7.4 Hydroxy Compounds (A Level Only)

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7.4.1 ALCOHOLS

Reaction of Alcohols With Acyl Chlorides

- **Acyl chlorides** are **reactive** organic compounds with a **-COCl** functional group
- The carbonyl carbon is **electron-deficient** and has a **partial positive charge**
- It is therefore susceptible to **nucleophilic attack**
- The carbon-chlorine bond breaks and **white fumes** of **hydrogen chloride**, HCl are formed

Reaction with alcohols and phenols

- Acyl chlorides react with **alcohols** and **phenols** to form **esters** in a **nucleophilic substitution** reaction
- The -OH group acts as a **nucleophile** and attacks the carbonyl carbon to **substitute** the chlorine atom
- Forming esters using acyl chlorides is **more effective** compared to using carboxylic acids as:
    - Acyl chlorides are more **reactive** (so the ester is produced faster)
    - Acyl chloride reactions go to **completion** (so more of the ester is produced)

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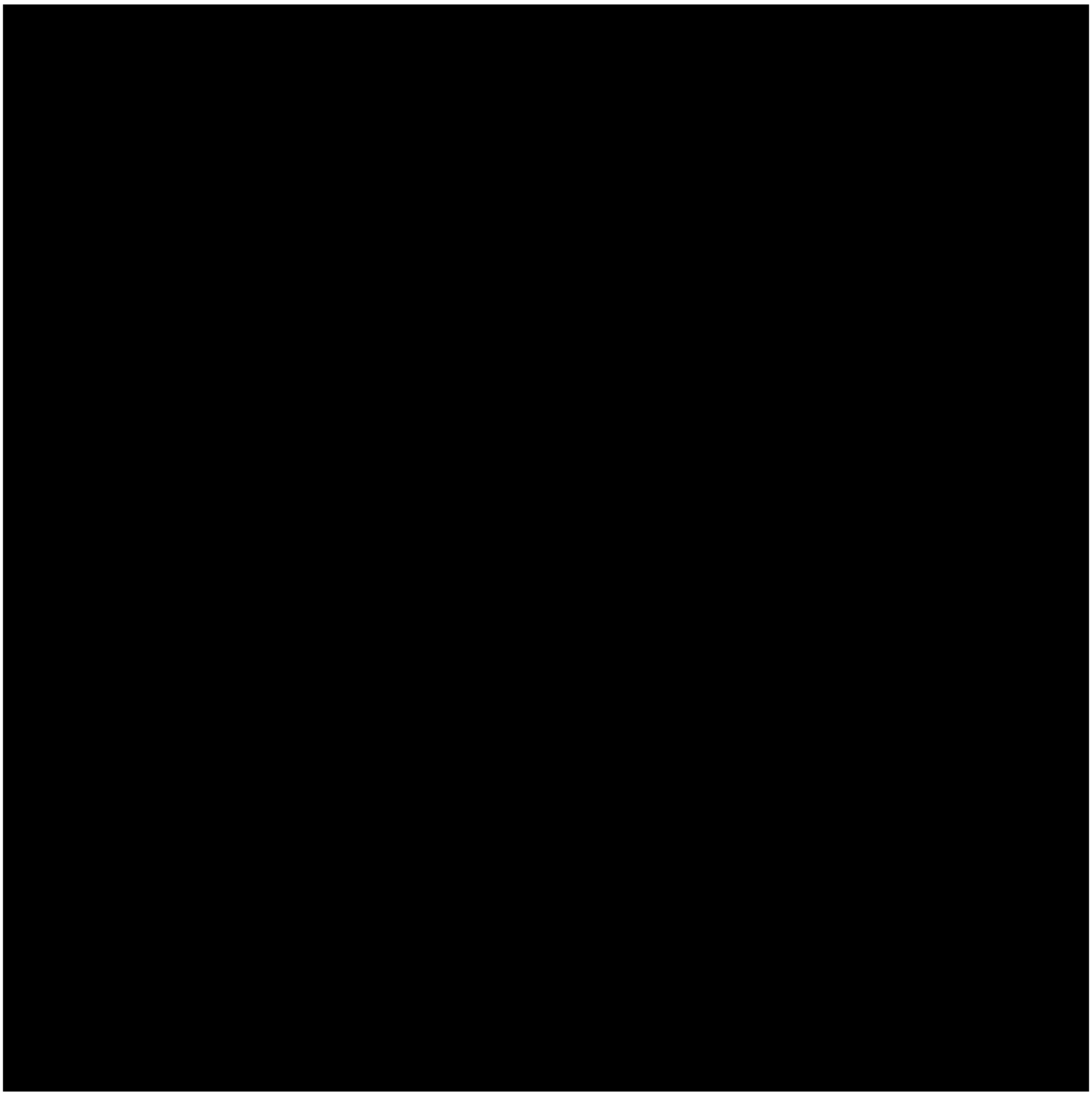
Reaction with alcohols

- The reaction of acyl chlorides with alcohols is **vigorous** and white fumes of HCl gas are formed



Acyl chlorides react vigorously with alcohols to form esters

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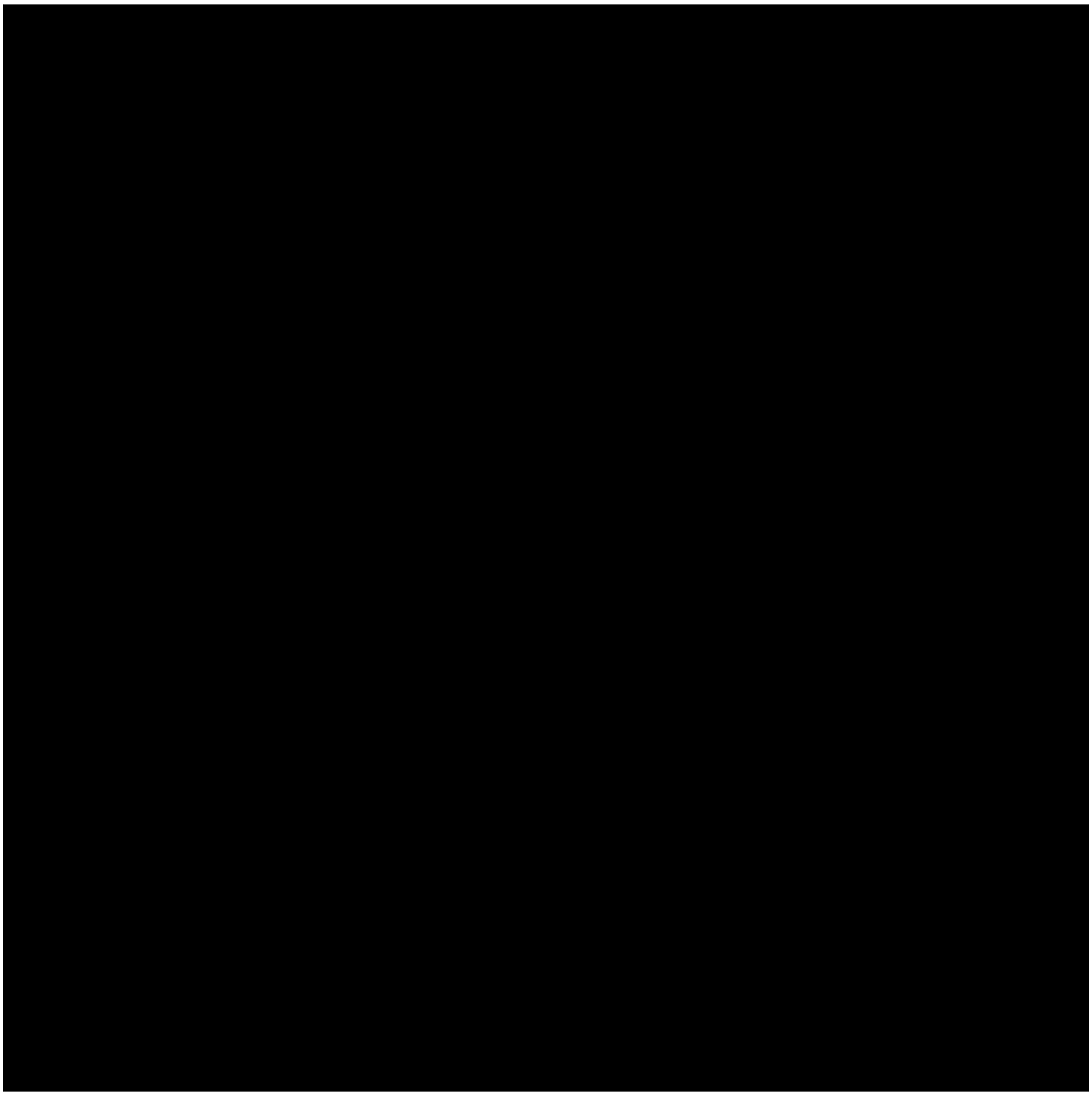
Reaction with phenols

- For the reaction of acyl chlorides with phenols to occur, **heat** and a **base** are required
  - The base is needed to deprotonate the phenol and form a **phenoxide ion**
  - The phenoxide ion is a better nucleophile than the original phenol molecule and will be able to attack the carbonyl carbon



Acyl chlorides react with phenols when heated and in the presence of a base to form esters

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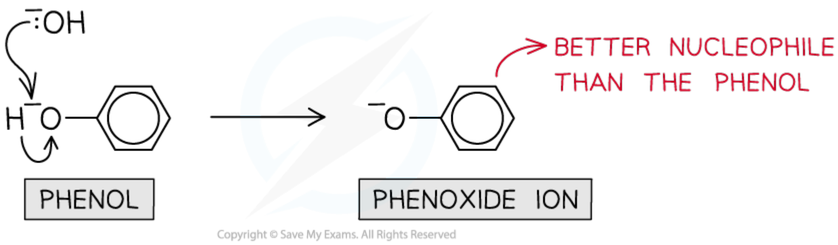

A base is needed to form a phenoxide ion which is a better nucleophile than phenol; now, nucleophilic attack on the carbonyl carbon can more readily occur

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7.4.2 REACTIONS OF PHENOL

Reactions of Phenol

- Phenols can undergo many types of reactions as both the **electron-rich benzene ring** and the **polar -OH** group can participate in chemical reactions
- Some of the reactions of phenols include:
  - With bases
  - With reactive metals
  - With diazonium salts
  - Nitration
  - Bromination

Reactions of the -OH group in phenols

- The -OH group in phenols has a **slightly acidic character**
- It can therefore act as an **acid** and take part in **acid-base reactions**

Reaction with bases

- Phenols are **only slightly soluble** in water due to the large non-polar benzene ring
- However, they do dissolve in alkaline solutions and undergo **acid-base** reactions with **bases** to form a **soluble salt** and **water**

Phenols are weak acids and undergo acid-base reactions in alkaline solutions

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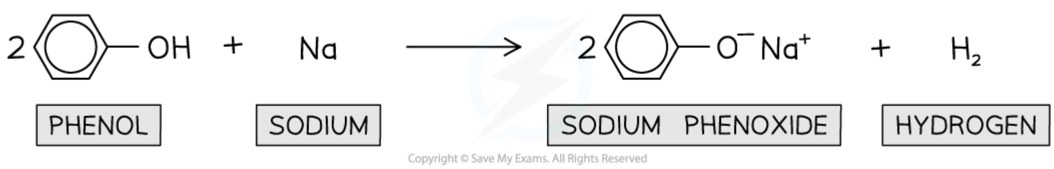
Reaction with reactive metals

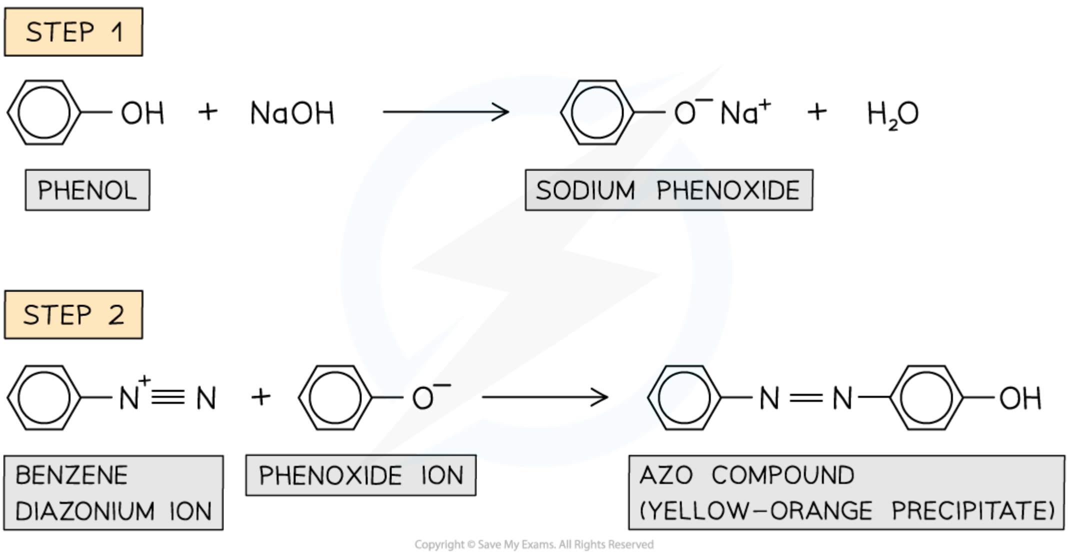
- **Molten phenols** react **vigorously** with reactive metals such as **sodium** (Na)
- This is also an **acid-base** reaction
- Now, a soluble salt is formed and **hydrogen gas** is given off



Molten phenols react vigorously with reactive metals to form a soluble salt and hydrogen gas

Reaction with diazonium ions

- **Diazonium ions** are very reactive compounds containing an -N_2^+ group
- When phenols are **dissolved** in sodium hydroxide (NaOH), a solution of **sodium phenoxide** is obtained
- This solution is cooled in **ice** and **cold diazonium ion** is added to the sodium phenoxide
- After the reaction has occurred, a **yellow-orange** solution or precipitate of an **azo compound** is formed
- These are compounds in which **two benzene** rings are linked by a **nitrogen bridge**



Azo compounds are formed from the reaction of phenols with diazonium ions

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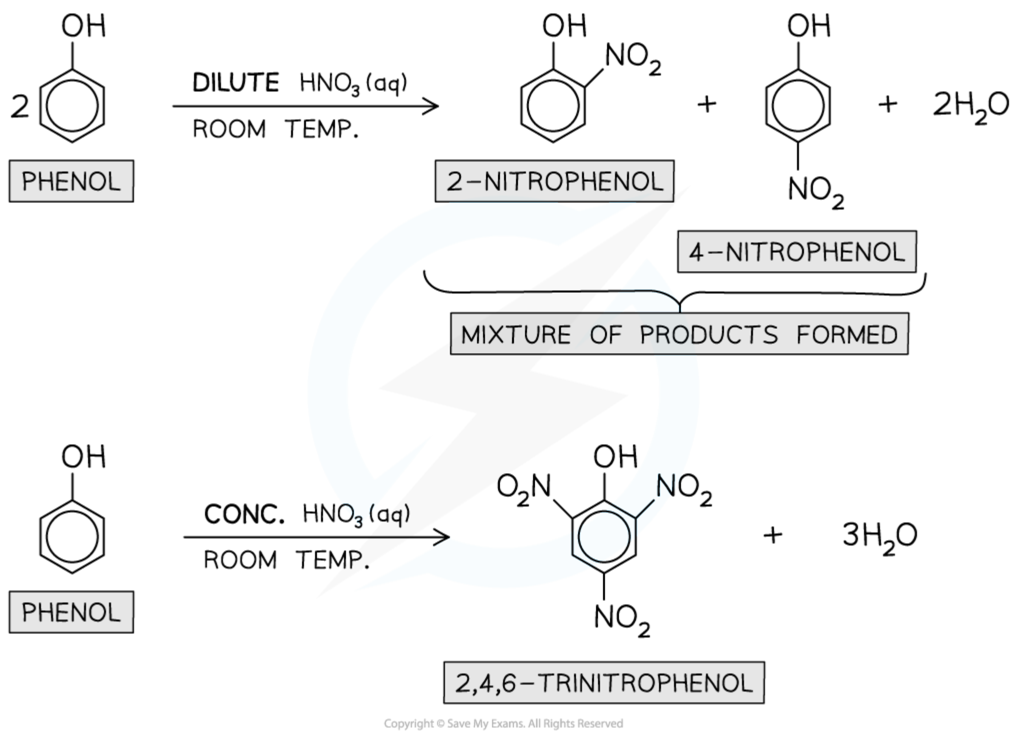
Reactions of the aromatic ring in phenols

- Phenols react more **readily** with **electrophiles** compared to benzene
- This is because one of the lone pairs of electrons on the oxygen atom in -OH overlaps with the π bonding system
- This increases the **electron density** of the benzene ring making it more **susceptible** to **electrophilic attack**
- The -OH group in phenols is **activating** and **directs** incoming electrophiles to the **2, 4, and 6 positions**

Nitration

- Phenols can undergo **electrophilic substitution** reactions when reacted with **dilute nitric acid** (HNO_3) at **room temperature** to give a mixture of **2-nitrophenol** and **4-nitrophenol**
    - When **concentrated HNO_3** is used, the product will be 2,4,6-trinitrophenol instead
- A hydrogen atom in the benzene ring is **substituted** by a nitro (-NO_2) group
- This is also known as the **nitration** of phenol



Phenols undergo nitration when reacted with dilute HNO_3 at room temperature

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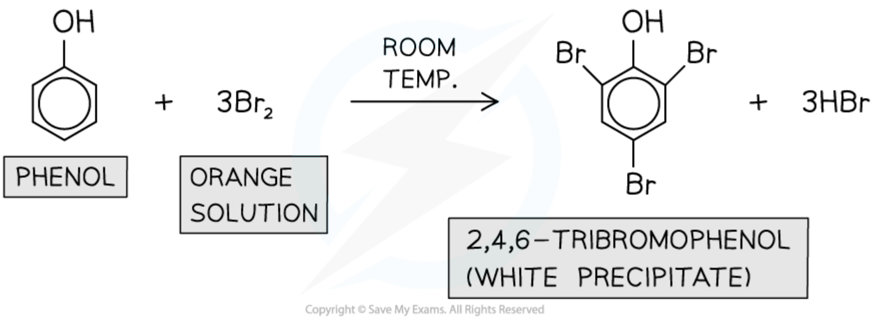
Bromination

- Phenols also undergo **electrophilic substitution** reactions when reacted with **bromine water** at **room temperature**
- Phenol **decolourises** the **orange** bromine solution to form a **white precipitate** of 2,4,6-tribromophenol
- This is also known as the **bromination** of phenol



Phenols undergo bromination when reacted with bromine water at room temperature

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7.4.3 ACIDITY OF PHENOLS

Relative Acidities of Water, Phenol & Ethanol

- The pK_a is a measure of the acidity of a substance
- The values of water, phenol, and ethanol show that phenol is a **stronger** acid than ethanol and water

Relative acidity of ethanol, water & phenol table

Acid	Dissociation	pK_a (at 25 °C)
Ethanol	$C_2H_5OH(aq) \rightleftharpoons C_2H_5O^-(aq) + H^+(aq)$	16
Water	$H_2O(l) \rightleftharpoons OH^-(aq) + H^+(aq)$	14
Phenol	$C_6H_5OH(aq) \rightleftharpoons C_6H_5O^-(aq) + H^+(aq)$	10

- The order of acidity can be explained by looking at their **conjugate bases** which are formed from the dissociation of the compounds

Delocalisation of charge density

- In the **phenoxide ion** (which is the conjugate base of phenol) the charge density on the oxygen atom is **spread out** over the entire ion
- As a result, the electrons on the oxygen atom are **less available** for bond formation with a proton (H^+ ion)
- The **conjugate base** of ethanol is the **ethoxide ion**
- The **ethyl** group in the ion is an **electron-donating** group that donates electron density to the oxygen atom
- As a result, the electron density on the oxygen atom is **more readily available** for bond formation with an H^+ ion

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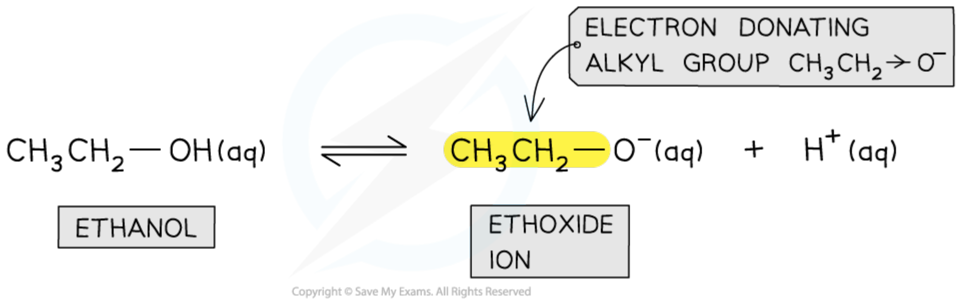

The electron-donating alkyl group in the ethoxide ion concentrates charge density on the oxygen atom which can more easily bond an H^+ ion

- The **conjugate base** of water is the **hydroxide ion**
- Since the charge density of the oxygen atom cannot become delocalised over a ring, the hydroxide ion more readily accepts an H^+ ion compared to the phenoxide ion
  - Water is, therefore, a **stronger base** compared to phenol
- However, as there are no **electron-donating** alkyl groups, less negative charge is concentrated on the oxygen atom which therefore less readily accepts an H^+ ion compared to the ethoxide ion
  - Water is, therefore, a **weaker base** compared to ethanol

The hydroxide ion lacks an aromatic ring and electron-donating alkyl groups so water is a stronger base than phenol but a weaker base than ethanol

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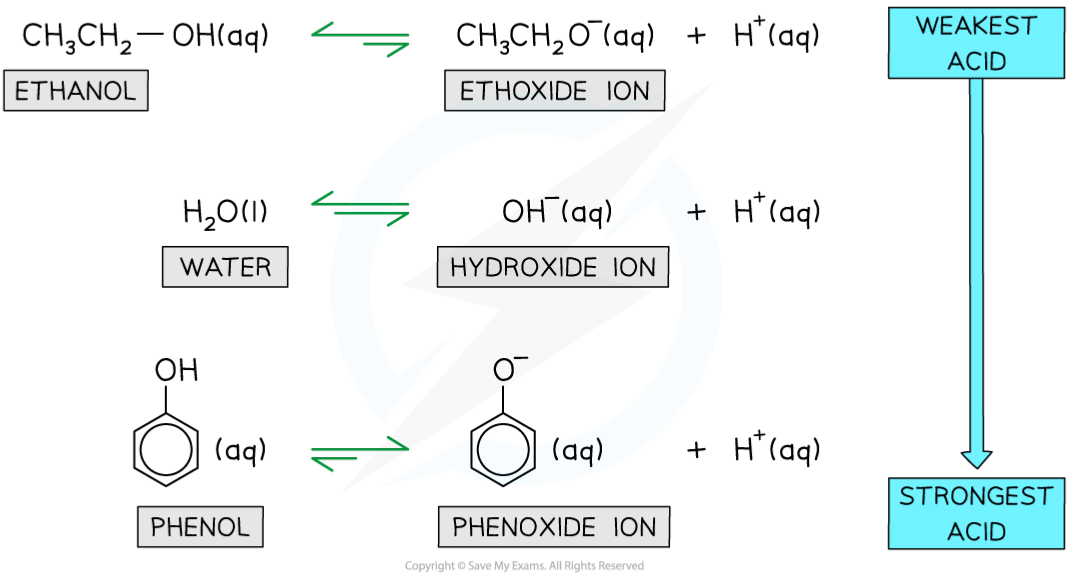
- Therefore, the position of equilibrium lies:
  - Further to the **right-hand side** favouring the **dissociated phenoxide ions**
  - Further to the **left-hand side** favouring the **undissociated ethoxide and hydroxide ions**



Relative equilibrium positions for the dissociation of ethanol, water, and phenol