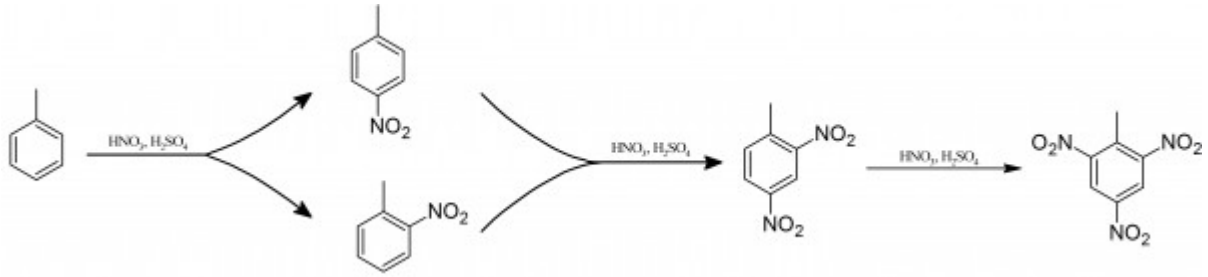
Preparation of 2,4,6-trinitrotoluene



A mixture of 294 g of concentrated sulfuric acid (d=1.84 g/ml) and 147 g of nitric acid (d=1.42 g/ml) is added slowly from a dropping funnel to 100 g of toluene in a tall 600 ml beaker, while the liquid is stirred vigorously with an electric stirrer and its temperature is maintained at 30° C to 40° C by running cold water in the vessel in which the beaker is standing. The addition of acid will require from an hour to an hour and a half. The stirring is then continued for half an hour longer without cooling; the mixture is allowed to stand over night in a separatory funnel; the lower layer of spent acid is drawn off; and the crude mononitrotoluene is weighed. One-half of it, corresponding to 50 g of toluene, is taken for the dinitration.

The mononitrotoluene is dissolved in 109 g of concentrated sulfuric acid (d=1.84 g/ml) while the mixture is cooled in running water. The solution in a tall beaker is warmed to 50° C, and a mixed acid, composed of 54.5 g each of nitric acid (d=1.50 g/ml) and sulfuric acid (d=1.84 g/ml), is added slowly drop by drop from a dropping funnel while the mixture is stirred mechanically. The heat generated by the reaction raises the temperature, and the rate of addition of the acid is regulated so that the temperature of the mixture lies always between 90° C and 100° C. The addition of the acid will require about 1 hour. After the acid has been added, the mixture is stirred for 2 hours longer at 90-100° C to complete the nitration. Two layers separate on standing. The upper layer consists largely of 2,4-dinitrotoluene, but probably contains a certain amount of 2,4,6-trinitrotoluene. The trinitration in the laboratory is conveniently carried out without separating the 2,4-dinitrotoluene from the spent acid.

While the dinitration mixture is stirred actively at a temperature of about 90° C, 145 grams of fuming sulfuric acid (oleum containing 15% free sulfur trioxide) is added slowly by pouring from a beaker. A mixed acid, composed of 72.5 g each of nitric acid (d=1.50 g/ml) and 15% oleum, is now added drop by drop with good agitation while the heat of the reaction maintains the temperature at 100-115° C. After about three-quarters of the acid has been added, it will be found necessary to apply external heat to maintain the temperature. After all the acid has been added (during 1,5 to 2 hours), the heating and stirring are continued for 2 hours longer at 100-115° C. After the material has stood over night, the upper 2,4,6-trinitrotoluene layer will be found to have solidified to a hard cake, and the lower layer of spent acid to be filled with crystals.

The acid is filtered through a Buchner funnel (without filter paper), and the cake is broken up and washed with water on the same filter to remove excess of acid. The spent acid contains considerable TNT in solution; this is precipitated by pouring the acid mixture into a large volume of water, filtered off, rinsed with water, and added to the main batch. All the product is washed three or four times by agitating it vigorously with hot water under which it is melted. After the last washing, the TNT is granulated by allowing it to cool slowly under hot water while the stirring is continued. The product, filtered off and dried at ordinary temperature, is equal to a good commercial sample of crude TNT. It may be purified by dissolving in warm alcohol at 60° C and allowing to cool slowly, or it may be purified by digesting with 5 times its weight of 5% sodium bisulfite solution at 90° C for half an hour with vigorous stirring, washing with hot water until the washings are colorless, and finally granulating as before. Pure 2,4,6-trinitrotoluene, m.p. 80.8°, may be procured by recrystallizing this material once from nitric acid (d=1.42 g/ml) and once from alcohol.

Chemistry of Powder and Explosives, by T. L. Davis, 148-149, 1941

2,4,6-trinitrotoluene is prepared by nitrating 2,4-dinitrotoluene with the nitrating mixture containing 83% of concentrated sulfuric acid and 14.5% of fuming nitric acid. Furthermore, for the complete nitration, the nitric acid should be counted with 100% excess.

To the round bottom flask containing calculated amount of nitrating mixture, 40 g of dinitrotoluene are slowly placed. The reaction mixture is starting gently to heat until the temperature reaches 80° C. Slowly the temperature is raised to 110° C and keep at that temperature for 1 hour. After nitration is complete the reaction flask is cooled to 80° C. At this temperature distilled waters is slowly added to the reaction mixture and the reaction product is separated as a yellow oil in a separation funnel. Then the reaction product is further washed with distilled water, diluted sodium carbonate solution in order to remove the inorganic acids. 2,4,6-Trinitrotoluene contains some inorganic acids. To fully remove those acids 2,4,6-trinitrotoluene should be washed many times with distilled water and diluted sodium carbonate solution. Finally, 2,4,6-trinitrotoluene is recrystallized from a mixture of 95% of ethyl alcohol and 5% of toluene. Interestingly 2,4,6-trinitrotoluene also could be recrystallized from conc. nitric acid.