Experiment 15

SYNTHESIS OF ACID-BASE INDICATORS

Objective

The purpose of this experiment is to learn the structures, synthesis, and the color change of the acid-base indicator phenolphthalein and its derivatives.

Lab techniques

- Using the alcohol lamp.
- Operating the precipitation and decantation.

Introduction

I. Preparation of phenolphthalein indicator and its color change

Phenolphthalein is a commonly used acid-base indicator. It is colorless when pH of solution is lower than 8; and appears purple red when pH is greater than 10. The synthesis of phenolphthalein is a series of aromatic electrophilic substitution reactions. An electrophile (electron-deficient substance) replaces a hydrogen atom on the benzene ring, known as an addition-elimination reaction. This reaction occurs more readily when the benzene ring bears an electron-donating group and the electrophilic substituent is either *ortho*- or *para*-directing on the ring, since the reaction produces intermediate carbocations that are stabilized in these two arrangements. The general mechanism for a substitution reaction is shown as Fig. 15-1.

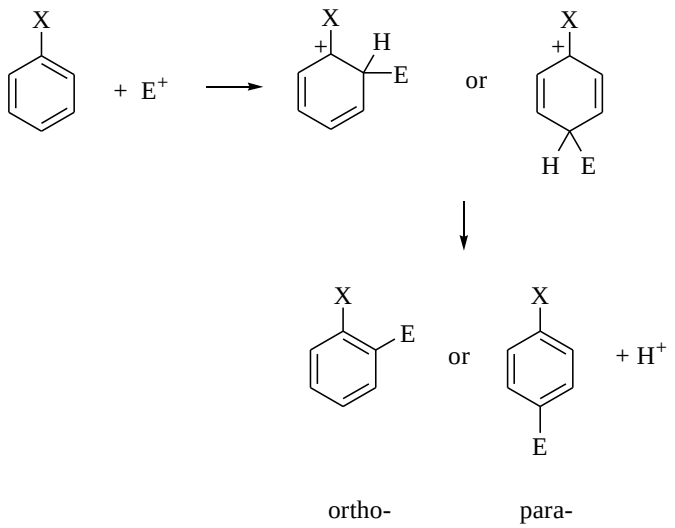
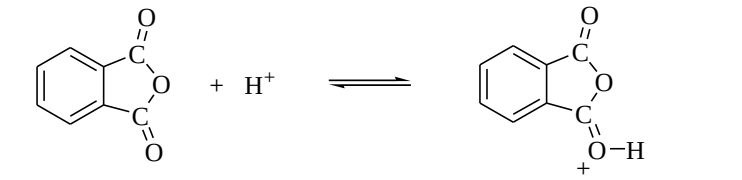


Figure 15-1 General mechanism for an electrophilic substitution reaction

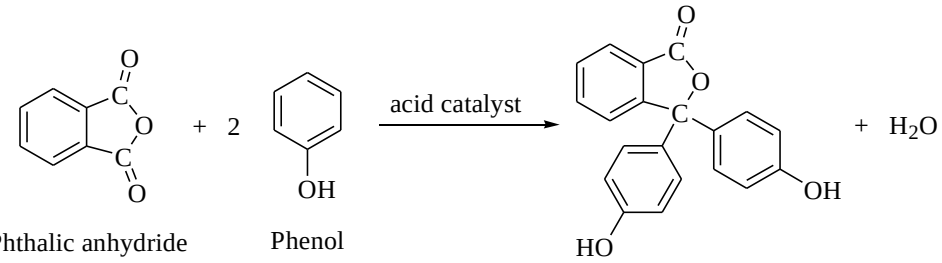
In the synthesis of phenolphthalein, the aromatic reactant is phenol, which bears an electron-donating group, i.e. a hydroxyl group (-OH). The electrophilic reagent is the protonated phthalic anhydride (protonated by H_2SO_4) as equation 15-1.



Phthalic anhydride

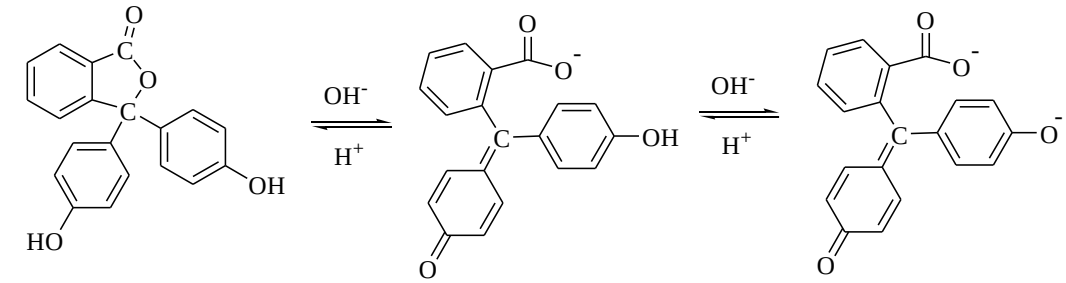
Protonated phthalic anhydride (electrophilic) (15-1)

The synthesis of phenolphthalein from phthalic anhydride is shown as equation 15-2.



Phthalic anhydride Phenol Phenophthalein (15-2)

Since sulfuric acid is present in the reaction process, the product is in the acid form. If sodium hydroxide is added to neutralize it, the weakly acidic hydroxyl group of the phenolic portion will dissociate and a quinoid structure will be produced. Further addition of the base to make the solution alkaline will cause deprotonation to produce a dianion that is purple-red. The reaction is reversible; if acid is added, equilibrium shifts to left to form colorless phenolphthalein (Fig. 15-2).



Phenolphthalein in acidic medium (colorless)

Phenolphthalein in neutral medium (pale yellow)

Phenolphthalein in alkaline medium (purple red)

Figure 15-2 Structures and colors of phenolphthalein

II. Effect of substituent on color

If we replace phenol with guaiacol to react with phthalic anhydride, we get 3´, 3´´-diguaiacol phthalein. Under alkaline condition, this compound is blue, since its absorption wavelength shifts to the long wavelength range due to the presence of two additional substituents. This example demonstrates how the color of organic compounds can be influenced by a change in substituents, and thus the interesting phenomenon of color change (Fig. 15-3).

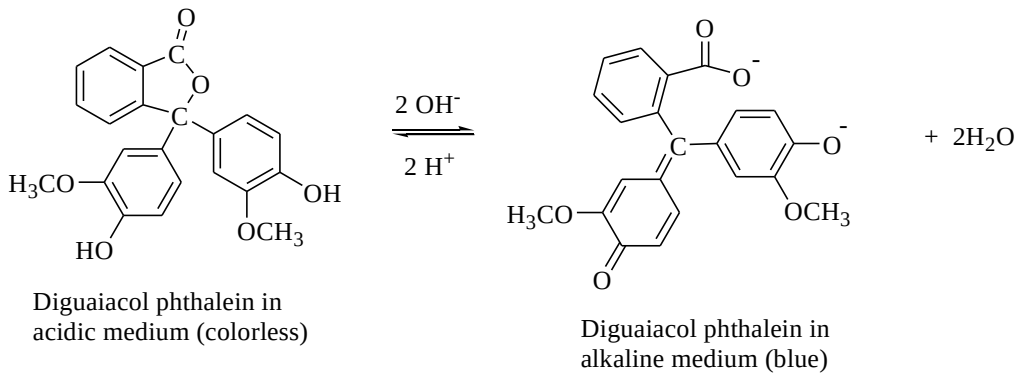
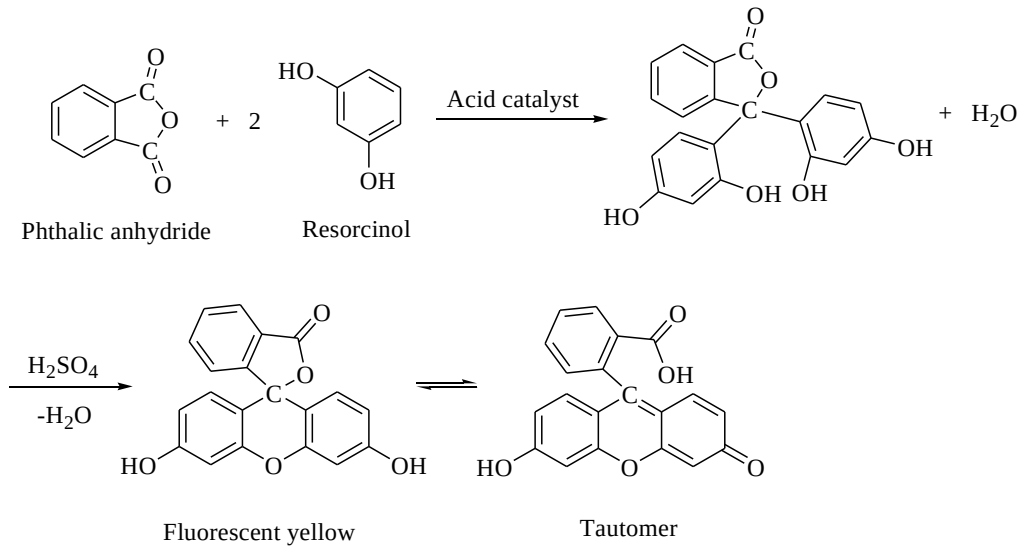
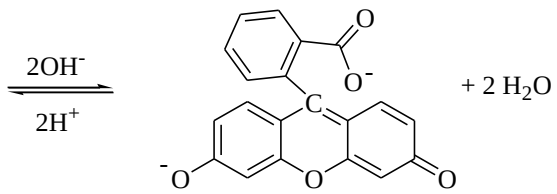


Figure 15-3 Structures and colors of diguaiacol phthalein

III. Synthesis of fluorescent yellow

On the other hand, if we replace phenol with resorcinol to react with phthalic anhydride, the product will have two adjacent hydroxyl groups that can lose water and thus produce fluorescent yellow. This fluorescent yellow exists as tautomers in the solution state. When alkali is added, the acidic hydroxyl groups on the phenolic portion are deprotonated to give a dianion, and green fluorescence is produced. If polyvinyl alcohol is added to this solution, we obtain fluorescent ink (Fig. 15-4).



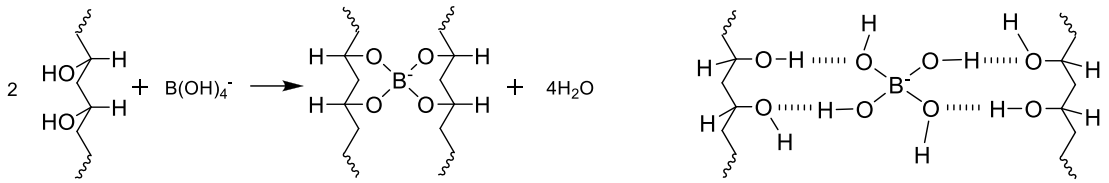


Green fluorescent substance in alkaline medium

Figure 15-4 Structures and colors of fluorescent substances

IV. Synthesis of green fluorescent elastomer

Polyvinyl alcohol (PVA) is a long chain polymer which is usually contained in the glue. If we add and stir sodium tetraborate to PVA solution, it will produce cross linking between polymer chains (Fig. 15-5) that increase its viscosity and may turn into an elastomer. In the fourth part of the experiment we add some synthesized fluorescent substance into PVA/borax solution and obtain a green fluorescent elastomer.



(a) Cross-linking with covalent bonding (b) Cross-linking with hydrogen-bonding

Figure 15-5 The cross-linking between PVA polymer chains

Apparatus

Test tubes (10), test tube holder, test tube rack, graduated cylinder (10 mL), glass rod, beaker (100 mL), alcohol lamp, matchstick, cotton buds, droppers, latex gloves, UV light, activated carbon mask (self-prepared), and digital camera (self-prepared).

Chemicals

Phthalic anhydride, $C_6H_4(CO)_2O$
Phenol, C_6H_5OH
Guaiacol, $CH_3OC_6H_4OH$
Resorcinol, $C_6H_4(OH)_2$
Concentrated sulfuric acid, 18 M H_2SO_4
1 M Sodium hydroxide, NaOH
1 M Hydrochloric acid, HCl(aq)
95% and 10% Ethanol, C_2H_5OH
Polyvinyl alcohol solution (glue)

4% Sodium tetraborate, $Na_2B_4O_7 \cdot 10H_2O$

Procedure

★ The chemicals used in this experiment are volatile and corrosive. Wear latex gloves and avoid chemicals contacting eyes and skin.

★ Perform heating in the fume hood.

I. Preparation of phenolphthalein indicator and test its color change

1. Brush 5 test tubes clean and oven dry in advance.
2. Take 1/2 small spatula (ca. 0.05 g) of phthalic anhydride and put it into a dry test tube. In fume hood, add 2 drops of phenol and 1~2 drops of concentrated sulfuric acid (18 M) to the test tube. Mix thoroughly with a glass rod.
   Caution: Phenol and sulfuric acid are corrosive and should be handled with care.
3. Holding the test tube with test tube holder, heat it for 5 s over the flame of the alcohol lamp, remove from the flame, and stir the mixture with a glass rod. **Repeat heating and stirring reactants several times until all of the solid reactant has disappeared** and the mixture appears dark orange. Stop heating and allow the mixture to cool; then add 3 mL DI water to the test tube. Take the test tube out of hood and operate the following steps on the benchtop.
   Note: Operate the heating of reactants and adding of water in fume hood. Record the color changes as the reaction proceeds. Do not overheat the reactants to avoid the black-brown byproduct.
4. Use a glass rod to stir and mix the solution in the test tube thoroughly. The product (phenolphthalein) is insoluble in water and will precipitate out. Allow the solid product to settle for a few minutes and decant the solution. Add 1~2 mL of 95% ethanol to the remaining solid in the test tube. Stir the solution with a glass rod to dissolve the solid. Transfer an aliquot of this phenolphthalein ethanol solution (ca. 0.5~1 mL) with dropper to a clean test tube for the following test.
5. Add 1 M NaOH(aq) to the phenolphthalein solution drop by drop, and stir it until the solution is basic. Observe and record the color change. Add 1 M HCl(aq) to the solution drop by drop until it is acidic, observe and record the color change.

II. Effect of substituents on color

6. Repeat synthetic procedures as in part I, but replace phenol with 2 drops of guaiacol. Compare color changes of two products upon addition of base and acid.
   Note: This reaction is faster than the first one. Heat the reactants until the solids disappear and the color changes to blue-purple. Do not overheat the reactants to avoid the black-brown byproduct.

III. Synthesis of fluorescent yellow

7. Take 1/2 small spatula (ca. 0.05 g) of phthalic anhydride and 1/2 small spatula of solid resorcinol; put them in a test tube. Add 1~2 drops of concentrated sulfuric acid (18 M) and stir the mixture with a glass rod.
8. Repeat steps 3~4 to synthesize the fluorescent yellow. Take small amount of product to a test tube and add 1~2 mL of 95% ethanol to dissolve it (Fig. 15-6).
   Note: The fluorescent yellow may decompose at its melting point (315°C). Hence, during heating, the test tube should be continuously moved into and out of the flame to avoid overheating.
9. Transfer 2~3 drops of this fluorescent yellow 95% ethanol solution to another test tube. Dilute it with 10% ethanol until the color is very light yellow.
10. Add 1 M NaOH drop by drop to the diluted solution in step 9 and observe the color. You may use a piece of black paper as background.
11. Observe the fluorescence under a UV lamp with the long wavelength (366 nm) and switch to short wavelength (254 nm), alternatively.
    Caution: Avoid UV light shining on skin or eyes that may cause injury.
12. Take about 0.5 mL of the fluorescent yellow 95% ethanol solution obtained in step 8, add several drops of 1 M NaOH and proper amount of PVA glue. When the solution is uniformly mixed, wet a cotton bud with the sticky solution and try to write with this highlighter.

IV. Synthesis of Green fluorescent elastomer

13. Take 3 drops of fluorescent yellow 95% ethanol solution obtained in step 8 and some PVA glue in a 100 mL beaker. Add 1~2 drops of 1 M NaOH, stir with glass rod and mix well.
14. Add sodium tetraborate solution drop by drop. Stir the mixture with glass rod, and observe the color, viscosity, and elasticity change of PVA polymer.
15. After finishing the experiment, rinse the test tubes and glass rod with 10% alcohol, dispose the solution into the waste container, then clean up the glassware.

<table>
<tr><td rowspan="3">Add ½ small spatula of phthalic anhydride
⇓
Add 2 d. conc. sulfuric acid</td><td>(1) Phenol (2 d.)</td><td rowspan="3">Stir and mix
⇓
Heat to react
⇓
Observe change in color and viscosity</td><td rowspan="3">Add water
⇓
Products precipitate out
⇓
Decant the supernatant</td><td rowspan="3">Dissolve products with 95% alcohol</td></tr>
<tr><td>(2) Guaiacol (2 d.)</td></tr>
<tr><td>(3) Resorcinol (½ small spatula)</td></tr>
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Figure 15-6 Summary of the synthesis of phenolphthalein and its derivatives