Experiment 27
Amines and Amides

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Name:

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Key Objectives

1. Structure of Amines and Amides
2. Physical properties of Amines and Amides
3. Diagnostic tests for Amines and Amides

Discussion

Structure of Amines and Amides

Amines and Amides are organic compounds containing nitrogen. Amines have the functional group $R{-}NH_2$. Amines may be classified similar to alcohols depending on the number of R-groups attached to the nitrogen atom as shown in Figure 27.1). Amides are the nitrogen derivatives of carboxylic acids as shown in Figure 27.1), having a carbonyl carbon attached to the amine group. As with Amines the hydrogen's maybe replaced with R-groups.

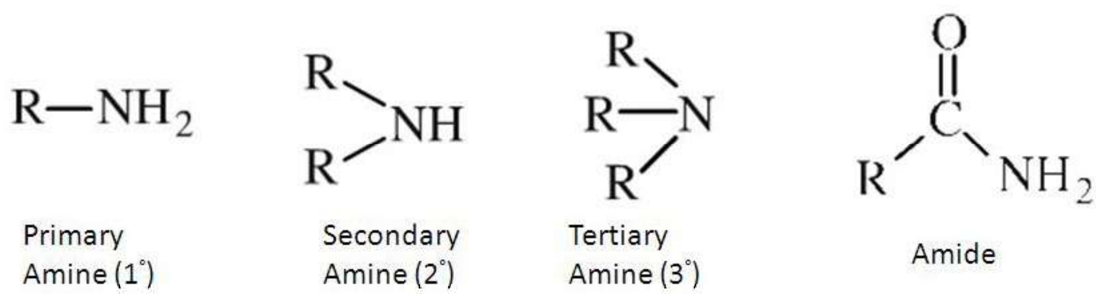


Figure 27.1: Structure of primary, secondary and tertiary amines. A primary amide is also shown (not shown are secondary and tertiary amides). credit: author

Physical Properties of Amines and Amides

In general, primary and secondary amines form weak hydrogen bonds compared to water or alcohols because nitrogen is significantly less electronegative than oxygen. Primary and secondary amides can also form hydrogen bonds and also have a carbonyl carbon allowing additional dipole-dipole interactions to occur. Amide hydrogen bonds are stronger than those found in water due to the electron withdrawing properties of the carbonyl carbon.

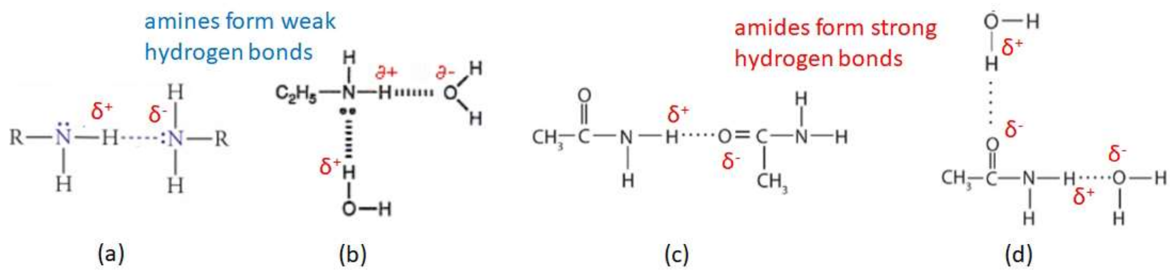


Figure 27.2: Hydrogen bonding between (a) amine an amine (b) amine and water (c) amide and amide and (d) amide and water. Generally amines form weak hydrogen bonds and amides form strong hydrogen bonds. credit: author

All of the amines can form hydrogen bonds with water, though tertiary amines only accept a hydrogen bond from water (due to having a lone pair of electrons). Solubility falls off as the hydrocarbon chains get longer after about six carbons, due to the increasing influence of the London Dispersion forces in the alkane chain. The hydrocarbon chains have to force their way between water molecules, breaking the attractive hydrogen bonds between water molecules. However, they don't replace them by anything as strong, and so the process of forming a solution becomes less and less energetically feasible as chain length grows.

Despite being able to form hydrogen bonds, primary and secondary amines have boiling points between alkanes and alcohols as the hydrogen bonds formed between amines is relatively weak compared to the hydrogen bonds formed between alcohols Tertiary amines can only form a dipole-dipole interaction between themselves. Amides on the other had have very high boiling points, higher than even carboxylic acids due to the electron withdrawing properties of the carbonyl carbon making the amide hydrogen bonds very strong compared to those of alcohols.

Amines with low molecular weights have sharp penetrating odors similar to ammonia. Amines with higher molecular weights smell like decaying fish. Two compounds responsible for the odor of decaying animal tissue have the common graphic names putrescine and cadaverine as shown in Figure 27.3.

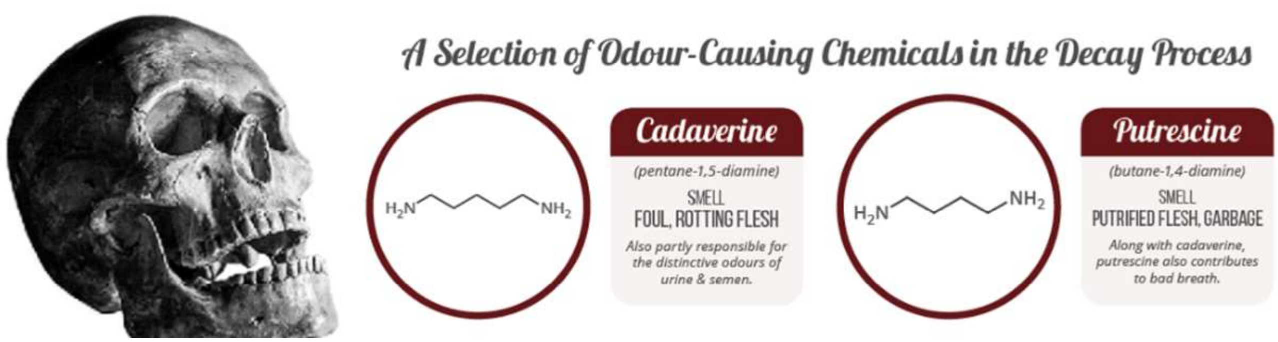


Figure 27.3: Amines are responsible for some really really really nasty smells! credit: `http://www.compoundchem.com/wp-content/uploads/2014/10/The-Chemistry-of-the-Smell-of-Death.png`

Amines and amides are a part of many important biological molecules like amino acids, proteins, DNA, RNA and are also found in many drugs and important medicines. amines exhibit physiological activity. Amides are often used as polymers, both commercially, as in nylon, and biologically forming the backbone of proteins. Figure 27.4 shows several examples of important amines and amides.

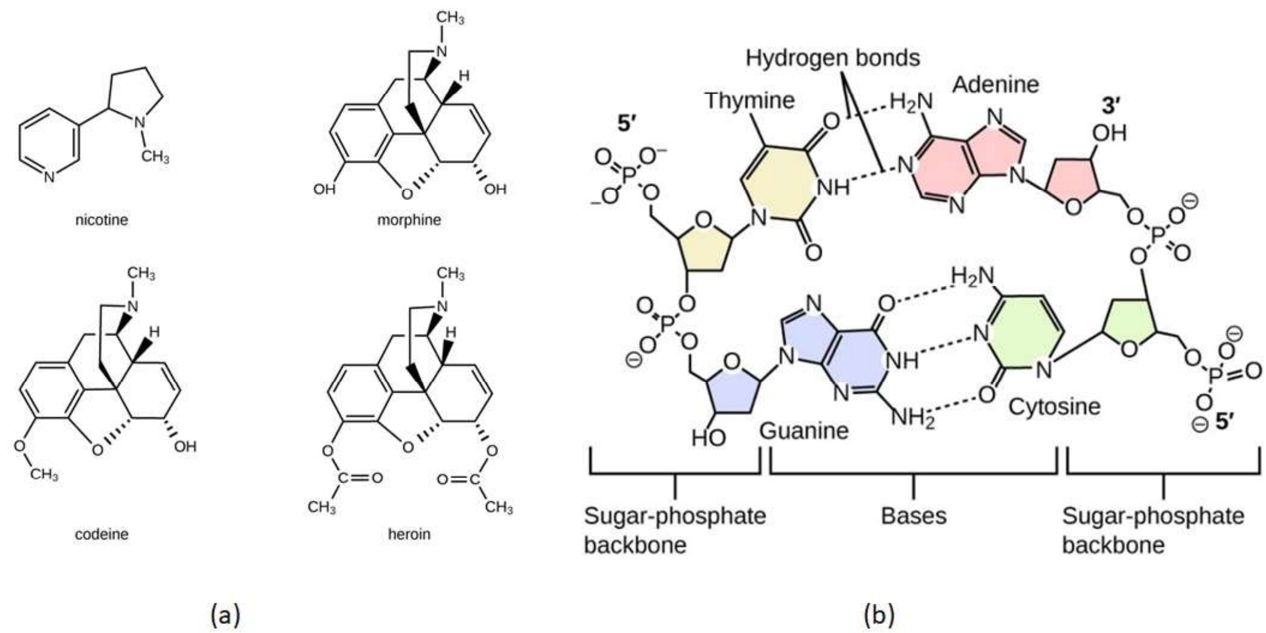
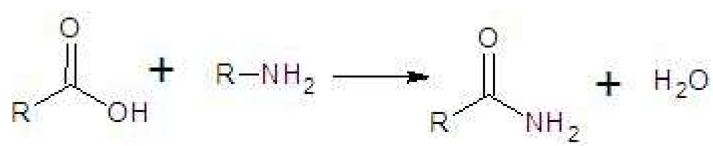


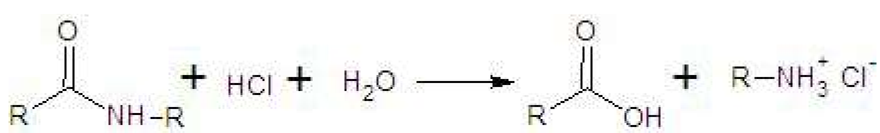
Figure 27.4: Some examples of important amines and amides (a) Found in drugs and medicines (b) component of DNA and RNA. credit: `https://courses.lumenlearning.com/chemistryformajors/chapter/amines-and-amides/`

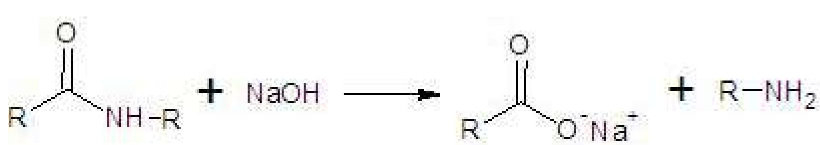
Chemical Properties - Amides

Amides are formed by the reaction of a carboxylic acid with ammonia or an amine.



Amides like Esters may be hydrolysed in either acid or base conditions.





Chemical Properties - Amines

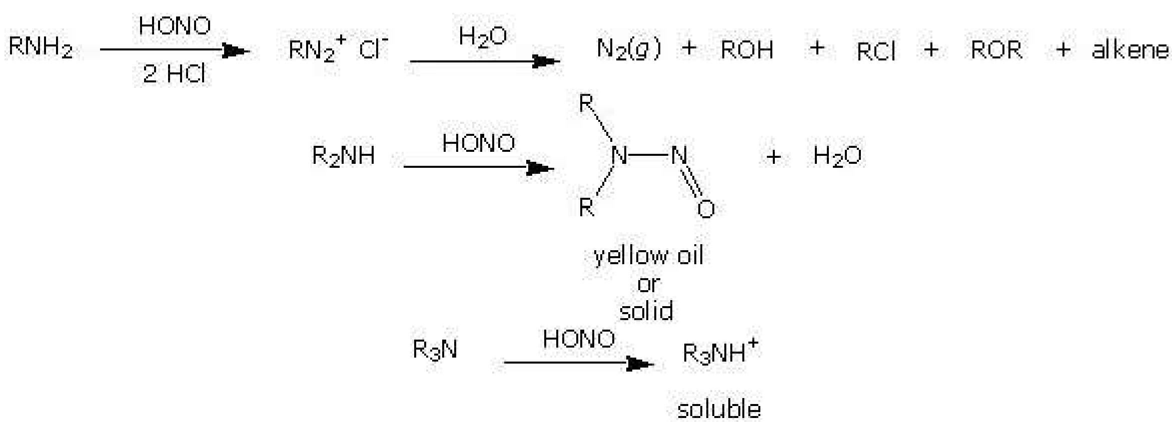
Amines are considered weak bases due to the unshared pair of electrons which can attract a proton from a water molecule.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + HO^-$$

Because amines are bases, they can react with acids to form amine salts. These salts often much more soluble then the original amine.

$$R{-}NH_2 + HCl \longrightarrow R{-}NH_3^+ Cl^-$$

Primary, Secondary and Tertiary amines maybe distinguished from each other by their reaction with Nitrous Acid (HONO). Primary amines react to form N_2 gas, secondary amines form a yellow oil or solid, while tertiary amines do not react.



Procedure

A. Solubility of Amines in Water and Acid

1. Perform the following in the hood.
2. Add 5 drops of each amine to a separate test tube.
3. Carefully detect the odor of all the compounds by carefully wafting. Record your observations.
4. Add 2 mL of water to each test tube. Stir vigorously. Record your observations.
5. Wait 2-3 minutes and record your results.
6. Determine the pH of each solution using a stirring rod and pH paper.
7. Add 10% HCl drop-wise to each solution until the solution is acidic to blue litmus paper. Record your results. Note any color changes or odors.
8. Write a balanced chemical reaction for each neutralization that occurred in the previous step.
9. Dispose of the contents of the test tubes in the appropriately labeled waste bottle".

B. Solubility of Amides in Water and Acidic Solutions

1. Add 5 drops or a pea sized sample of each amide to a separate test tube.
2. Carefully detect the odor of all the compounds by carefully wafting. Record your observations.
3. Add 2 mL of water to each test tube. Stir vigorously. Record your observations.
4. Wait 2-3 minutes and record your results.
5. Determine the pH of each solution using a stirring rod and pH paper.
6. Add 10% HCl drop-wise to each solution until the solution is acidic to blue litmus paper. Record your results. Note any color changes, odors or changes in solubility.
7. Write a balanced chemical reaction for each neutralization that occurred in the previous step.
8. Place each test tube in boiling water bath. Carefully hold a wet strip (using water) of red litmus paper over the mouth of each test tube. Record your results. Heat the test tubes for 5 minutes.
9. Carefully detect the odor of all the compounds by carefully wafting. Record your observations.
10. Dispose of the contents of the test tubes in the appropriately labeled waste bottle".

C. Solubility of Amides in Basic Solutions

1. Add 5 drops or a pea sized sample of each amide to a separate test tube.
2. Add 2 mL of water to each test tube. Stir vigorously. Record your observations.
3. Record the pH.
4. Add 2 mL of 10% NaOH solution. Stir vigorously. Record your observations. Note any color changes or odors.
5. Wait 2-3 minutes and record your results.
6. Record the pH.
7. Place each test tube in boiling water bath. Carefully hold a wet strip (using water) of red litmus paper over the mouth of each test tube. Record your results. Heat the test tubes for 5 minutes.
8. Carefully detect the odor of all the compounds by carefully wafting. Record your observations.
9. Dispose of the contents of the test tubes in the appropriately labeled waste bottle".

D. Distinguishing Primary, Secondary and Tertiary Amines

1. Perform the following in the hood. Dissolve 0.5 mL of the amine in 2.5 mL of water. Carefully (drop-wise) add 1.5 mL of concentrated HCl.
2. Cool the resulting solution in an ice-water bath for 5 minutes.
3. In a separate test tube dissolve 2.0 g of sodium nitrite in 10.0 mL of water.
4. Add 2.5 mL if the sodium nitrite solution (made in the previous step) 5 drops at a time to the test tube containing the amine to be tested. Keep the test tube immersed in the ice water bath at all times except to briefly mix the solution between adding drops. Test for the formation of nitrous acid after each addition of sodium nitrite by placing a drop of the solution on starch-iodide paper, a blue color indicates the formation of nitrous acid. Continue the addition until the mixture gives a positive test for nitrous acid.
5. Remove 2.0 mL of the resulting solution and slowly warm it to room temperature in a water bath. Record your observations.
6. Dispose of the contents of the test tubes in the appropriately labeled waste bottle".

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Results

A. Solubility of Amines in Water and Acid

	1-hexanamine	diethyl amine	triethylamine	N-methylaniline
Odor				
Initial Solubility in Water				
Solubility in Water after 2-3 minutes				
pH				
Reaction Products for Amine + H_2O				
Observations after addition of HCl (Odor, Color, Solubility)				
Reaction product after addition of HCl				

Table 27.1: Results - Solubility in Water and Acid

B. Solubility of Amides in Water, and Acidic Conditions

	Acetamide	Benzamide	Acetanilide	TBA
Odor				
Intitial Solubility in Water				
Solubility in Water after 2-3 minutes				
pH				
Observations after addition of HCl (Odor, Color, Solubility)				
Observations after heating: (pH paper)				
Observations after heating: (Odor, color and Solubility)				

Table 27.2: Results - Amide Solubility in Water and Acidic Solutions

C. Solubility of Amides in Basic Conditions

	Acetamide	**Benzamide**	**Acetanilide**	**TBA**
Initial pH				
Observations after addition of NaOH (Odor, Color, Solubility)				
pH				
Effect of gas formed on Red Litmus Paper				
Observations after heating (Odor, Color, Solubility)				
Chemical Reaction				

Table 27.3: Results - Amide Solubility in Basic Conditions

D. Primary, Secondary and Tertiary Amines

	1-hexanamine	Diethylamine	Triethylamine	N-methylaniline
Initial Observations				
Observations on addition of sodium nitrite (in icewater)				
Observations on warming to room temperature				
Conclusion: 1°, 2°, or 3°				

Table 27.4: Results - Primary, Secondary and Tertiary Amines

Questions

1. Which amines were soluble in water?

2. Which amines were insoluble in water?

3. What conclusion(s) can you make relating amine structure and solubility in water? Explain.

4. Write the chemical equation for the hydrolysis of acetamide under acidic conditions (assume HCl).

5. Write the chemical equation for the hydrolysis of acetamide under basic conditions (assume NaOH).

6. Amines are responsible for the nasty odor of many substances including the odor of fish. Explain why lemon juice might remove the odor of fish.

7. You have 3 unknowns, a carboxylic acid, an ester, and an amine. Describe how you might distinguish between them. (Don't bother asking me, I don't know the answer).

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Prelab Questions

1. Draw the structure of the following organic molecules. For ionic compounds simply give the chemical formula. For amines and amides label them as primary, secondary or tertiary.

(a) Aniline	(b) N-methylaniline
(c) Diethylamine (N-ethylethanamine)	(d) Triethylamine (N,N-diethylethanamine)
(e) 1-hexanamine	(f) Acetamide (ethanamide)
(g) Benzamide	(h) Acetanilide (N-phenylethanamide)
(i) Sodium Nitrite	(j) Nitrous Acid

Amazing! We keep bumping into each other. It must be fate. I like to listen to music, do you? What is your favorite band?