

CAIE Chemistry A-level

19: Nitrogen Compounds 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 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:

$$\begin{array}{c} \mathsf{CH}_3\mathsf{CH}_2\mathsf{CI}+\mathsf{NH}_3\to\mathsf{CH}_3\mathsf{CH}_2\mathsf{NH}_3^+\mathsf{CI}^-\\ \mathsf{CH}_3\mathsf{CH}_2\mathsf{NH}_3^+\mathsf{CI}^-+\mathsf{NH}_3\to\mathsf{CH}_3\mathsf{CH}_2\mathsf{NH}_2+\mathsf{NH}_4^+\mathsf{CI}^-\end{array}$$

Nitriles and Hydroxynitriles

Formation of Nitriles

Nitriles are formed when a halogenoalkane reacts with **cyanide**. The reaction requires **warm**, **ethanolic potassium cyanide** (ethanolic means dissolved in ethanol).



Nucleophilic Addition

When aldehydes and ketones react with HCN to form hydroxynitriles, a nucleophilic addition reaction occurs.

The **carbonyl bond** (C=O) is **highly polar**. The negative **cyanide ion** acts as a **nucleophile** and attacks the slightly positive carbon atom. The C=O bond breaks, leaving only a **single bond** between the **carbon and oxygen** atoms. The negatively charged oxygen then bonds to a **hydrogen ion** (from HCN or any added acid).





<u>Hydrolysis</u>

Nitriles can undergo hydrolysis to form carboxylic acids. The C≡N nitrile bond reacts with water to produce the carboxylic acid.

• Acid hydrolysis

The nitrile is heated under **reflux** with a dilute acid (such as **hydrochloric acid**). A **carboxylic acid** and a **salt** are produced.

The reaction of propanenitrile with a dilute acid:

$$CH_{3}CH_{2}CN + 2H_{2}O + HCI \rightarrow CH_{3}CH_{2}COOH + NH_{4}CI$$

• Alkaline hydrolysis

The nitrile is heated under **reflux** with an alkali (such as **sodium hydroxide**). This produces a **carboxylic acid** and **ammonia**. The reaction takes place in two stages. First, carboxylate ions are produced (e.g. **sodium carboxylate** forms if sodium hydroxide is used). A **strong acid** must then be added to provide hydrogen ions to liberate the carboxylic acid. Hydrochloric acid is commonly used.

The formation of propanoic acid from propanenitrile:

Stage 1: $CH_3CH_2CN + NaOH + H_2O \rightarrow CH_3CH_2COONa + NH_3$

Stage 2: $CH_3CH_2COONa + HCI \rightarrow CH_3CH_2COOH + NaCI$

▶ Image: Contraction PMTEducation

