Expt: 3

ESTIMATION OF PHENOL
(Back Titration Method)

Aim: Determine the amount of phenol present in the whole of the given an aqueous solution of phenol.

Principle:

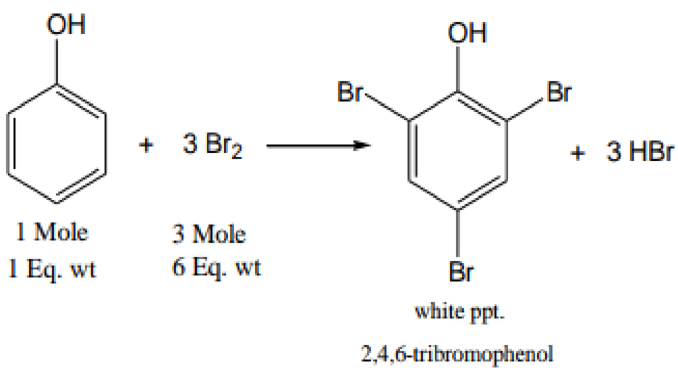
A known volume of the $KBrO_3$- KBr solution (in-situ generated Bromine) is acidified with HCl and then the solution of KI is added so that liberated bromine (eqn.1) can react with KI to give an equivalent amount of iodine (eqn.2)

$$KBrO_3 + 5KBr + 6HCl \rightarrow 3\,Br_2 + 3H_2O + 6KCl \qquad \text{...............(1)}$$

$$Br_2 + 2KI \rightarrow 2\,KBr + I_2 \qquad \text{...............(2)}$$

The liberated iodine is titrated against standardized sodium thiosulphate using starch as an indicator.

The given aqueous solution of phenol is made up to 100 ml exactly. A known volume of this made-up solution is treated with a measured $KBrO_3$- KBr solution. On acidifying this mixture, the bromine liberated (eqn.1) brominates the phenol and the excess of bromine is made to liberate I_2 from KI. This is then titrated against sodium thiosulphate as before. The relevant equations are:



.............(3)

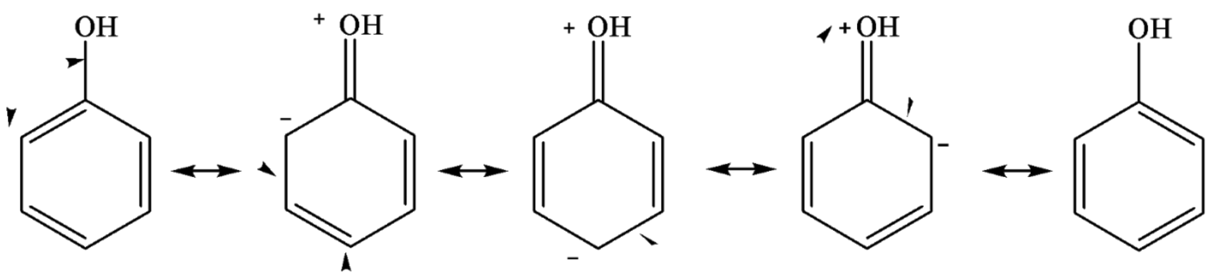
From (eqn.3) it is seen that $C_6H_5OH = 3Br_2$ = 6 equivalents and so the equivalent weight of phenol is $C_6H_5OH/6$ or 15.66.

$$\underset{\text{Excess unreacted (1 Mole)}}{Br_2} + \underset{\text{(2 Mole)}}{2\,KI} \longrightarrow \underset{\text{Free iodine}}{I_2} + 2\,KBr \quad ....(4)$$

$$\underset{\text{(1 Mole)}}{I_2} + \underset{\text{(2 Mole)}}{2\,Na_2S_2O_3} \longrightarrow 2\,NaI + \underset{\text{Sodium tetrathionate}}{Na_2S_4O_6} \quad ....(5)$$

Comments:

1. Standard solution of Br_2 is difficult to prepare and hence the stable $KBrO_3$ – KBr mixture serves as a source for bromine on acidification.
2. OH group attached to the benzene ring is ortho/para directing and it is one of the powerful activating groups in electrophilic aromatic substitution. Thus, phenol forms 2, 4, 6 – aromatic substitution directly with the evolution of HBr. (decolorization of bromine water by olefinic and acetylenic compounds).
3. **Resonance Structures of Phenol:** Bromination of phenol falls under reaction type-electrophilic substitutions. Resonance structures shown below indicate that ortho and para carbons tend to be electron-rich sites and hence the attacking electrophile, viz, the brominium ion (Br^-) preferentially attacks two 'ortho' sites and 'para' site simultaneously. In fact, derivation of phenol into sym-tribromophenol is a well-known reaction in organic qualitative analysis.



4. Aniline is another organic substrate, which undergoes facile bromination by Br_2 water or acidified $KBrO_3$-KBr mixture to give.

2, 4, 6 – tribromoaniline with the evolution of HBr. Since the reaction proceeds quantitatively, the Back titration method can be used for quantitative estimation of phenol in solution.

Materials Required:

Chemicals:

1. $KBrO_3$ – KBr mixture
   [0.1N] 15 g of KBr and 2.8 g of $KBrO_3$ dissolved in 1 lL of water.
2. Conc. HCl
3. 5% KI (5 gm of KI in 100 ml dist. Water)
4. Std. $Na_2S_2O_3$ aq. (0.1 N) (24.8 gm into 1 L of dist. Water)
5. Freshly prepared 2% starch solution (2 gm in 100 ml dist. Water)

Glassware:

1. 250mL Reagent Bottle – 2No.
2. Measuring Cylinder 25mL – 1No.
3. Measuring Cylinder 50mL – 1No.
4. Measuring Cylinder 10mL – 2No.
5. 50mL Burette – 1No.
6. 250mL Conical Flask – 1No.
7. Standard Flask 100mL – 1no.
8. Burette Stand – 1No.

Procedure:

1. Note the bottle number of phenol solution. Make up the given phenol solution to exactly 100 ml using a 100 ml volumetric or standard measuring flask, taking care to avoid loss of phenol, while transferring. Shake the made-up solution to make it uniform in strength.

2. ***Correction of volumes to 0.1 N $Na_2S_2O_3$ & 0.1 N Br_2 solutions or Blank titration:***

Pipette out 25 ml of the given $KBrO_3$-KBr mixture into a 250 ml reagent bottle, add 5 ml of conc. HCl followed by 10 ml of 5% aq. KI, shake vigorously, and titrate against the given standard sodium thiosulphate solution. When the contents of the bottle turn light yellow, 1 to 2 ml of freshly prepared 2% starch solution is added, the solution will turn deep blue. Titration is continued until the deep blue colour just gets discharged. This is the endpoint of the titration. Titration is repeated until concordant titre values are got. Let the titre value be V_1 ml.

3. ***Titration with phenol Solution:***

Pipette out 25 ml of the KBrO3- KBr solution followed by 5 ml of conc. HCl. Immediately stopper the bottle, shake well and set aside for 3 to 5 minutes. Add 20 ml of the made-up phenol solution into a reagent bottle and shake well for 10-15 minutes. Open the bottle, wash the stopper into the bottle, add 10 ml of 5% aq. KI and titrate against the same $Na_2S_2O_3$ aq. using starch as an indicator. The endpoint is the same as in (2). Estimation is repeated with another 20 ml of phenol solution. If the titre values agree, calculate the weight of phenol in the whole of the given phenol solution. Let the titre value be V_2 ml.

4. From (2) and (3) calculate the volume of Bromine (in-situ generated) solution in terms of an equivalent amount of thiosulphate that has reacted with unreacted KBrO3-KBr solution.

Experimental Readings:

Normality of thiosulphate aq. Sodium =

($KBrO_3$- KBr solution + Conc. HCl + KI) Vs $Na_2S_2O_3$

S .No	Volume of $KBrO_3$-KBr solution (ml)	Burette readings		Volume of $Na_2S_2O_3$ required (V_1) ml
		Initial	Final	
1.	25			
2.	25			

(Phenol solution + KBrO3- KBr solution + Conc. HCl + KI) Vs $Na_2S_2O_3$

S .No	Volume of $KBrO_3$-KBr solution (ml)	Burette readings		Volume of $Na_2S_2O_3$ required (V_2) ml
		Initial	Final	
1.	25			
2.	25			

Volume of $Na_2S_2O_3$ (V_2) ml =

Chemical factor:

2 moles of $Na_2S_2O_3$ $\equiv$ 1mole of I_2 $\equiv$ 1 mole of Br_2

So,

6moles of $Na_2S_2O_3$ $\equiv$ 3moles of I_2 $\equiv$ 3moles of Br_2 $\equiv$ 1mole of Phenol

6Eq.wt of $Na_2S_2O_3$ $\equiv$ 6Eq.wt of I_2 $\equiv$ 6Eq.wt. of Br_2 $\equiv$ 1Eq.wt of Phenol

6 x 1000 mL of 1 N Br_2 $\equiv$ 94.11 g of phenol

6000 mL of 0.1 N Br_2 $\equiv$ 9.411 g of phenol

1 mL of 0.1 N Br_2 $\equiv$ (9.411 / 6000) g of phenol

1 mL of 0.1 N Br_2 $\equiv$ 0.001569 g of phenol.

Calculate the volume of bromine reacted with phenol.

Volume of total 0.1 N Br_2 solution added (corrected) = 25 mL

25 mL - V_2 = V_3 mL of $Na_2S_2O_3$ which represent volume of Br_2 reacted with phenol.

Calculate the amount of phenol by using the chemical factor

Each 1 mL of 0.1 N Br_2 $\equiv$ 0.001569 g of phenol.

V_3 x 0.001569 = g of Phenol in 20 mL unknown sample.