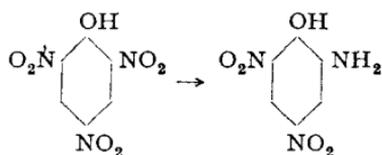
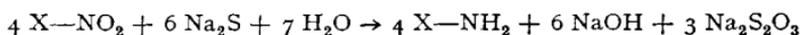


Picramic Acid



In a glass or iron container of at least 2.5-liter capacity, a solution of 10 grams of picric acid and 10 grams of 35 per cent sodium hydroxide in 600 cc. water is heated to 55°C., and to this is added, with vigorous stirring over a period of 10 minutes, a solution of *crystalline* sodium sulfide in 100 cc. water. When this addition is completed, an additional 127.5 grams of pulverized picric acid is added in teaspoon portions, and simultaneously a solution of 220 grams of sodium sulfide in 400 cc. water is introduced, the additions of the two reagents being completed at the same time (within about 10 minutes in all). If the temperature goes above 65°, ice is added. Stirring is continued for 10 minutes more, then the mixture is poured onto 400 grams of ice, precipitating the sodium picramate completely. After 10 hours, the mixture is filtered, and the precipitate is washed with 10 per cent salt solution. Free picramic acid is obtained by dissolving the sodium salt in 500 cc. water, warming the solution to 80°, and acidifying, with stirring, with dilute sulfuric acid. The mixture, which should be just acid to Congo red, is allowed to cool and stand for 10 hours. The product is then filtered off, yielding about 100 grams of pure material.

Variation. The partial reduction of picric acid can be effected in various ways. Instead of adding the picric acid gradually, and thus using it to neutralize the alkali formed:



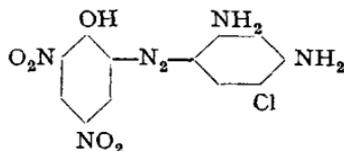
(see also page 114) the sodium salt can be reduced and the necessary amount of hydrochloric acid added simultaneously.

For example, 0.6 mole (137.5 grams) of picric acid is mixed with 1.2 liters of water and 36 grams of soda ash at 50°. Solution is not complete. When the carbon dioxide has been expelled, a solution of 1 mole (240 grams) of crystalline sodium sulfide in 450 cc. water is added, with good stirring, during the course of 30 minutes. Simultaneously, a mixture of 108 grams of 30 per cent hydrochloric acid and 300 cc. water is added at such a rate that this addition requires about 1 minute longer than that of the sodium sulfide solution. Stirring is then continued, with-

out heating, for 30 minutes, and the mixture is filtered after 12 hours. The precipitate is washed with 100 cc. saturated salt solution. This crude sodium picramate is dissolved in 2 liters of water, and the solution is filtered and poured into a hot (90°) solution of 70 cc. 30 per cent hydrochloric acid in 400 cc. water. The pure picramic acid is precipitated completely after 24 hours, and is filtered off, washed with a small amount of water, and dried at 80°. The yield is about 100 grams, or 83 per cent of the theoretical amount.

Of the two procedures given, the first is better suited for large scale work, because the additions of the reagents can be regulated better.

Picramic acid has recently become very important as an azo dye component. Its diazo compound, reacted with unsulfonated couplers, gives very fast chrome dyes for wool, characterized by the fact that they can be used with chromic acid in the dye bath. Examples are the metachrome dyes, e.g., metachrome brown:



These dyes are generally very difficultly soluble and are often explosive in the dry state. Hence, they must be mixed with a large quantity of Glauber salt or marketed as a paste with water.

The diazo compound of picramic acid was the first diazonium compound discovered and led to the important work of Peter Griess.