Chem Factsheet

www.curriculum-press.co.uk Number 154

Chemistry of Phenols

To begin, try the simple test below:

Statement	True	False
1. Phenols have an –OH group attached to a saturated carbon atom		
2. Electrons from a lone pair on the oxygen of the –OH group become delocalised		
3. The donation of an oxygen lone pair decreases the electron density on the ring system		
4. Phenol can be made directly from benzene and an OH group		
5. Phenol's –OH group loses its hydrogen very easily		
6. The reaction of phenol with iron(III) chloride to give a violet precipitate can be used as a test for phenol		
7. Phenol can take part in a coupling reaction to produce an azo dye		
8. Phenol is a non-toxic crystalline compound		

Statements 2, 6, and 7 are correct, and 1, 3, 4, 5 and 8 are incorrect.

Phenol is a toxic corrosive crystalline compound, C_6H_5OH.

> *Functional groups in aliphatic compounds behave differently to functional groups attached to benzene rings.*

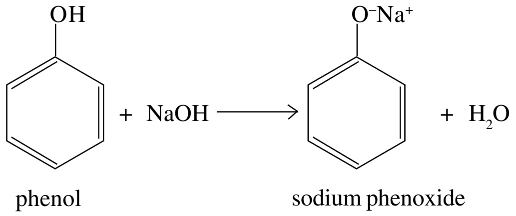
The Acidity of Phenol

> *In aqueous solution phenol is a very weak acid (pH 5-6 at 0.1M), commonly known as carbolic acid, and is slightly dissociated to give the phenoxide ion*:
> $C_6H_5OH + H_2O \rightleftharpoons C_6H_5O^- + H_3O^+$

Phenol is more acidic than alcohols (which are so weakly acidic that they can be considered as neutral). The charge density from one lone pair of the oxygen atom becomes delocalised over the unsaturated ring system. The hydrogen of the OH experiences less attractive force due to the lower negative charge on the oxygen and so is more weakly held and more easily lost to form the H_3O^+ ion.

However, the electronegativity of oxygen will still draw the negative charge towards it, resulting in phenol being a *very weak* acid. You can also describe the phenoxide ion as being *stabilised* by the incorporation of a p-orbital of the oxygen atom into the benzene ring – this stabilisation encourages formation of this ion and hence the tendency to ionise. The p-orbitals overlap sideways above and below the benzene ring.

The hydroxide ion in sodium hydroxide solution is strongly basic so phenol will react to give a colourless solution of sodium phenoxide:



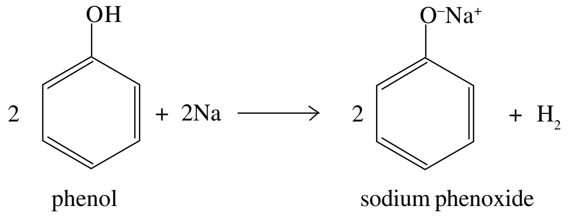
Phenol is not acidic enough to react with sodium carbonate or sodium hydrogencarbonate, or one can also say that these bases are not strong enough to take the hydrogen ion from the phenol. Carboxylic acids will react with these bases to liberate carbon dioxide.

A useful *order of acidity* to remember is: *carboxylic acids › phenols › alcohols and water.*

Reaction of Phenol with Sodium to form Salts

NOTE Safety aspects make this unsuitable as a student practical!

Phenol is gently warmed in a dry tube until it is molten. A small piece of sodium is then added and fizzing occurs as hydrogen gas is given off, leaving sodium phenoxide:



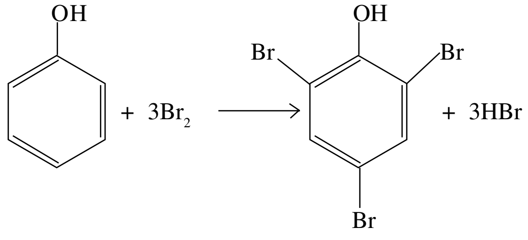
Electrophilic Substitution Reactions of Phenol

> *Electrophiles are positive ions or parts of molecules with a positive charge + or δ+, making them able to accept a pair of electrons.*

The delocalisation of one lone pair from an oxygen p-orbital into the ring electron system causes the electron density around the ring to be higher than for benzene. Thus the OH substituted benzene ring will be **more attractive to electrophiles**. This means that it will undergo electrophilic substitution more readily.

> *The donation of oxygen's lone pair into the ring system increases the electron density around the ring and causes the ring to be much more reactive than it is in benzene itself.*

If bromine water is added to an aqueous solution of phenol, the **orange brominesolution is decolourised** and a **white precipitate of 2,4,6-tribromophenol is formed**:



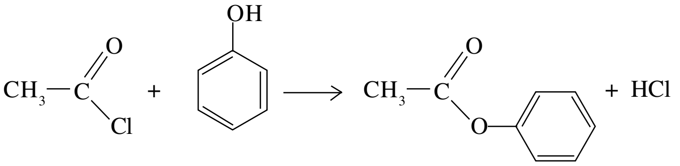
phenol 2,4,6-tribromophenol

[Compare this with the bromination of benzene which needs pure bromine in the presence of a catalyst e.g. Fe.]

The –OH group has a 2,4-directing effect, which means that incoming groups will tend to go into the 2-position (next to the –OH group) or the 4-position (opposite the –OH group) much faster than into the 3-position.

Ethanoylation Reaction of Phenol

Phenol reacts with ethanoyl chloride, CH_3COCl to form phenyl ethanoate and misty-white fumes of hydrogen chloride gas:



ethanoyl chloride phenol phenyl ethanoate

This is an example of the general reaction of the –OH group in a phenol which will react with an acyl chloride to form an ester. [You could compare this with the esterification of an alcohol by reaction with a carboxylic acid and concentrated sulphuric acid and note that the **phenolic group *cannot* be esterified in this way**.]

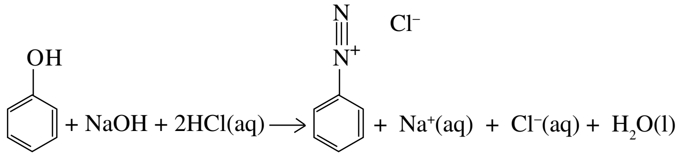
Reaction of the –OH (phenolic) Group with Aqueous Iron(III) Chloride

Most phenolic groups will react with aqueous iron(III) chloride to form a complex, which displays an intense colour: violet, blue or green. ***Phenol gives an intense violet colour***. Alcohols do not give this colour and the reaction may be used to distinguish alcohols from phenols.

The Coupling Reaction of Benzenediazonium Ions with Phenol

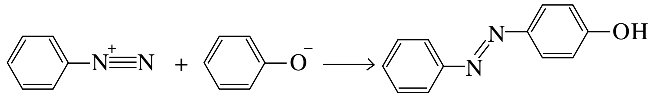
An azo dye can be synthesised from phenylamine (aminobenzene) and phenol. Phenylamine is first reacted with excess nitrous acid (nitric(III) acid) at 5°C to produce benzenediazonium ions.

[**Note**: The nitrous acid is prepared from sodium nitrite (sodium nitrate(III)) and hydrochloric acid *in situ*]:



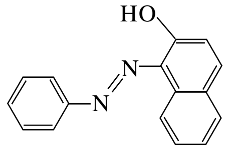
Benzenediazonium ions react with phenols to form coloured compounds called **azo dyes.**

e.g. with phenol, in alkaline conditions, a yellow product is formed

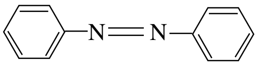


benzenediazonium ion phenoxide ion 4-hydroxyazobenzene

The yellow colour is due to the π-electrons of the –N=N- bonds and the π-electrons of the benzene rings overlapping, to give an electron system which extends over the structure. This is called a **conjugated electron system**, and it absorbs electromagnetic radiation. If it absorbs in the visible region, as here, it is known as a **chromophore.** A similar example is the coupling of benzendiazonium chloride with naphthalene-2-ol, in alkaline conditions, to give a red dye which has the structural formula:



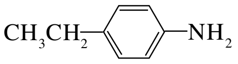
If you are required to draw the structural formula of a product given the formula of the initial compound, remember the **azo dye linkage** is:



So you can just add the OH and any other group required, according to the question.

Sample Question on Coupling Reactions

4-ethylaminobenzene, which has the structural formula:



reacts with nitrous acid to form a product which undergoes a ***coupling reaction*** with phenol to produce an ***azo-dye.***

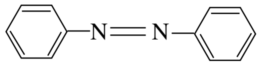
(i) Explain the terms
- (a) Coupling reaction (1 mark)
- (b) azo-dye (1 mark)

(ii) Draw the structural formula of the product dye produced by the coupling reaction. (1 mark)

Solution to Sample Question on Coupling Reactions

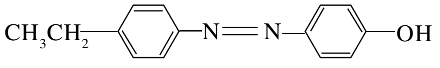
(i) (a) A coupling reaction is electrophilic attack in which <u>**two benzene rings are linked together**</u> to form one larger molecule. (1 mark)

(b) An azo dye is a coloured substance which has the linkage:



(1mark)

(ii) Structural formula of dye produced



(1mark)

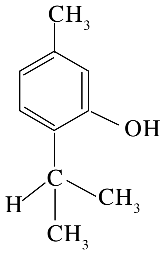
Uses of Phenol

Production of plastics, antiseptics, disinfectants and resins for paints.

Practice Questions

1. (a) Give the reagents for making 2,4,6-tribromophenol from phenol. (1 mark)
   (b) Describe the appearance of the organic product. (1 mark)
   (c) Give the equation for the reaction. (1 mark)

2. Thymol (shown below) is a phenol.



   (a) Describe a test to distinguish thymol from an alcohol, and give the positive result of this test. (2 marks)
   (b) Thymol reacts with aqueous bromine. Draw the structural formula of organic product of this reaction. (1 mark)

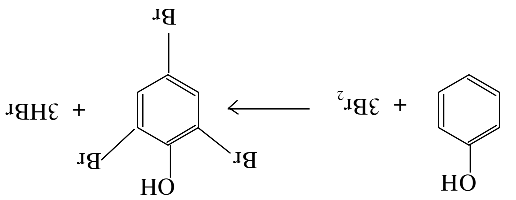
3. Explain why carboxylic acids liberate CO_2 from carbonates and hydrogencarbonates whereas phenol does not. (1 mark)

4. 2,4,6-trinitrophenol was the first chemical to be used as an artificial dye, and has also been used in explosives.
   (i) Draw the structure of 2,4,6-trinitrophenol. (1 mark)
   (ii) Give one test to show the presence of the phenol group in 2,4,6-trinitrophenol. (2 marks)
   (iii) 2,4,6-trinitrophenol dissolves in sodium hydroxide solution. Draw the structure of the organic species. (1 mark)
   (iv) 2,4,6-trinitrophenol reacts with ethanoyl chloride, CH_3COCl
      (a) draw the structure of the organic product (1 mark)
      (b) write a balanced equation for the reaction (1 mark)
      (c) name the class of compounds to which the organic product belongs. (1 mark)

5. State the hazards of using phenol in the laboratory and corresponding precautions which you might take. (2 marks)

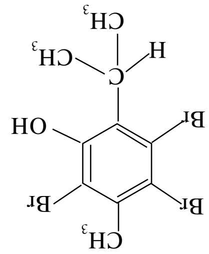
Answers

1. (a) aqueous phenol and bromine water
   (b) white precipitate
   (c)



phenol 2,4,6-tribromophenol

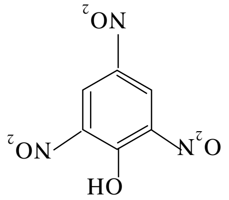
2. (a) Add aqueous iron(III) chloride to thymol.
   The result is an intense violet coloured solution.
   (b)



   Mono-, di-, tri- bromination accepted in any vacant position

3. Carboxylic acids are stronger acids than phenols. Phenols are not strong enough acids to react with carbonates and hydrogencarbonates.

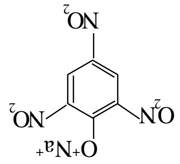
4. (i)



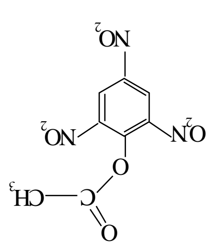
   The bond to the ring from the NO_2 group must come from the nitrogen each time (not from the oxygen.)

   (ii) test: Add iron(III) chloride solution
   result: gives a purple colour

   (iii)



   (iv)(a)



   (b) $C_6H_2(NO_2)_3OH + CH_3COCl \rightarrow C_6H_2(NO_2)_3OCOCH_3 + HCl$
   (c) Ester

5. Hazards: toxic/corrosive
   Precautions: wear gloves/pipette filler/wash spillages with cold water/eye protection

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