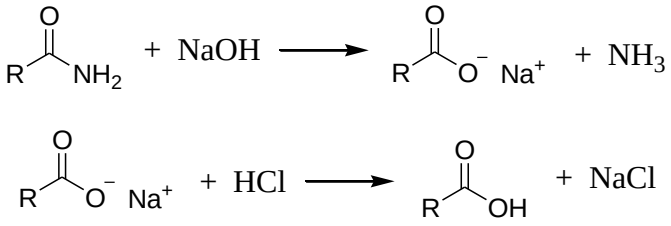
Hydrolysis of amides can take place in either acid or base. Primary amides hydrolyze in acid to ammonium salts and carboxylic acids. Neutralization of the acid and ammonium salts releases ammonia, which can be detected by odor or by litmus.



$$NH_4Cl + NaOH \rightarrow NH_3 + NaCl + H_2O$$

Secondary and tertiary amides would release the corresponding alkyl ammonium salts which, when neutralized, would yield the amine.

In base, primary amides hydrolyze to carboxylic acid salts and ammonia. The presence of ammonia (or amine from corresponding amides) can be detected similarly by odor or litmus. The carboxylic acid would be generated by neutralization with acid.



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Procedure

Caution: Amines are toxic chemicals. Avoid excessive inhaling of the vapors and use gloves to avoid direct skin contact. Anilines are more toxic than aliphatic amines and are readily absorbed through the skin. Wash any amine or aniline spill with large quantities of water. Diethyl ether is extremely flammable. Be certain there are NO open flames in the immediate area. Discard all solutions in properly labeled organic waste containers.

Properties of Amines

1 Place 5 drops of liquid or 0.1 g of solid from the compounds listed in the following table into labeled clean, dry test tubes (100 x 13 mm).

Test Tube No.	*Nitrogen Compound*
1	6 M NH_3
2	Triethylamine
3	Aniline
4	N,N-Dimethylaniline
5	Acetamide

2 Carefully note the odors of each compound. **Do not inhale deeply. Merely wave your hand across the mouth of the test tube toward your nose (i.e., wafting motion) in order to note the odor**. Record your observations on your data sheet.

3 Add 2 mL of distilled water to each of the labeled test tubes. Mix thoroughly by sharply tapping the test tube with your finger. Note on the data sheet whether the amines are soluble or insoluble.

4 Take a glass rod and test each solution for its pH. Carefully dip one end of the glass rod into a solution and touch a piece of pH paper. Between each test, be sure to clean and dry the glass rod. Record the pH by comparing the color of the paper with the chart on the dispenser.

5 Carefully add 2 mL of 6 M HCl to each test tube. Mix thoroughly by sharply tapping the test tube with your finger. Compare the odor and solubility of this solution with previous observations.

6 Place 5 drops of liquid or 0.1 g of solid from the compounds listed in the table into labeled clean, dry test tubes (100 x 13 mm). Add 2 mL of diethyl ether to each test tube. Stopper with a cork and mix thoroughly by shaking. Record the observed solubilities.

7 IN THE HOOD, carefully place a drop of triethylamine and a drop of concentrated HCl on a watch glass, side by side without touching. Record your observations.

Hydrolysis of Acetamide

1. Dissolve 0.5 g of acetamide in 5 mL of 6 M H_2SO_4 in a large test tube (150 x 18 mm). Heat the solution in a boiling water bath for 5 min.
2. Hold a small strips of moist pH paper just inside the mouth of the test tube WITHOUT touching the sides, note any changes in color; record the pH reading. Remove the test tube from the water bath, holding it with a test tube holder. Carefully note any odor.
3. Place the test tube in an ice water bath until cool to the touch. Now *carefully add, dropwise with shaking*, 6 M NaOH to the cool solution until basic. (You will need more than 7 mL of base). Hold a piece of moist pH paper just inside the mouth of the test tube without touching the sides. Record the pH reading. Carefully note any odor.

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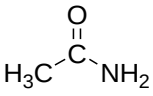
Data and Calculations for Experiment 13

Properties of amines

	Odor		Solubility		pH	
	Original Soln	*with HCl*	*H_2O*	*Ether*	*HCl*	*H_2O*
6 M NH_3						
Triethylamine						
Aniline						
N,N – Dimethylaniline						
Acetamide						

Triethylamine and concentrated hydrochloric acid observation:

Write the chemical equation for the reaction of triethylamine with concentrated hydrochloric acid:

Hydrolysis of Acetamide, 

Solution	*pH Reading*	*Odor Noted*
1. Acid		
2. Base		

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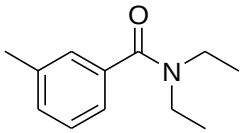
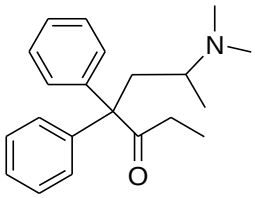
Questions

1. Effective mosquito repellents contain DEET (N,N–diethyl–3–methylbenzamide). If you were to synthesize this compound, what carboxylic acid and amine would you begin with?



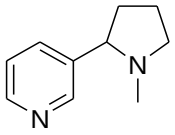
DEET

2. Metadone, a narcotic analgesic shown below, is dispensed as its hydrochloride salt. Explain the usefulness of the salt rather than the amine.



Metadone

3. Nicotine is an alkaloid, meaning base-like. What structural feature is present in the molecule that would make it react as a base?



Nicotine

4. Write the equations that account for what happens in the hydrolysis of the acetamide solution in (A) acid and in (B) base. See the data sheet for the structure of acetamide.

   A.

   B.