

Notes on organic nitrogen compounds

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1 Introduction

Organic nitrogen compounds consists of amines, amides, amino acids, and proteins.

2 Formation and reactions of amines

Amines are organic compounds based on ammonia, where one or more of the hydrogen atoms have been substituted with either an alkyl or an aryl group. They are mostly associated with smelly odours. When ammonia is heated under pressure with a halogenoalkane, some of the hydrogen atoms on the ammonia are replaced by the alkyl groups, producing amines:



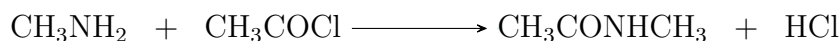
which is then followed by:



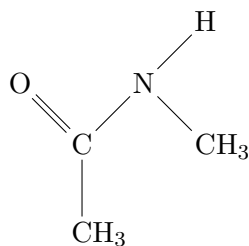
finally followed by:



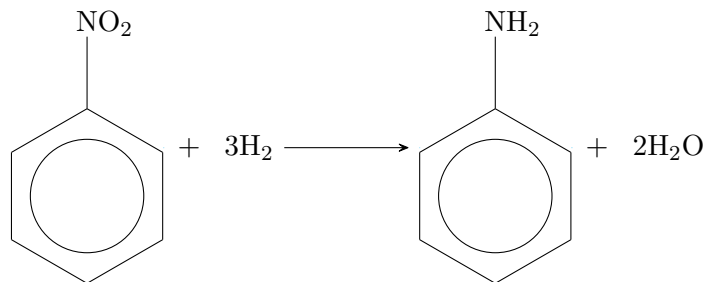
The number of alkyl groups indicates whether the amine is primary, secondary, or tertiary. A tertiary amine has three alkyl groups, and a secondary amine has two alkyl groups, leaving the primary amine which only has one alkyl group. The degree of the amine affects the properties of the amine. Amides can be produced using either a primary or secondary amine to react with an acyl chloride by substituting the N—H bond with an RCO— group:



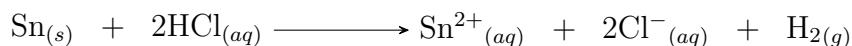
And this is the structure of the product N-methylethanamide:



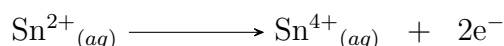
Nitrobenzene can be reduced to form phenylamine using a mixture of tin and concentrated hydrochloric acid:



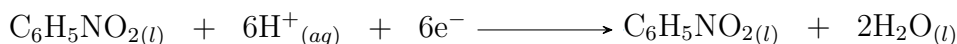
The reaction is carried out in reflux condensation apparatus. The tin reacts with the hydrochloric acid to produce tin (II) ions and hydrogen:



Then the tin (II) ions are further oxidised to tin (IV) ions which then go on to reduce the NO_2 group in the nitrobenzene to NH_2 group:



which is then followed by:



After this, the round bottom flask is then cooled and sodium hydroxide solution is added to dissolve the initial precipitate of tin (IV) hydroxide. Tin (IV) hydroxide ($\text{Sn}(\text{OH})_4$) is amphoteric, so with excess alkali, the soluble $\text{Sn}(\text{OH})_6^{2-}$ ion is produced.

Water is then added, and steam distillation takes place to separate the mixture of phenylamine and water. The distillate collected initially will be cloudy because it is an emulsion of phenylamine and water. Powdered sodium chloride is added to the distillate and the mixture is transferred to a separating funnel.

This is shaken well and since phenylamine is significantly less soluble in saturated sodium chloride solution in comparison to water, the phenylamine is separated from the water. This process is called salting out. Ethoxyethane is added and shaken, relieving the pressure occasionally by opening the tap.

The layers are allowed to separate and then the lower aqueous layer is run off into a small beaker. The ethoxyethane layer is then transferred to a small conical flask, and further extraction of the aqueous layer with further portions of ethoxyethane is carried out.

The ethoxyethane extracts are combined. This is known as solvent extraction. Pellets of potassium hydroxide are added to dry the ethoxyethane extract and remove any excess acid. This mixture is distilled off, collecting the fraction at around 182°C .

2.1 Properties of Amines

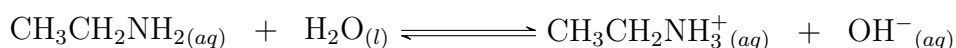
Alkylamines with short carbon chains usually exist as gases or volatile liquids. Primary and secondary amines can sometimes form hydrogen bonds with each other due to the electronegative nitrogen atom connected to at least one hydrogen atom, like that in ammonia.

In tertiary amines, hydrogen bonding is not possible, so the only interactive forces are van der Waals forces otherwise known as London dispersion forces. This phenomenon explains why trimethylamine boils at a lower temperature in comparison to both methylamine and dimethylamine.

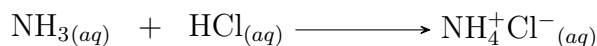
Aryl amines are usually less volatile and are usually liquids at room temperature. They are not as soluble in water since the aromatic properties of the benzene group severely outweigh the ability for the -NH_2 to form hydrogen bonds with the water. They are instead more likely to dissolve in an organic solvent.

Short chain amines are miscible in water, since amine can form hydrogen bonds with the amine molecules. A solution of an amine in water is alkaline and are more basic than ammonia in water. The nitrogen atom acts as a proton acceptor, and therefore a base.

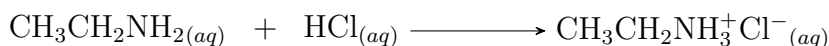
The alkyl amines are usually stronger bases than ammonia due to their shift of electrons from the alkyl group, increasing the electron density on the nitrogen atom, meaning the nitrogen atom can hold a proton with more strength.



Ammonia can form salts with acids:



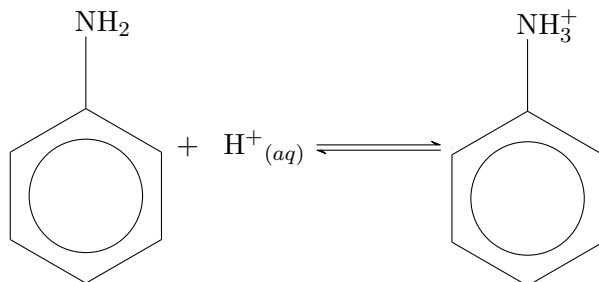
Amines can also form salts with acids using the same way:



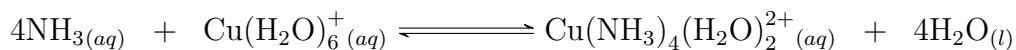
The above reaction can be monitored by temperature change since it is exothermic. The ethylamine will lose its fishy smell during the reaction. Phenylamine, an example of an aryl amine, is a weaker base than ammonia since the nitrogen atom donates electron density to the π system of delocalised electrons in the benzene ring.

This means there is less electron density on the nitrogen atom, and therefore the nitrogen atom has less strength to hold onto a proton.

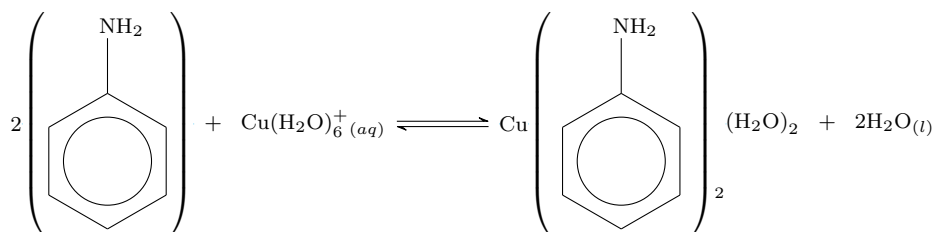
Phenylamine will however form a salt with strong acids, where the excess H^+ ions move the equilibrium to the right, thus allowing the production of the salt:



Ammonia also forms complex ions with transition metal cations:



Amines form a complex in a similar manner:



2.2 Making Paracetamol