

23.16: Reactions of Amines—General Features

The basic properties of amines

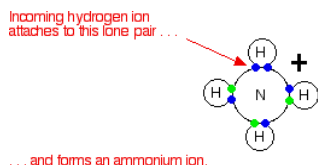
We are going to have to use two different definitions of the term "base" in this page. A base is

- a substance which combines with hydrogen ions. This is the Bronsted-Lowry theory.
- an electron pair donor. This is the Lewis theory.

The easiest way of looking at the basic properties of amines is to think of an amine as a modified ammonia molecule. In an amine, one or more of the hydrogen atoms in ammonia has been replaced by a hydrocarbon group. Replacing the hydrogens still leaves the lone pair on the nitrogen unchanged - and it is the lone pair on the nitrogen that gives ammonia its basic properties. Amines will therefore behave much the same as ammonia in all cases where the lone pair is involved.

The reactions of amines with acids

These are most easily considered using the Bronsted-Lowry theory of acids and bases - the base is a hydrogen ion acceptor. We'll do a straight comparison between amines and the familiar ammonia reactions. Ammonia reacts with acids to produce ammonium ions. The ammonia molecule picks up a hydrogen ion from the acid and attaches it to the lone pair on the nitrogen.



If the reaction is in solution in water (using a dilute acid), the ammonia takes a hydrogen ion (a proton) from a hydroxonium ion. (Remember that hydrogen ions present in solutions of acids in water are carried on water molecules as hydroxonium ions, H_3O^+ .)

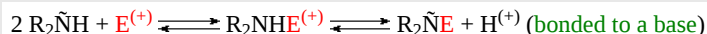
If the acid was hydrochloric acid, for example, you would end up with a solution containing ammonium chloride - the chloride ions, of course, coming from the hydrochloric acid. You could also write this last equation as:

... but if you do it this way, you must include the state symbols. If you write H^+ on its own, it implies an unattached hydrogen ion - a proton. Such things don't exist on their own in solution in water. If the reaction is happening in the gas state, the ammonia accepts a proton directly from the hydrogen chloride:

This time you produce clouds of white solid ammonium chloride

Electrophilic Substitution at Nitrogen

Ammonia and many amines are not only bases in the Brønsted sense, they are also nucleophiles that bond to and form products with a variety of electrophiles. A general equation for such **electrophilic substitution of nitrogen** is:



A list of some electrophiles that are known to react with amines is shown here. In each case the electrophilic atom or site is colored red.

Electrophile	$\text{RCH}_2\text{-X}$	$\text{RCH}_2\text{-OSO}_2\text{R}$	$\text{R}_2\text{C=O}$	R(C=O)X	$\text{RSO}_2\text{-Cl}$	HO-N=O

Name	Alkyl Halide	Alkyl Sulfonate	Aldehyde or Ketone	Acid Halide or Anhydride	Sulfonyl Chloride	Nitrous Acid
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