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DIRECT SULFURATION OF SIMPLE ORGANIC COMPOUNDS[1]

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Palmer and co-workers (1, 2) found that a wide variety of organic compounds reacted directly with molten sulfur to form sulfur dyes and other organic compounds. The method employed in this process consisted essentially in passing the vaporized organic reactant into molten sulfur at various temperatures (approximately 200° or above). Hydrogen sulfide was evolved in various amounts during the reactions. The sulfur compounds were produced in the excess molten sulfur at the bottom of the reactor and were purified by extraction with carbon disulfide and other solvents. The products prepared above 300° were sulfur dyes.

Heretofore all of the solid products obtained from the sulfuration of organic compound vapors have been amorphous. Recently, by modifying the apparatus and procedure we have isolated *crystalline* material formed during the preparation of a sulfur dye from nitrobenzene. The yields of the crystalline material varied from 4 to 5.5%, while at the same time about 55% of the original material was converted into an amorphous, green sulfur dye. Instead of the emission of hydrogen sulfide, sulfur dioxide was produced. Because of the exactness of technique required in obtaining the crystalline material the following procedure is given in detail.

EXPERIMENTAL

Preparation of the crystalline product. The apparatus is shown in Figure 1. The vaporization chamber, A, is a wide-mouth 500-ml. Erlenmeyer flask, provided with a good cork stopper drilled to accommodate the Y-tube B. The latter should be 18–20 mm. in diameter, with the vertical limb projecting approximately 12 cm. above the flask A. Addition of the nitrobenzene is accomplished by means of the Pyrex dropping-funnel, C. A length of tubing is sealed to the funnel stem so that the open end extends just below the end of the Y-tube. The side arm D is bent to make an angle of 45° with the upper limb of the Y-tube. The inclined condenser, E, measures 120 cm. in length. Current practice is to join the condenser to the Y-tube with a good cork stopper because ground joints occasionally have caused trouble. A tube attached to the upper end of the condenser carries the sulfur dioxide to absorbing bottles or to a fume hood. Heating is conveniently accomplished by a Wood's alloy bath.

The flask A is charged with 40 g. of flowers of sulfur, and the assembly B C E is then placed in position, taking precautions to have all joints gas-tight. Since wide-mouth Erlenmeyer flasks sometimes have imperfectly shaped necks it may be necessary to obtain a good seal by wrapping the cork with one layer of thin asbestos sheeting. When the latter is slightly moistened a good seal can be obtained by pressing the stopper firmly into the neck of the flask. After the alloy in the heating-bath has been melted the entire assembly is lowered so that the bottom of the vaporization flask A is 2.5–3 cm. below the surface of the bath. The temperature of the molten alloy is raised to 330–340°.

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When the flask is well filled with sulfur vapor the addition of nitrobenzene from funnel C is begun. It may require five minutes to add the first 5-ml. portion. During the addition, vapor should pass up into the condenser. While the bath temperature is kept in the 330–340° range, the remainder of the 50 ml. of nitrobenzene is added slowly. The rate should be sufficiently rapid to cause the reflux ring to gradually rise in the condenser until it has gone approximately two-thirds up the length of the tube. However, at no time should a large pool of liquid be permitted to accumulate on the surface of the sulfur.

After the reaction has been in progress for 20–40 minutes a crystalline solid begins to deposit on the wall of the condenser. Eventually, *i.e.* after about 20 ml. of nitrobenzene have been introduced, the addition of each 5-ml. portion will require from 12–20 minutes. By adopting this rate the reflux ring in the condenser will gradually recede. This is important in preventing too much of the crystalline deposit from being dislodged from the walls and washed back into the vaporization flask. The time required for the addition of 50 ml. of nitrobenzene is about 2 hours (±10 minutes). Heating should be continued until reflux has practically ceased, which may require an additional period of 15–30 minutes.

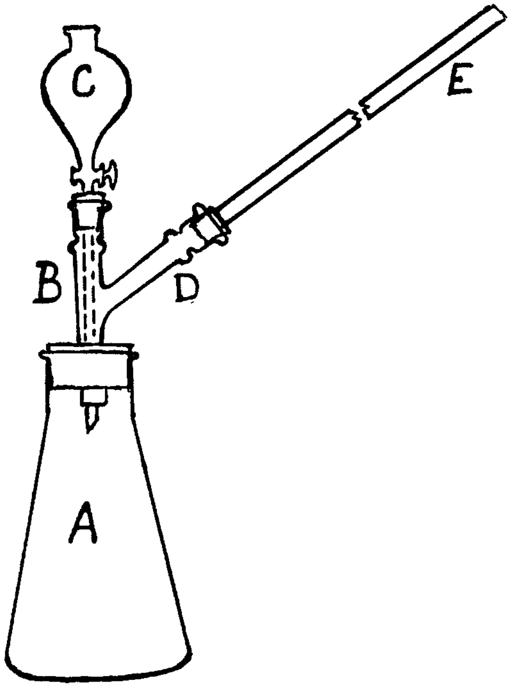

FIGURE 1.

The condenser is removed from the assembly and clamped in a vertical position overnight in order to permit the excess nitrobenzene to drain from the solid deposit. Final traces of the liquid are removed by drawing air through the tube for a number of hours. Finally the solid product can be scraped out by means of a heavy glass rod, the end of which has been flared to form a disc. The yield of dried, microcrystalline product is usually 5–5.5 g. In order to remove any free sulfur which might have been deposited with the crystalline material the latter is placed in a Soxhlet apparatus and subjected to prolonged extraction with C. P. benzene or with anhydrous ether.

Analyses of the crystalline material. When the crude crystals were allowed to stand exposed to air for approximately one week and recrystallized from absolute ethyl alcohol, elemental and sulfate analyses, and molecular weight determinations showed the recrystallized substance to be practically pure aniline sulfate $(C_6H_5NH_2)_2 \cdot H_2SO_4$). The crude white crystals when freshly prepared also contained a small amount of unstable aniline-sulfur dioxide addition product (3).

TABLE I

BEHAVIOR OF THE CRYSTALLINE PRODUCT

TREATMENT GIVEN	RESULTS
1. Barium hydroxide solution	Released NH_3.
2. Potassium carbonate solution	Released NH_3.
3. Potassium ferricyanide solution	Reagent reduced.
4. Chloroplatinic acid, 2%	Solid gradually yields lathlike crystals.
5. Chloroauric acid, 2%	Reduction. Blue ppt. and metallic gold.
6. Palladium chloride, 1%	Curd-like orange-colored ppt. plus slender prismatic crystals.
7. Ferric nitrate solution	Green ppt.
8. Ferric chloride solution	Green ppt.
9. Silver nitrate solution	White ppt. which rapidly turned brown. After thorough washing the brown ppt. was identified as silver sulfide.
10. 30% Hydrogen peroxide	No visible change.
11. Oxygen gas	Bubbled through solution 25 hrs. No change observed.
12. Sodium hydroxide solution, 10%	Aniline, NH_3, and small unidentified residue.
13. Fusion with sodium hydroxide	Aniline and NH_3.
14. Ammonium hydroxide solution (conc'd)	Aniline.
15. Heated to 250°	Green sulfur dye residue, SO_2, and aniline.
16. Glacial acetic acid	H_2S evolution over a long period.
17. Benzyl alcohol	H_2S evolution.
18. 1,4-Dioxane	H_2S evolution over a long period.
19. Benzothiazole	Slight evolution of H_2S.
20. Nitrobenzene	Copious H_2S evolution; charred residue.
21. *o*-Nitrotoluene	H_2S evolution.
22. *o*-Toluidine	H_2S evolution.
23. Dimethylaniline	H_2S evolution.
24. Mesityl oxide	Slight H_2S evolution; discoloration of liquid.
25. Acetylacetone	H_2S evolution.
26. Acetonylacetone	Abundant H_2S evolution; solution becomes pink, then passes through red, carmine, purple to deep blue.
27. Diacetone alcohol	H_2S evolution; solution turns pink, finally brown.
28. Acetone	No H_2S.

The behavior of an aqueous solution of the crystalline material (crystals extracted from benzene or ether and placed in well-stoppered small bottle) toward various reagents at room temperature, the effect of boiling the material in various organic liquids, and the substances produced upon heating are given in Table I.

Similar results with the boiling organic liquids were obtained from crystals recrystallized from water.

The dried crystalline product obtained by the sulfuration of nitrobenzene had a faint odor of sulfur dioxide; even after having been extracted for 50–60 hours a trace of sulfur dioxide odor persisted. This was especially true upon opening a bottle in which the crystals had been stored for several weeks. The material gave a positive carbylamine test, indicating the presence of one or more potential amino groups. At room temperature the solubility of the material in water is a little over 7%, while in most of the common organic solvents tried, the solubility at room temperature is negligible. The material is practically insoluble in C. P. ether, benzene, toluene, chloroform, chlorobenzene, ligroin, etc. At 25°, 100 g. of absolute alcohol will dissolve 1.24 g.

Green amorphous sulfur dye (Flask A, Fig. 1). The quantity of unreacted sulfur present in different runs varies from practically 30–40% of the melt. After removal of the unreacted sulfur the color of the residue is almost black but it leaves a green streak on unglazed porcelain. Although the solid is not affected by common solvents it imparts a blue-green color to cotton. When produced at higher temperatures the nitrobenzene-sulfur dye imparts a deep green color to cotton.

SUMMARY

1. A new procedure is given for the preparation of crystals and a green sulfur dye by the sulfuration of nitrobenzene. Sulfur dioxide is also evolved.
2. Analyses, molecular weights, and certain properties of the freshly prepared crystals show the presence of aniline sulfate and a small amount of aniline-sulfur dioxide addition product.
3. The fresh crystalline product obtained by heating sulfur with nitrobenzene has the property of being converted, by treatment with alkali, chiefly into *aniline*, and some ammonia with a small amount of an unidentified solid; heat alone converts it into a *sulfur dye*, sulfur dioxide, and a small amount of aniline.
4. This apparent intermediate crystalline material should give us information about the structure of the *simplest* sulfur dyes.

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