

CAIE Chemistry A-level

34: Nitrogen Compounds (A-level only)

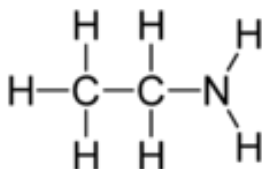
Notes

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Primary Amines

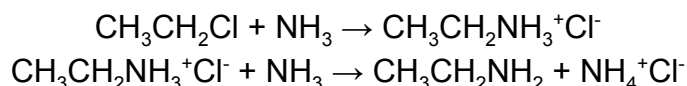
Primary amines have the formula RNH_2 where R is an alkyl group. The structure of **ethylamine** is shown below:



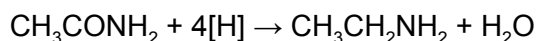
Formation of Alkyl Amines

Alkyl amines can be made in several ways:

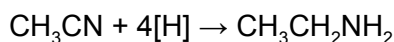
- From **halogenoalkanes**:
 - Heat the halogenoalkane in a sealed tube with **concentrated ammonia** in an ethanol solvent (reflux cannot be used as ammonia is too volatile). To ensure that a **primary amine** is formed, rather than an ammonium salt, an **excess of ammonia** must be used.
 - E.g. using 1-chloroethane:



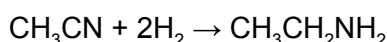
- Reduction of amides** with LiAlH_4 :
 - LiAlH_4 is the **reducing agent** and this can be shown in the equation as $[\text{H}]$.
 - E.g. for the reduction of ethanamide:



- Reduction of nitriles** with LiAlH_4 :
 - Nitriles contain the group $-\text{CN}$. The **reducing agent** is LiAlH_4 which can be shown in the equation as $[\text{H}]$.
 - E.g. for the reduction of ethanenitrile:

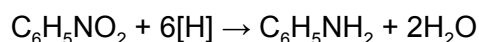


- Reduction of nitriles** with H_2/Ni :
 - A nickel catalyst is used to reduce a nitrile with hydrogen gas. The reaction is similar to the one above.
 - E.g. for the reduction of ethanenitrile:



Phenylamine

Phenylamine is formed by **reducing nitrobenzene** with **tin** and **concentrated HCl**. The mixture is heated under **reflux** for about 30 minutes. **Sodium hydroxide** is then added to the product to **remove a proton** from the $-\text{NH}_3^+$ group. This can be summarised by the following equation:



Basicity of Amines

Amines are **basic** because the **lone pair** on the nitrogen in the amine group can **accept a proton**/ hydrogen ion. Amines react with acids in the same way as ammonia, forming **alkyl ammonium salts**. Amines also form an **equilibrium in water**, producing hydroxide ions and alkyl ammonium ions.

There are two factors that affect the **strength of a base**:

- How easily the lone pair can **accept a hydrogen ion**
- The **stability** of the ions formed

In **ethylamine**, the alkyl group has a tendency to **push electrons away** from itself. This causes an increase in the **negative charge of nitrogen** which makes the lone pair on the nitrogen more attracted to hydrogen ions. In addition to this, this electron-pushing effect means that the **charge is more spread out** in ethylamine than in **ammonia** so the **ethylammonium ion is more stable** than the ammonium ion. The combination of these two factors means that **ammonia is a weaker base** than ethylamine.

The amine group in **phenylamine** is directly attached to the **benzene ring** meaning that the **lone pair** on the nitrogen is **delocalised into the pi system**. As a result, the lone pair cannot combine with a hydrogen ion. The nitrogen atom is very electronegative meaning it draws electrons towards itself. However, this **charge is much weaker** than in ammonia or ethylamine. In addition to this, if the lone pair combined with a hydrogen ion, the delocalised pi system would be disrupted, making the molecule less stable. Both of these factors mean that **phenylamine is a weaker base than ammonia and ethylamine**.

The relative basicity of the three compounds discussed:

ethylamine > ammonia > phenylamine.

Phenylamine and Azo Compounds

Reactions of Phenylamine

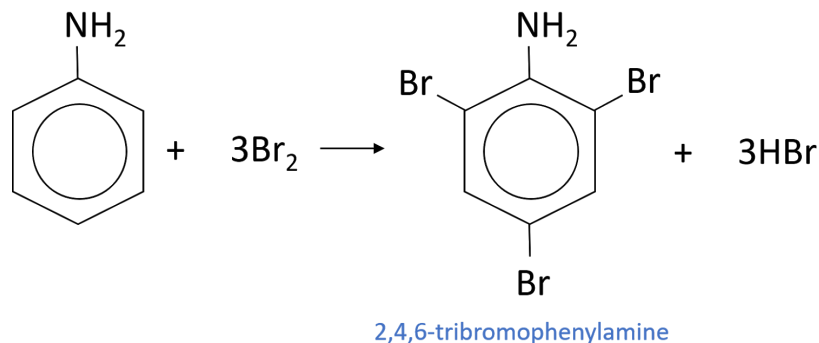
The **-NH₂** group in phenylamine activates the **benzene ring** meaning that it is **more reactive**. This is because the **lone pair** on nitrogen is delocalised into the pi system, increasing the electron density meaning **electrophiles are more attracted**.

The **-NH₂** has a **2,4-directing effect** meaning that groups will generally be substituted at the 2-position and the 4-position (with the carbon that is bound to the amine group being 1-position).



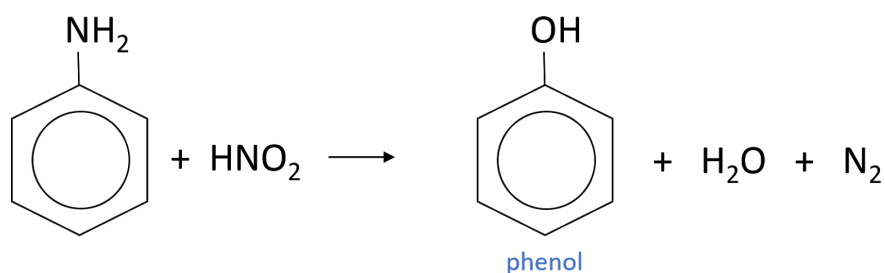
Phenylamine and Bromine

Phenylamine reacts with **aqueous bromine** at room temperature without a catalyst. During this reaction, the bromine water is **decolourised** and a **white precipitate** is formed. The product has multiple substitutions.

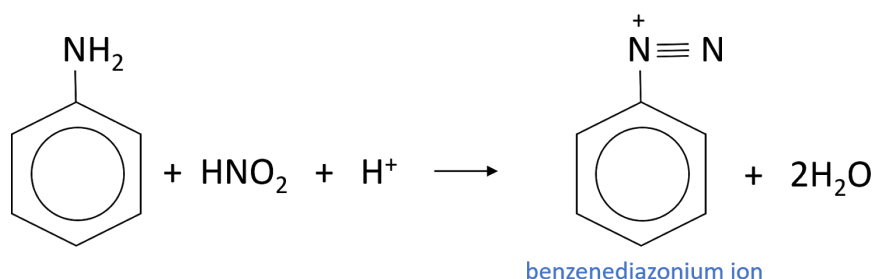


Phenylamine and Nitrous acid

Phenylamine also reacts with **nitrous acid** (HNO_2). Nitrous acid is typically made in situ as it **decomposes rapidly**. Phenylamine is dissolved in hydrochloric acid and sodium or potassium nitrate is added. If the reaction mixture is warmed, **phenol** is produced:

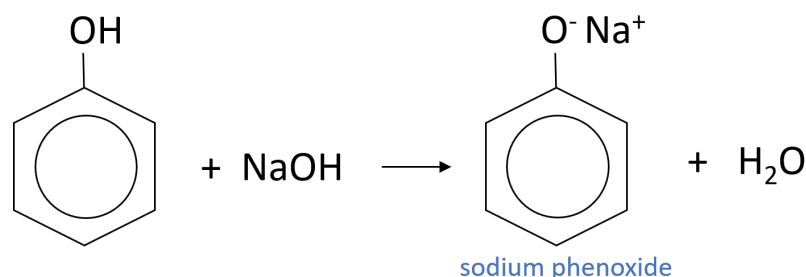


If the reaction vessel is **stood in ice** (to ensure the temperature stays below 5°C), a **diazonium salt** is produced. The **diazonium ion** (containing an $-\text{N}_2^+$ group) combines with the negative ion from the acid to form a salt - these reactions are further covered in the next section.

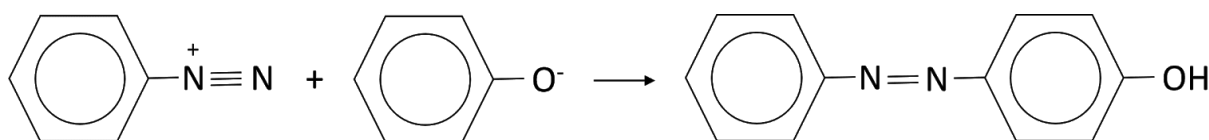


Formation of Dyes

Phenol first reacts with **sodium hydroxide** to form a solution of **sodium phenoxide**:

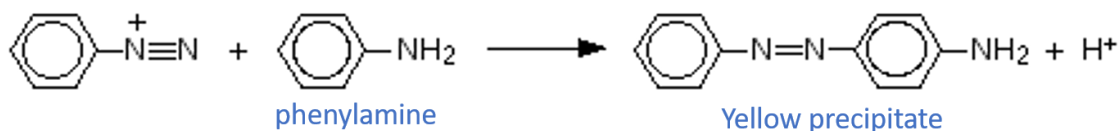
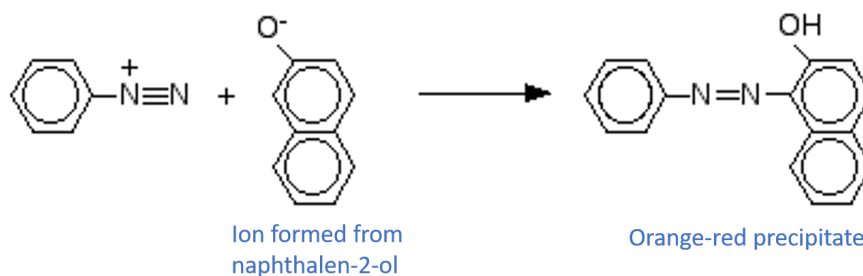


The sodium phenoxide solution is **cooled in ice** before a cool solution of **benzenediazonium chloride** is added. This reaction forms a **yellow-orange** solution or precipitate. The product is an **azo compound** (two benzene rings joined by a nitrogen bridge):



In the equation above, **coupling** takes place in the 4-position (opposite the oxygen in the phenoxide ion). Unless the **4-position** is already occupied, coupling will always occur in this position. If the 4-position is occupied, the **2-position** will be used.

Below are some examples which used a similar reaction to form **azo dyes**:



['Reactions of diazonium salts', Jim Clark, Chemguide](#)



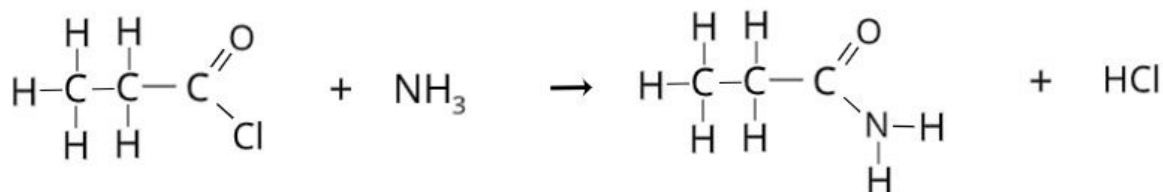
Amides

Amides contain the **-CONH₂** group. They are **neutral** despite the fact that they contain an -NH₂ group. This is because the **lone pair** on the nitrogen is **delocalised** into the pi bond between oxygen and carbon meaning the nitrogen atom is **unable to attract a hydrogen ion**, so is a much weaker base than amines. The delocalisation also makes the molecule more **stable** so disrupting the delocalisation to accept a hydrogen ion would require a lot of energy.

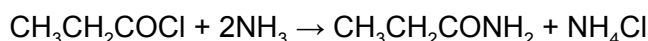
Formation of Amides

Reactions with ammonia

When acyl chlorides react with ammonia, an **amide** and **hydrogen chloride** gas is produced. Amides are organic compounds with the group **-CONH₂**. The suffix for naming an amide is **-amide** so for the reaction below, the product formed is **propanamide**.

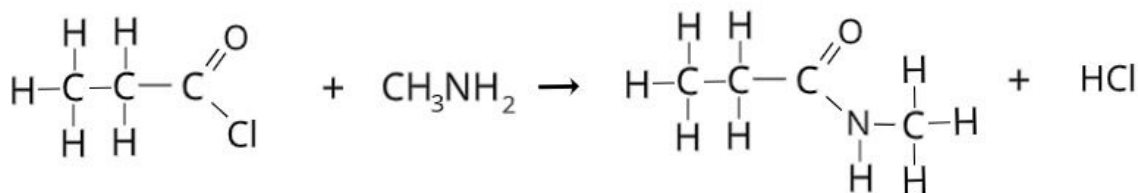


The hydrogen chloride produced reacts with the **excess ammonia** to produce ammonium chloride so the overall equation for the reaction can be written as:

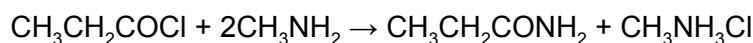


Reactions with primary amines

A **primary amine** is an organic compound with an **-NH₂** group bonded to an alkyl group, like methylamine, CH₃NH₂. The product formed from the reaction between a primary amine and acyl chloride is called an **N-substituted amide**. The product formed below is N-methylpropanamide - the methyl group comes from the alkyl group on the primary amine.



The **hydrogen chloride** produced reacts with the **excess primary amine** so the overall equation for the reaction can be written as:



If an amino acid has a carboxylic acid or amine group in the R group, only one acidic and one basic group will be involved in the formation of the zwitterion. In **water, proton transfer** will occur to form a charged ion.

Addition of an alkali

If an **alkali** (OH^- ions) is added to a solution of an amino acid, the NH_3^+ group in the zwitterion **donates a hydrogen** to the OH^- ions to form water. The organic compound is no longer a zwitterion as it only contains a **negative charge**.

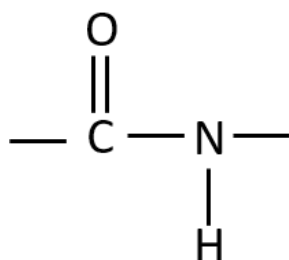
Addition of an acid

If an **acid** (H^+ ions) is added to a solution of an amino acid, the COO^- group **accepts a hydrogen ion** from the solution. The organic compound is no longer a zwitterion as it only contains a **positive charge**.

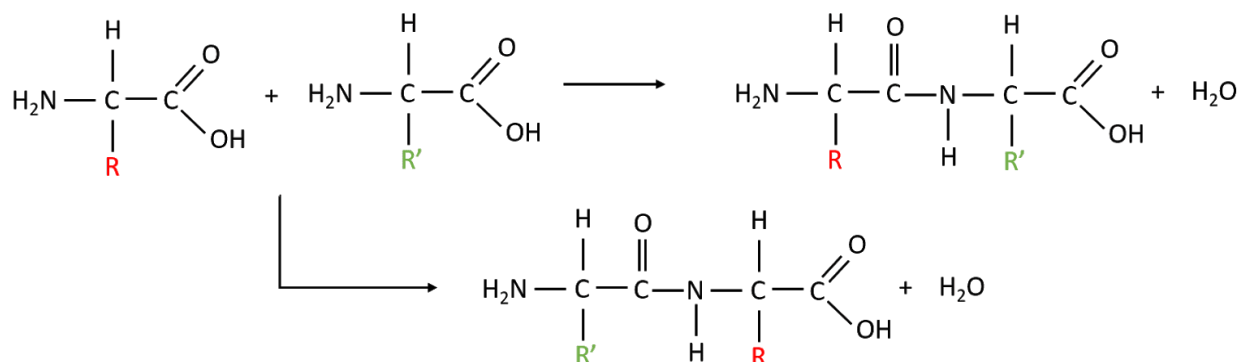
If **alkali** is added to the **positive amino acid ion**, formed when acid was added, the **proton in the $-\text{COOH}$ group** will be **donated to the OH^- ions** to form water. This proton would be donated before the proton in $-\text{NH}_3^+$ as the **$-\text{COOH}$ proton is more acidic**. This reforms the **zwitterion**. If exactly the right amount of alkali is added, the amino acid can have **no overall charge**. During **electrophoresis** (see 'Electrophoresis' below), the amino acid won't travel towards the cathode or the anode. The pH at which the amino acid doesn't move during electrolysis is the isoelectric point. This pH varies between amino acids.

Peptide Bonds

A peptide bond is formed during a **condensation reaction** between **two amino acids**. A water molecule is lost.



When two amino acids combine, a **dipeptide** is formed:



A **tripeptide** forms when three amino acids join together.



Electrophoresis

Below is one way in which electrophoresis can be used to **separate amino acids**:

1. A piece of moistened filter paper is placed on a microscope slide.
2. Crocodile clips are attached to each end of the paper and connected to a battery.
3. A drop of amino acid solution is added to the middle of the paper.
4. The apparatus is left for a period of time to enable separation to occur.
5. Ninhydrin is sprayed onto the paper to make the colourless amino acid solution visible. The paper is dried and warmed gently, causing the amino acids to be seen as coloured spots.

Instead of damp filter paper, a **gel soaked in buffer solution** is typically used. The gel would have troughs to hold the amino acid solution.

Analysing electrophoresis results:

- Zwitterions don't move towards the **anode or cathode**. For an amino acid to form its zwitterion in solution, the **pH** must be the **isoelectric point** of that specific amino acid.
- Amino acids that travel towards the **cathode** (negative electrode) are **positively charged**. This may occur when an amino acid has an extra amine group in the R group. In solution, this compound would have a net charge of 1+.
- Amino acids that travel towards the **anode** (positive electrode) are **negatively charged**. This may occur when an amino acid has an extra carboxylic acid group in the R group. In solution, this compound will have a net charge of 1-.
- **Smaller ions will travel faster** than larger ions as there is less resistance to their movement through the fibres of the paper/ the matrix in the gel.

A **buffer with a low pH** will cause the -COOH groups to remain as -COOH groups. Any NH_2 groups will accept a proton to become $-\text{NH}_3^+$ groups. All the amino acids will be **positively charged** so will move towards the cathode.

A **buffer with a high pH** will cause the -COOH groups to donate a proton and become $-\text{COO}^-$ groups. Any $-\text{NH}_2$ groups will remain as $-\text{NH}_2$ groups. All the amino acids will be **negatively charged** so will move towards the anode.

Electrophoresis and Peptides

Electrophoresis can also be used either to **separate peptides** in **order of relative molecular mass** or to **estimate the relative molecular mass** of a peptide. This is done by treating the peptides with **SDS** and heating them to denaturing the peptides. The secondary and tertiary structure of the peptides are lost and the molecule becomes **amino acid chains surrounded by negative charges** (from the SDS molecules that cover the chain). During electrophoresis, the peptide molecules move towards the anode, with smaller molecules moving fastest.

