Production and use of indigo

Aims of the experiment

- Producing the dye indigo
- Understanding one of the most important dyestuff syntheses
- Dying substances with indigo
- Explaining the dying process

Principles

The 1870 discovered indigo synthesis made it possible, for the first time, to synthetically produce indigo, one of the oldest and most important natural dyes. The Indigo synthesis was discovered in 1870 by Adolph von Bayer

Indigo was used since antiquity by a variety of cultures to dye clothing, rugs, and earthenware jugs or for tattooing purposes. The Greeks and Romans used it as a pigment for painting.

Originally, in Europe it was recovered through the fermentation of woad. Beginning in the 12th century, it was recovered from the indigo plant *Indigo feratinctoria* which comes from India.

After synthetic production of indigo became possible in the 19th century, it started being used in large amounts for the production of work clothes and uniforms. Indigo as a dye for blue jeans invented by Levi Strauss in 1873 is a particularly famous use. Even today, dying of jeans is still the main use of indigo. With an annual worldwide production of 30,000 tons, indigo is still the most used textile dye.

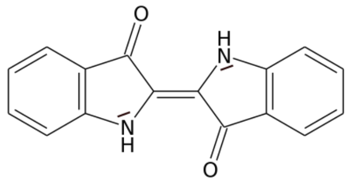

Fig.2: Structure of indigo.

In the experiment presented here, indigo will be produced according to the Bayer-Drewsen reaction from 2-nitrobenzaldehyde and a piece of material will be dyed with it. In the evaluation, the dying processes with indigo will be considered more closely. The calculation of yield and the reaction mechanism are be elucidated in experiment C2.4.1.1.

Risk assessment

When carrying out the experiment, wear goggles, an apron and gloves. Be careful in particular when adding the sodium hydroxide pellets, as they are very corrosive. Keep the bottles of organic solvent away from possible flame sources.

Fig.1: Set-up of the experiment.

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Sodium dithionite	
 **Signal word** **Hazard**	**Hazard statements:** H251: Can heat up by itself; can ignite. H302: Harmful if swallowed. EUH031: Poisonous gases will develop in contact with acid. **Safety statements:** P370+P378: In case of fire: Use sand to extinguish.
Acetone	
 **Signal word** **Hazard**	**Hazard statements:** H225: Highly flammable liquid and vapour. H319: Causes serious eye irritation. H336: May cause drowsiness or dizziness. EUH066: Repeated contact can lead to brittle or cracked skin. **Safety statements:** P210: Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking. P233: Keep container tightly closed. P305+P351+P338: IF IN EYES: Rinse carefully with water for several minutes. Remove contact lenses if present and easy to do so. Continue rinsing.
Ethanol	
 **Signal word:** **Hazard**	**Hazard statements:** H225: Highly flammable liquid and vapour. **Safety statements:** P210: Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.
2-nitrobenzaldehyde	
 **Signal word:** **Caution**	**Hazard statements:** H302: Harmful if swallowed. H315: Causes skin irritation. H319: Causes serious eye irritation. H335: May cause respiratory irritation. **Safety statements:** P261: Avoid breathing dust/fume/gas/mist/vapour/aerosol. P305+P351+P338: IF IN EYES: Rinse carefully with water for several minutes. Remove contact lenses if present and easy to do so. Continue rinsing.

Equipment and chemicals

1	Erlenmeyer flask, DURAN, 100 ml, squat	664 246
1	Spatula with spoon end, 150 mm	666 967
1	Electronic balance 440-3N, 200 g : 0.01 g	667 7977
1	Graduated pipette 5 ml	665 996
1	Pipetting ball	666 003
1	Measuring cylinder, 10 ml, with plastic base	665 751
1	Büchner funnel, 45 mm diam.	665 161
1	Water jet pump	375 56
1	Rubber collar (Guko)	665 060
1	Suction flask 250 ml	664 865
1	Vacuum rubber tubing, 8 mm diam., 1 m	667 186
1	Beaker, DURAN, 100 ml, squat	664 101
1	Beaker, DURAN, 150 ml, squat	602 043
1	Beaker, DURAN, 250 ml, squat	664 103
1	Measuring cylinder, 100 ml, with plastic base	665 754
1	Magnetic stirrer with hotplate, round	666 839
1	Watch glass dish, 80 mm diam.	664 154
1	Glass stirring rod 200 mm x 8 mm diam.	665 212ET10
1	Stirring thermometer, -30...+110 °C/1 K	382 21
1	Round filter type 595 40 mm diam.	661 030
1	2-nitrobenzaldehyde, 5 g	673 9390
1	Acetone, 1 l	670 0410
1	Soda lye, 1 mol/l, 500 ml	673 8420
1	Ethanol, absolute, 500 ml	671 9711
1	Sodium dithionite, 250 g	673 6310
1	Sodium hydroxide, pellets, 250 g	673 6810

Additionally required:
- Distilled water
- Cotton strips

Set-up and preparation of the experiment

Synthesis of indigo

In a 100 ml Erlenmeyer flask, 1 g of 2-nitrobenzaldehyde is weighed out. Acetone, 1 N sodium hydroxide and distilled water are prepared. Also, a 5 ml graduated pipette with a pipetting ball is provided and a 10 ml measuring cylinder.

The porcelain Büchner funnel is inserted in to the suction flask with the rubber collar. The suction flask is then connected to the water jet pump through a tube. A type 595 round filter is placed in the Büchner funnel in such a way that all holes of the funnel are covered. A 100 ml beaker is prepared with 50 ml of ethanol.

Dying with indigo

To dye the material, a 150 ml beaker is filled with 100 ml of distilled water and placed on a magnetic stirrer with hotplate. 2 g of sodium dithionite is weighed out onto a watch glass. Sodium hydroxide pellets and ethanol are also needed.

Performing the experiment

Synthesis of indigo

The weighed out 2-nitrobenzaldehyde is dissolved in 3 ml of acetone. Then, 3 ml of distilled water and 1 ml of 1 N soda lye are added. The solution changes colour to dark brown in the process. After 5 minutes, the solution is filtered. To do so, the water jet pump is first turned on. The filter is made wet with a bit of ethanol.

Note: Check to see that the filter is situated correctly! All holes of the funnel must be covered by filter paper.

Only then are the contents of the Erlenmeyer flask poured over the filter in small steps. Contents remaining in the Erlenmeyer flask are flushed out with ethanol and also added to the Büchner funnel. After the liquid in the Erlenmeyer flask is filtered, the residue in the Büchner funnel is washed again with a bit of ethanol. Then the pump is turned off. The residue obtained will still look a bit brown, but can be used for dying.

Dying with indigo

To produce the water-soluble dye solution (vat), 3 ml of ethanol is first added to a 250 ml beaker. Some of the residue obtained is scraped from the filter using a spatula and stirred into the ethanol.

Note: If yields are low, swirl the filter in ethanol.

10 ml of water and 6 sodium hydroxide pellets are added and stirred with a glass stirring rod until the sodium hydroxide has dissolved.

100 ml of water is heated to 70° C on a hotplate with a magnetic stirrer. The temperature is tracked with a stirring thermometer. The heated water is added to the indigo solution. Then, the weighed out sodium dithionite is dissolved into it. The yellow-green solution obtained is the vat.

A pre-wetted strip of cotton is swirled in the vat for a bit to dye the strip. Subsequent drying in air (if necessary over night) results in the strip changes colour to blue.

Observation

1. After adding the sodium hydroxide to 2-nitrobenzaldehyde and acetone, the solution turns dark brown.

2. During nutsch filtering, a blue-brown mixture is obtained.

3. The colour of the vat is greenish yellow.

4. When a white piece of material is held in the vat and swirled in it, it initially remains white. Only over time whilst drying in air does it turn blue.

5. When the vat sits for a while, a blue layer forms on the surface.

Result of the experiment

The reaction of the indigo synthesis

In indigo synthesis 2 molecules of acetone formally react with 2 molecules of 2-nitrobenzaldehyde with splitting of 2 molecules of acetic acid and 2 molecules of water to form indigo.

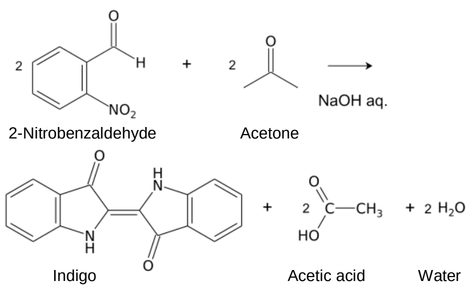

Fig. 3: Overall reaction equation of indigo synthesis.

Reaction of the dyeing process

For the dyeing process, the vat is produced first. In the process, the blue indigo is initially reduced to the colourless leucoindigo:

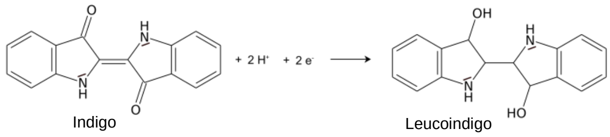

Fig. 4: Reduction of indigo to leucoindigo.

The electron-donating reaction is the oxidation of sodium dithionitrite in the base:

$$Na_2\overset{+III}{S_2}O_3 + 2\,OH^- \rightarrow 2\,Na\overset{+V}{S}O_3 + 2\,H^+ + 4\,e^-$$

The leucoindigo is colourless since the two halves of the π system are no longer conjugated with one another. Because the central bond is able to rotate, the πorbitals of both systems are no longer on a single plane. Thus, what we have are two isolated π systems, each with only 10 electrons. The absorption maximum of the leucoindigo is in the UV range. For this reason, it appears colourless.

When dried in air, the leucoindigo oxidises back to indigo due to the oxygen in the air. The same thing happens at the surface of the vat when it stands in air for a while.

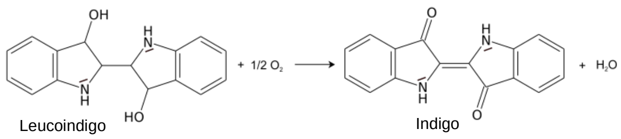

Fig. 5: Oxidation of leucoindigo in air.

The greenish-yellow colour of the vat results as a mixed colour of small amounts of indigo in the vat and the yellow colour of the sodium dithionitrite in the aqueous solution.

The contaminant due to indolone still present plays no role since it reacts completely to form indigo in the vat because it is continuously removed from the reaction equilibrium due to the reaction forming leucoindigo.

Cleaning and disposal

The wash water contains ethanol, therefore, it must be added to the container for organic solvent waste.

The rest of the vat can be added to the container for inorganic solvent waste.