Synthesis of Dyes

Faith B. Cramer
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Faith B. Cramer, Class of 1945
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Group Adviser

Faith B. Cramer

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Introduction

The dyeing property is dependent upon structure; the character of the dyestuff is derived from some group contained in it, called the chromophore. The most important chromophores are C=C, C=O, C=S, C=N, N=O, N=N. Chromophores vary in their effectiveness to produce color. In general, color deepens as the molecular weight increases, especially as the number of chromophores increases.

The fundamental substance containing the chromophore is the chromogen. The chromogen is not a dyestuff, but is converted into this by the entrance of some salt-forming group which destroys the chemically inert character of the chromogen.

The groups conferring salt-forming properties upon the chromogen are auxochromes, which fall into two groups:

a) acidic: SO₂H, COOH, OH
b) basic: NH₂, OH, NR₂

Often a colorless chromogen becomes colored upon introduction of an auxochrome. Benzophenone, for example, becomes yellow when the -NH₂ group is introduced. Azobenzene, which is red, becomes a dye when the -NH₂ is introduced in the para position. Certain auxochromes have a higher effectiveness than others.

Generally speaking, only those organic compounds containing acid or basic groups can be dyestuffs. They are unsaturated, readily reduced by nascent hydrogen, producing leuco compounds. The leuco compounds, in turn, yield the dyestuff again upon oxidation, or break up into bodies of lower molecular weight, which are not reconverted by oxidation.

In dye manufacture, there are certain original substances, such as benzene, naphthalene, anthracene, phenol, cresol, etc.—coal tar derivatives—which by various means are converted into intermediates. The intermediates are such compounds as will by simple reactions form the dyes. They comprise:

a) nitro compounds (nitrobenzene, nitroaniline)
b) amine compounds (aniline, toluidine, naphthylamine)
c) phthalic acids (phthalimide, phthalic anhydride)
d) sulfonic acids
e) halogen compounds
f) phenolic compounds and aminophenols
g) aldehydes and carboxylic acids
h) derivatives having several functions within the molecule (mixed compounds).
Classification of Dyes

Dyes are variously classified. The common methods are according to (a) whether the dyes are acidic or basic; (b) method of application; (c) structure of the dye.

Those dyes containing -NH₂, -NHR, -NR₂ groups will form salts with acids and are termed basic. Those possessing -SO₂H and COOH, or -OH, groups form salts with bases and are termed acid dyes.

Some of the general classifications according to method of application are (1) substantive dyes, or direct dyes; (2) adjective or mordant dyes; and (3) ingrain dyes. Substantive dyes adhere directly to the cloth to be dyed without the aid of supplementary chemicals. Mordant dyes are unable to dye directly, but may do so with the aid of a mordant, usually the hydroxides or basic salts of aluminum, chromium, tin and iron, which form insoluble compounds with the dyes. If the cloth is first dipped in a solution of the mordant, the insoluble dye-mordant compound is firmly fixed within the fiber as it forms. Ingrain dyes are actually formed within the cloth as the result of chemical action between two substances with the cloth is successively treated. Vat dyeing is similar.

Chemically, dyes are classified according to structure. The syntheses done in connection with this paper were chosen by this means. The general scheme follows:

<table>
<thead>
<tr>
<th>Name of dyestuff group</th>
<th>Chromophore</th>
<th>Typical dyestuff synthesized in lab</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Nitroso or oxime</td>
<td>=N=</td>
<td>Resorcin Blue</td>
</tr>
<tr>
<td>2. Nitro</td>
<td>=N=</td>
<td>Naphthol Yellow S</td>
</tr>
<tr>
<td>3. Azo</td>
<td>=N=N=</td>
<td>Methyl Orange</td>
</tr>
<tr>
<td>4. Triphenyl-methane</td>
<td></td>
<td>Magenta</td>
</tr>
<tr>
<td>5. Oxyketone</td>
<td></td>
<td>Alizarin</td>
</tr>
<tr>
<td>6. Pyronines</td>
<td></td>
<td>Eosin</td>
</tr>
</tbody>
</table>
7. Diphenylamines
   (a) Indamines
   (b) Indophenols
   (c) Thiazines
   (d) Oxazines
   (e) Safranines
Laboratory Preparations

1. Fast Green 0
2. Naphthol Yellow S
3. Magenta
4. Eosin
5. Methylene Blue
6. Methyl Orange
7. Purpurin
FAST GREEN 0 (RESORCIN GREEN)

(a) chemicals: Resorcinol 20 gms.
Concentrated HCl 45 gms.
Sodium nitrite 25.5 gms.
Sodium chloride 100 gms.

(b) procedure: The resorcinol is dissolved in 800 cc. water and the hydrochloric acid added together with 100 gms. salt. Ice is added until the temperature is 0°C, and into this solution which is stirred mechanically, the sodium nitrite dissolved in 100 cc. water is allowed to flow very slowly, the temperature not being allowed to rise above 8°C. This takes about a half hour. When all the nitrite has been added, the liquid shows a faintly acid reaction. After standing for one hour, the brownish-yellow precipitate is filtered, washed with ice-cold water and the paste dried on a porous plate. The yield obtained was 34.6 gms.

(c) properties: Greyish-brown powder, soluble in hot water. Dyes iron-mordanted cotton green; iron-mordanted wool dark green.

(d) equation:

\[
\text{Resorcinol} + 2 \text{HNO}_3 \rightarrow \text{Fast Green O}
\]
(a) chemicals:  
- a-Naphthol 100 gms.  
- Concentrated H$_2$SO$_4$ 400 gms.  
- Concentrated HNO$_3$ 174 gms.  
- Sodium carbonate  
- Potassium chloride 75 gms.

(b) procedure: The sulfuric acid is warmed to 100°C in a round-bottom flask, and the naphthol (powdered) is added all at once. The temperature is now raised to 120°C and kept at this point for 3-4 hours. The sulfonation mixture is then poured into 600 cc. water and stirred mechanically. As soon as the temperature is about 30°C, the solution is poured into a mixture of 90 gms. HNO$_3$ and 33 cc. water, the temperature being kept below 35°C. A further 84 gms. HNO$_3$ is now added, during which addition the temperature may rise to 40°C. The nitration mixture is now filtered on woollen cloth. According to Cain and Thorpe, it is washed free from acid with salt solution; the drained paste stirred with hot water at 80°C, sodium carbonate added until neutral, and the dyestuff precipitated by adding potassium chloride. However, the nitration mixture passed through the cloth easily, so the solution was simply heated to 80°C, the sodium carbonate added, etc. The precipitated dye is filtered and dried on a porous plate. The dye appeared as a muddy-yellow wet powder. Yield: 61.6 gms.

Attempts to find a solvent suitable for purification of the dye were unsatisfactory. A portion of the dye was recrystallized from hot alcohol; three liters of alcohol yielded 2.4 gms. pure dye. After recovery of the alcohol, another gram of dye was obtained.

(c) properties: orange-yellow powder; dyes wool and silk yellow from an acid bath.

(d) equation:

\[
\text{a naphthol} + 2\text{HNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{Naphthol Yellow S} + 3\text{H}_2\text{O}
\]
MAGENTA

(a) chemicals: Aniline 20 gms.
Commercial toluidine—64%ortho, 36%para
Concentrated HCl 67 gms.
Nitrobenzene 55 gms.
Iron wire 3 gms.

(b) procedure: 14 gms. aniline and 54 gms. toluidine are mixed together in a porcelain basin and the HCl added. The mixture of hydrochlorides is heated until the temperature is 130° when it is transferred to a round-bottom flask, in which has been placed the rest of the aniline and toluidine together with the nitrobenzene. The mixture is heated in an oil bath to 100° when the iron, dissolved in two mols of HCl (to form ferrous chloride) is slowly added.

The flask is now connected to a reflux condenser and the temperature raised gradually to 180° which is maintained 6-8 hours. The temperature never rose above 170° so the mixture was heated a longer time. The melt is finished when a sample withdrawn on a glass rod solidified on cooling.

The contents of the flask are then steam-distilled when a mixture of red oil and nitrobenzene passes over. The melt is now poured into 500 cc. boiling water, well-stirred, and 12 cc. concentrated HCl added slowly. As soon as an acid reaction is obtained, 25 gms. salt are added, and the whole boiled for a few minutes.

The aqueous solution which is poured off contains the hydrochlorides of aniline and toluidine which, as well as the previous distillates, is, on the large scale, used again in the manufacture. The residue is allowed to cool and should solidify to a green, brittle mass. This is then extracted with 1½ liters of boiling water containing 12 cc. HCl which dissolves the magenta. After filtering, the solution is allowed to cool, and upon standing, a little colouring matter separates out.

Using the above procedure, a dark powder was obtained at the point where a brittle mass should have appeared. The whole procedure was repeated, as a check, with the same results. Then it was tried again, using ferrous sulfate in place of the ferrous chloride, and heating at least 18 hours at 170°. This time, large shining crystals separated out on standing. Some of these were extracted with boiling water as directed, and a very little magenta was obtained. Yield: 131.1 gms. of the large crystals.

(c) properties: the hydrochlorides form glistening crystals with a greenish reflection, dissolving in water to a red solution; dyes silk and wool bluish-red direct; cotton after having been mordanted with tannin and tartar emetic.
(d) equation;

\[
\begin{align*}
\text{p-tolidine} & \quad \xrightarrow{[0]} \quad \text{p-aminobenzaldehyde} \\
\text{NH}_2 + \text{C} + \text{HCHO} & \quad \rightarrow \quad \text{CH} + \text{NH}_2 + \text{H}_2\text{O} \\
\text{Magenta} & \quad \xrightarrow{[0]} \quad \text{carbabil base}
\end{align*}
\]
EOSIN

(a) chemicals: Fluorscein 15 gms.
Bromine 33 gms.
Alcohol 60 gms.

(b) procedure: The fluorscein is placed in a flask, the alcohol added, and the bromine dropped in slowly from a small dropping funnel. When half the bromine has been added, the dibromide which is formed is in solution; but on further addition of bromine, the tetrabromide separates out. After standing for two hours, the precipitate is filtered, washed first with alcohol, then with water, and converted into the sodium salt by mixing it with a little hot water, carefully neutralizing with caustic soda (avoiding an excess of this reagent) and evaporating to dryness on a water bath. Yield: 25.6 gms free acid; 3.16 gms sodium hydroxide added, giving 24.9 gms sodium salt of eosin.

(c) properties: forms bluish-red crystals or a brownish-red powder, dissolving in water with a bluish-red color; dyes wool and silk yellowish-red.

(d) equation:

\[
\begin{align*}
\text{Fluorscein} & \quad + 4\text{Br}_2 & \rightarrow & \quad \text{Eosin (free acid)} \\
& \quad + 4\text{HBr} & & \\
\end{align*}
\]

\[
\begin{align*}
2\text{NaOH} & \quad \text{Na}_2\text{Eosin} \\
\text{Eosin (sodium salt)} & \quad \text{Na}_2\text{Eosin} \\
\end{align*}
\]
METHYL ORANGE

(a) chemicals:
- 5% Sodium carbonate 50 cc.
- Sulfanilic acid 11 gms.
- Sodium nitrite 3.5 gms.
- Concentrated HCl 7 gms.
- Dimethylaniline 6 gms.
- Glacial acetic acid 3 gms.
- Sodium hydroxide 7 gms.
- Salt 20 gms.

(b) procedure:
Place 50 cc. 5% Na₂CO₃ in a beaker, add 50 cc. water, and the sulfanilic acid. If the sulfanilic acid does not completely dissolve, add 5-10 cc. more Na₂CO₃. If necessary, then filter the solution with suction to remove the undissolved residue. Add the sodium nitrite (dissolved in 20 cc. water). Cool until the temperature is 3-5°C, then stir vigorously and add drop by drop a mixture of 7 gms. HCl and 10 cc. water. Test for complete diazotization with Potassium iodide-starch paper.

Add 3 gms. acetic acid to 6 gms. dimethylaniline; add this mixture to the diazonium salt solution immediately. Allow to stand with occasional stirring for 5-10 minutes. Finally make the solution alkaline by adding a solution of 7 gms. sodium hydroxide in 20 cc. water. The methyl orange separates at once; it may be made to precipitate more completely by adding 20 gms. salt. Filter with suction, using hardened filter paper, and crystallize the impure product from hot water. Cool the hot filtered solution with suction, wash with alcohol, and finally with ether.

Yield: 8.6 gms. pure dye

(c) properties:
- Bright orange powder, dissolves in water with an orange color; used as indicator—yellow in basic solution and red in acid solution.

(d) equation:

\[
\begin{align*}
\text{Sulfanilic acid} & \quad \text{Dimethylaniline} \\
\text{N} &= \text{N} + \text{N(CH₃)}₂ \quad \text{HCl} + \text{N} = \text{N} \quad \text{HCl}
\end{align*}
\]
METHYLENE BLUE

(a) chemicals: Dimethylaniline 24 gms.
Concentrated HCl 65 gms.
Sodium nitrite 7.1 gms.
Zinc dust 30 gms.
Sodium thiosulfate 50 gms.
Potassium dichromate 25 gms.
Sulfuric acid 53 gms.
Sodium chromate 8 gms.

(b) procedure: 12 gms. dimethylaniline are dissolved in a mixture of 40 cc. water and 65 gms. concentrated HCl, and the solution cooled to 12-15°C. This is stirred mechanically, and a solution of 7.1 gms. sodium nitrite run in slowly (delivery tube beneath the surface of the liquid) keeping the temperature below 15°. The nitroso compound is reduced by adding 20 gms. zinc dust carefully. Additional small amounts of zinc and acid were added until the clear red color of the solution indicated the reduction was complete. The solution is now diluted with water to 500 cc. and a solution of 12 gms. dimethylaniline in 10 cc. HCl added, and then a solution of 50 gms. sodium thiosulfate in a little water.

The mixture is oxidized by adding a concentrated solution of 25 gms. Potassium dichromate; Cain and Thorpe say to boil the mixture for two hours. Since a dark blue precipitate appeared immediately, this was not done.

53 gms. sulfuric acid first diluted with 100 cc. water are now added, and the solution boiled to expel SO₂. The leucocyanine blue is oxidized by adding 8 gms. neutral potassium chromate dissolved in a little water, and the resulting dye precipitated by adding salt.

The base is filtered, dissolved in a little boiling water to which a little HCl has been added, and the hydrochloride precipitated by common salt, filtered, and dried on a porous plate.

(c) properties: dark green, or red-brown bronzy powder, easily soluble in water, forming a blue solution; dyes tannin-mordanted cotton blue.

(d) equation:
PURPURIN

(a) chemicals:  
Alizarin 20 gms.
Concentrated H 2 O 200 gms.
Manganese dioxide 10 gms.

(b) procedure: Into 200 gms. sulfuric acid are mixed 20 gms. dryed and powdered alizarin, while stirring, in an oil bath at 100°C. The temperature is raised gradually to 150°C, where it is maintained, until a sample diluted with water, filtered and washed with water, dissolves in dilute caustic soda with a red, not violet, color. After cooling, the melt is mixed with 10 kg. cracked ice, the precipitate filtered and washed with H 2 O. The purpurin may be purified by extracting with alum mixture, and then alcohol.

(c) properties: yellow-red powder; the compound of purpurin with ammonia and the alkalies are of bright red color and are soluble in H 2 O.

(d) equation:

\[
\begin{align*}
\text{Alizarin} & \quad \text{[1]} \quad \text{Purpurin}
\end{align*}
\]


