Chem Factsheet

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Amines

To succeed in this topic you need to:-
- Remember organic nomenclature ideas from AS Chemistry (Factsheets 15, 16 and 17)
- Be familiar with terminology related to organic mechanisms (Factsheet 16)
- Understand the link between inter-molecular forces and boiling points
- Know the meaning of the term *weak* as applied to acids and bases
- Understand that acid-base equilibria involve proton transfer

After working through this Factsheet you will:-
- Know about the characteristic structures and properties of amines
- Know about the characteristic reactions of amines
- Know the standard methods of preparation of amines
- Know the mechanisms associated with the reactions of amines
- Understand the importance of amines

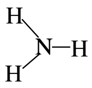
A discussion of amines is best divided into a series of categories: Structure and Nomenclature; Physical Properties; Basic Characteristics; Nucleophilic Behaviour and Preparations.

The Structure of Amines

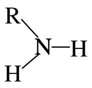
Amines are derivatives of ammonia, NH_3.

A primary amine is, in structural terms an ammonia molecule in which one of the hydrogen atoms has been substituted for by a hydrocarbon group such as an alkyl group, RNH_2.

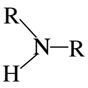
A secondary amine has two of the hydrogen atoms in ammonia replaced with such groups, R_2NH and a tertiary, three, R_3N. Quaternary ammonium salts (equivalent to ammonium salts, NH_4^+) are also found, R_4N^+.



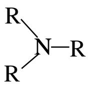
Ammonia



Primary amine



Secondary amine



Tertiary amine

There are, unfortunately, alternative naming systems for amines so you will have to check your specification to see which is required by your exam board. Firstly, there is the "alkylamine" style of naming:

CH_3NH_2	methylamine
$CH_3CH_2NH_2$	ethylamine
$(CH_3)_2NH_2$	dimethylamine etc.

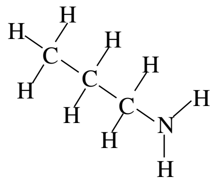
Alternatively, the "aminoalkane" style can be used:

CH_3NH_2	aminomethane
$CH_3CH_2NH_2$	aminoethane
$(CH_3)_2NH$	N-methylaminomethane etc.

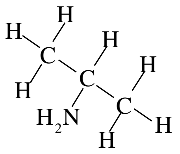
(The N indicates that the second CH_3 group is bonded to the N of the primary amine, CH_3NH_2, to form this secondary amine. Similarly, $CH_3CH_2N(CH_3)_2$ is N, N-dimethylaminoethane.

You might also encounter the system which uses "alkanamine" style. e.g. CH_3NH_2 (methanamine), $CH_3CH_2NH_2$ (ethanamine) etc.

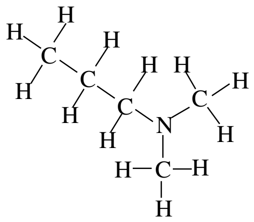
Alternative names for a few examples are shown below:



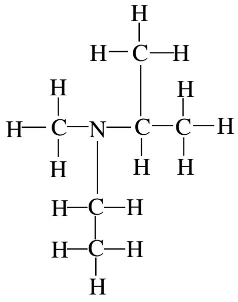
1-propylamine
or 1-aminopropane
or propan-1-amine



2-propylamine
or 2-aminopropane
or propan-2-amine



N,N-dimethyl-1-aminopropane
or dimethylpropylamine
or N,N-dimethylpropan-1-amine



N-ethyl-N-methyl-2-aminopropane
or ethylmethyl-2-propylamine
or N-ethyl-N-methyl-propan-2-amine

Preparation of Amines

Primary aliphatic amines can be made from halogenoalkanes, nitriles or nitro compounds.

1. Halogenoalkane method:

Ammonia (in *ethanolic solution* to minimise hydrolysis of the halogenoalkane to an alcohol and increase miscibility) is reacted with a halogenoalkane.

e.g. $CH_3CH_2Br + 2NH_3 \rightarrow CH_3CH_2NH_2 + NH_4Br$

In this reaction the ammonia molecules fill two different roles. The first acts as a nucleophile and attacks the δ+ carbon atom resulting in *nucleophilic substitution*.

$CH_3CH_2Br + NH_3 \rightarrow CH_3CH_2NH_3^+ + Br^-$

And then the second acts as a base, accepting a proton from the ethylammonium ion

$CH_3CH_2NH_3^+ + NH_3 \rightarrow CH_3CH_2NH_2 + NH_4^+$

The *problem with this method* is that the primary amines produced are themselves nucleophiles (in fact, a primary amine is a better/stronger nucleophile than ammonia as the electron-releasing character of the alkyl group makes the nitrogen more δ- and the lone pair more available in the primary amine than in ammonia) and so further substitution is possible, leading to secondary amines, tertiary amines and even quarternary ammonium salts. However, use of a large excess of ammonia can minimise production of secondary amines, tertiary amines and quarternary ammonium salts.

2. Nitrile Method

This involves *reduction* using either $LiAlH_4$ (in ether) or hydrogen gas with a nickel catalyst

In general: $RC{\equiv}N + 4[H] \rightarrow RCH_2NH_2$

Nitriles can readily be prepared from halogenoalkanes by nucleophilic substitution using KCN in ethanol.

$R\text{-}Br + KCN \rightarrow R\text{-}CN + KBr$

This method gives a more efficient method for producing amines as there is much less chance of unwanted by-products being formed. However, it is a two-stage process!

3. Nitro Compound Method

In the case of *aromatic amines* the most common method used is the *reduction of an aromatic nitro compound* using tin and concentrated hydrochloric acid or hydrogen gas with a nickel catalyst.

e.g. $C_6H_5NO_2 + 6[H] \rightarrow C_6H_5NH_2 + 2H_2O$

nitrobenzene phenylamine /aminobenzene

NB If a mixture of Sn and HCl is used then the acidity of the reaction mixture means that the initial product will actually be $C_6H_5NH_3^+$, which must be treated with an aqueous solution of sodium hydroxide to generate the amine.

$C_6H_5NH_3^+ + OH^- \rightarrow C_6H_5NH_2 + H_2O$

Both aliphatic and aromatic amines can be produced by reduction of a corresponding nitrile with Ni/H_2 but only aliphatic amines can be produced by nucleophilic substitution of the equivalent halogeno-compound.

Why is it not possible to form an aromatic amine by reacting ammonia with a halogenoarene such as bromobenzene?

The production of a primary amine from ammonia and a halogenoalkane depends on a nucleophilic attack by the lone pair of the nitrogen in ammonia on the δ+ carbon in the halogenoalkane. The delocalised electron cloud of the arene (benzene) group will repel the lone pair on the ammonia's nitrogen making such an attack impossible. In addition, the delocalisation strengthens the carbon-halogen bond in the halogenoarene and reduces its polarity by comparison with a halogenoalkane.

Physical Properties of Amines

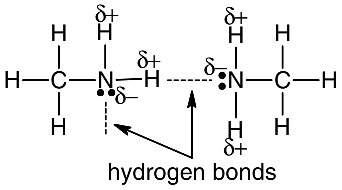
1. Boiling Points

Methylamine (b.pt.-6.3°C) and ethylamine (b.pt. 16.6°C) are both gases at room temperature but the remaining primary amines are liquids.

Why are boiling points of amines so much higher than similar sized alkenes and why do the boiling points of the amines increase with increasing chain length?

A useful comparison is between methylamine, CH_3NH_2, and ethane, CH_3CH_3, as they each have the same number of electrons and virtually the same shape (so that the strength of van der Waal's can be assumed to be almost identical) yet ethane's boiling point of -88.6°C is much lower than that of methylamine.

This difference is explained by the ability of amines to form intermolecular hydrogen bonds due to the polarity of the functional group, while alkanes can only form much weaker van der Waal's forces.



However, the increasing boiling points within the primary amines must be due to increasing van der Waal's forces since the hydrogen-bonding occurs between all amines.

It is worth noting that tertiary amines have much lower boiling points than primary or secondary amines as, although their structures contain a δ- nitrogen atom, there are no δ+ hydrogen atoms in the molecules. The only intermolecular forces present are therefore van der Waal's forces.

2. Solubility in Water

How does hydrogen bonding ability account for the solubility of short chain amines in water and why does the solubility decrease with increasing chain length of amine?

The ability to form hydrogen bonds also helps to explain the high solubility of short chain amines in water and the decreasing solubility with increasing M_r.

Any dissolving process depends on the solute-solvent attractions being strong enough to release enough energy to compensate for the endothermic breaking of the attractive forces between the solvent molecules in order for the solute particles to 'fit in between' them. Dissolving in water therefore depends on the solute being able to form strong enough attractions to compensate for the energy needed to break the hydrogen bonds between water molecules. Amines can form their own hydrogen bonds with water molecules. However, the longer the chain of the amine the greater the disruption of hydrogen bonding in water whilst the hydrogen-bonding ability of the amine remains constant, as it's due to the $-NH_2$ group. Hence, the balance becomes less favourable the longer the chain.

Basic Character of Amines

Ammonia is a weak base due to the ability of the lone pair on the nitrogen atom to accept hydrogen ions in a reversible reaction:

$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

Primary aliphatic amines are also weakly basic:

$RNH_2(aq) + H_2O(l) \rightleftharpoons RNH_3^+(aq) + OH^-(aq)$

Since they are basic, they react with acids to form salts which are related to ammonium (NH_4^+) salts:

e.g. $RNH_2 + HCl \rightarrow RNH_3^+Cl^- + H_2O$

The alkyl group attached to the $-NH_2$ group in an amine makes amines stronger bases than ammonia as the electron-releasing character of the alkyl group makes the lone pair of electrons on the nitrogen *more available* for co-ordinate bond formation to the H^+ ion, than it is in ammonia.

Primary aromatic amines are weaker bases than ammonia as the lone pair on the nitrogen atom delocalises with the delocalised electrons in the benzene ring and the electrons are *thus less available* for co-ordinate bond formation.

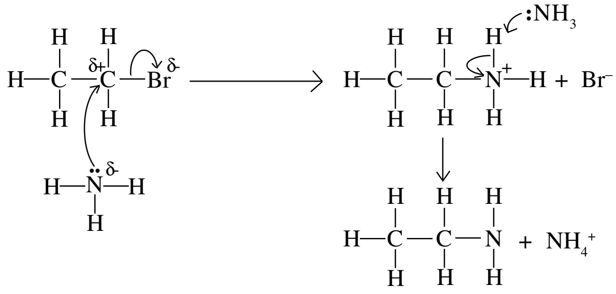
These effects are shown by the pK_b values which decrease with increasing basicity.

Name	Formula	pK_b
Phenylamine	$C_6H_5NH_2$	9.37
Ammonia	NH_3	4.76
Methylamine	CH_3NH_2	3.38
Ethylamine	$CH_3CH_2NH_2$	3.36

Nucleophilic Behaviour of Amines

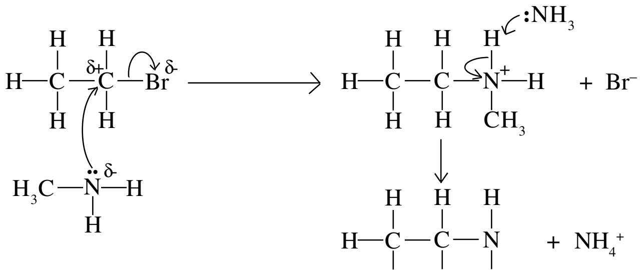
Ammonia and amines have nucleophilic properties since they can provide the lone pair on the δ- nitrogen atom to form a bond.

This is evident in the reaction of ammonia with a halogenoalkane

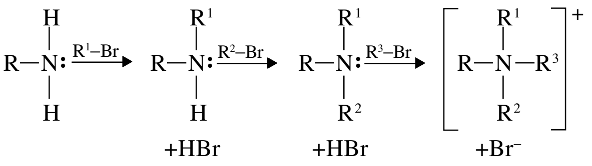


With a primary amine as the nucleophile the sequence will be exactly the same; resulting in the production of a secondary amine. A secondary amine will produce a tertiary amine and a tertiary amine reacting with a halogenoalkane leads to the formation of a quarternary ammonium salt.

e.g. with methylamine:



And overall:



Acylations

Amines, like many other molecules containing either N-H or O-H bonds, can be "*acylated*" using an acyl chloride, [RCOCl], or an acid anhydride, [RCO.OCO.R]. The result is the substitution of the H of N-H by an acyl group, RCO, to form an *N-substituted amide*. Acylations are usually considered as a general reaction applying to ammonia, water, alcohols, amines phenols etc – a thorough consideration, including the *nucleophilic addition-elimination mechanism* can be found in FactSheet 133.

However, as an example, ethylamine is acylated by ethanoyl chloride or ethanoic anhydride to form *N*-ethylethanamide.

$$CH_3CH_2NH_2 + \mathbf{CH_3CO}Cl \rightarrow \mathbf{CH_3CO}NHCH_2CH_3 + HCl$$

$$CH_3CH_2NH_2 + \mathbf{CH_3CO}.OCO.CH_3 \rightarrow \mathbf{CH_3CO}NHCH_2CH_3 + CH_3COOH$$

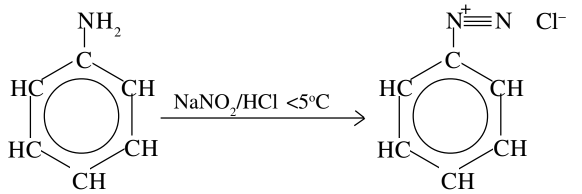
Cationic Surfactants (AQA Only)

The AQA syllabus expects you to *remember* that quarternary ammonium salts are used as cationic surfactants to reduce the surface tension of water and so improve its 'wetting' ability.

Diazotisation (EDEXCEL and OCR Only)

Reaction of an ***aromatic amine*** with cold nitrous acid, HNO_2, produces the diazonium ion, ArN_2^+, which, in turn, can be used in a coupling reaction with an aromatic amine or a phenol to produce a dyestuff.

Nitrous acid is itself unstable so it has to be generated *in situ* from an ice-cold mixture of sodium nitrite (nitrate(IV)) and hydrochloric acid.

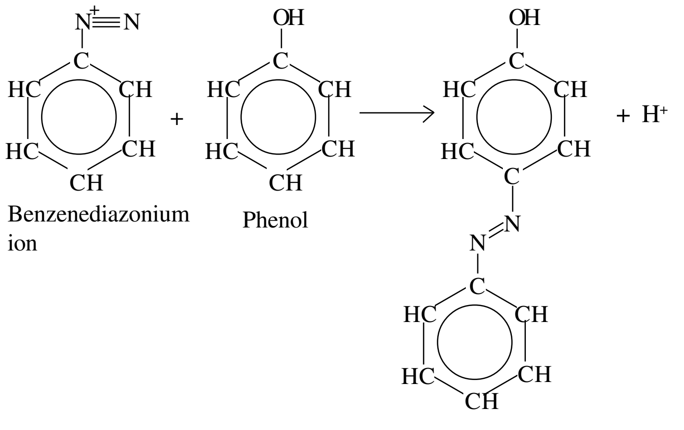


Phenylamine

Benzenediazonium chloride

The subsequent coupling reaction, with phenol, must be carried out below 10°C to avoid the hydrolysis of the benzenediazonium ion into phenol and nitrogen gas.

$ArN_2^+ + H_2O \rightarrow Ar\text{-}OH + H^+ + N_2$



Benzenediazonium ion

Phenol

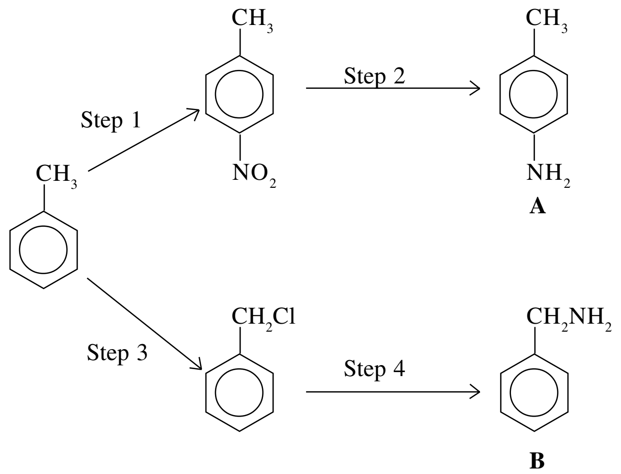
An Azo Dye

What is the diazonium ion behaving as in the coupling reaction and what name is given to the overall mechanism of the reaction?

The diazonium ion acts as an electrophile, attacking the electron dense benzene ring. The mechanism is electrophilic substitution – typical of benzene compounds.

Practice Questions

1. The following reaction scheme shows the formation of two amines, **A** and **B**, from methylbenzene.



(a) Give the reagents needed to carry out Step 2. Write equations for the reactions.
(b) Give the reagents needed to carry out Step 4. Write an equation for the reaction.

2. (a) Name and outline a mechanism for the formation of aminoethane from bromoethane.
(b) State why the amine formed is contaminated with other amines.
(c) Suggest how the reaction conditions could be modified to minimise this contamination.
(d) How can aminoethane be made from bromomethane?
(e) Suggest one reason why phenylamine (aminobenzene) ***cannot*** be prepared from bromobenzene in a similar way.
(f) Outline a synthesis of phenylamine from benzene.

3. (a) Draw the structure of a tertiary amine which is an isomer of butylamine.
(b) Pentylamine can also be prepared in a two-step synthesis starting from 1-bromobutane. Write an equation for each of the two steps in this synthesis.
(c) Explain why butylamine is a stronger base than ammonia.
(d) Explain why phenylamine (aminobenzene) is a weaker base than ammonia.
(e) Writing equations, explain why pentylamine is not very soluble in water but easily dissolved in dilute hydrochloric acid

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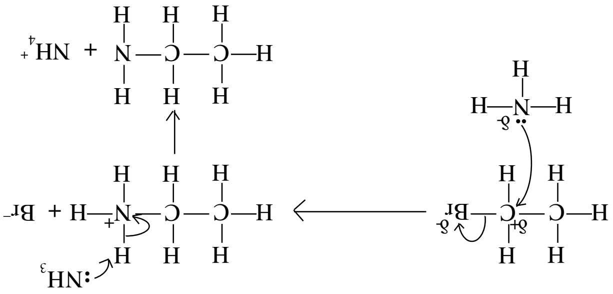
Answers

1. (a) *Tin and hydrochloric acid* for the main reduction reaction. This must be followed by *addition of dilute sodium hydroxide* to release the amine from the phenylammonium salt formed in the presence of the acid.
$CH_3C_6H_4NO_2 + 6[H] \rightarrow CH_3C_6H_4NH_2 + 2H_2O$
$CH_3C_6H_4NH_2 + HCl \rightarrow CH_3C_6H_4NH_3^+Cl^-$
$CH_3C_6H_4NH_3^+Cl^- + NaOH \rightarrow CH_3C_6H_4NH_2 + H_2O + NaCl$

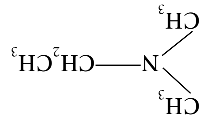
(b) Heat with *excess ammonia in ethanol.*
$C_6H_5CH_2Cl + 2NH_3 \rightarrow C_6H_5CH_2NH_2 + NH_4Cl$

2. (a) Nucleophilic substitution



(b) The ethylamine is nucleophilic and can react with further bromoethane to form secondary, tertiary and quaternary amines.
(c) Use a large excess of ammonia relative to the bromoethane.
(d) CH_3Br + KCN in ethanol → ethanenitrile, CH_3CN
Ethanenitrile reduced by $LiAlH_4$ or H_2 and Ni to aminoethane
(e) The C–Br bond is too strong (because of extended delocalisation) to allow substitution.
(f) Benzene + conc. HNO_3 + conc. H_2SO_4 → nitrobenzene
Nitrobenzene reduced by tin and HCl to phenylamine

3 (a)



(b) $CH_3CH_2CH_2CH_2Br + KCN \rightarrow CH_3CH_2CH_2CH_2CN + KBr.$
$CH_3CH_2CH_2CH_2CN + 4[H] \rightarrow CH_3CH_2CH_2CH_2CH_2NH_2$
(c) The butyl group attached to the $–NH_2$ group makes the amine a stronger base than ammonia because it is *electron-releasing / repelling*. This makes the *lone pair of electrons on the nitrogen more available* for accepting a H^+ ion.
(d) The phenyl group attached to the $–NH_2$ group makes phenylamine a weaker base than ammonia because it causes the *lone pair on the nitrogen atom to be delocalised* with the delocalised electrons in the benzene ring. This makes the electrons *less available* for accepting a H^+ ion.
(e) The carbon chain of pentylamine is sufficiently large to make van der Waal's forces the most significant between water and amine molecules. Formation of these releases *insufficient energy* to compensate for having to break much stronger hydrogen bonding between water molecules to allow mixing. Hence, this amine is not very water-soluble.

When hydrochloric acid is added, in the presence of such a strong acid, the basic amine forms an ionic chloride.

$CH_3CH_2CH_2CH_2CH_2NH_2 + HCl \rightarrow CH_3CH_2CH_2CH_2CH_2NH_3^+Cl^-$
These ions are able to form much stronger ion-dipole bonds with water molecules allowing the two to mix.