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SUPPORTING INFORMATION

Title: Synthesis and Characterization of New Energetic Nitroformate Salts
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Synthesis of Nitroform.[1] Anhydrous nitric acid (31.5 g (0.5 mol) was placed in a 250-mL Erlenmeyer flask provided with a two-holed stopper which has a slit cut in one edge to serve as an air vent and which holds a thermometer with the bulb reaching almost to the bottom of the flask. The flask is cooled below 10°C in ice water, and 51 g (0.5 mol) of acetic anhydride is slowly added from a burette in aliquots of about 0.5 mL through the second hole in the stopper. The temperature of the reaction mixture is never allowed to rise above 10°C. After about 5 mL of the acetic anhydride has been added the reaction becomes less violent, and larger portions, increasing gradually from 1 to 5 mL, may be introduced at a time with constant shaking. After all the acetic anhydride has been added, the stopper and the thermometer are removed. The neck of the flask is wiped clean with a towel, and the flask is then covered with an inverted beaker and allowed to increase to room temperature in the original ice bath. The mixture remains at room temperature for 7 days, and the tetranitromethane is separated by pouring the mixture into 300 mL of water in a 500-mL round-bottomed flask and steam distilled. The tetranitromethane passes over with the first 20 mL of the distillate. The heavy product is separated from the upper layer of water, washed first with dilute alkali, finally with water, and dried over anhydrous sodium sulfate. The yield of tetranitromethane is 12.2g (50%). *Caution! The product should not be distilled, as it may decompose with explosive violence.*

Tetranitromethane must be kept out of contact with aromatic compounds except in *very small* test portions, since violent explosive reactions can occur. To a solution of 6.9 g (122.4 mmol) of potassium hydroxide in 7 mL of water and 17 mL of ethanol was added dropwise 12 g (61.2 mmol) of tetranitromethane with stirring at a temperature maintained between 15-20 °C using an ice-water bath. The yellow precipitate of potassium nitroform was formed immediately. After the addition of tetranitromethane, the reaction mixture was stirred at room temperature for another 30 min. Then the precipitate was collected, washed with 10 mL of ice-water, 10 mL of ethanol, and finally 10 mL of ice-water, dried slowly under air. Potassium nitroformate was obtained 10.82 g (94 %) as yellow powder. *Caution! Potassium nitroformate cannot be stored.* Concentrated sulfuric acid (15 mL) was added slowly to a suspension of potassium nitroformate in hexane (250 mL) at 5-10 °C with stirring. During the addition of sulfuric acid the color of the reaction solution turned to colorless and a white precipitate (potassium sulfate) was formed. After stirring for a further 30 min at low temperature, the clear solution was poured into another pre-cooled flask, the residual white solid was washed with cool hexane (40 mL). The desired product was isolated from the combined hexane solution by recrystallization at -60 to -80 °C. Nitroform was obtained 6.9 g (80 %) as white crystalline solid, m.p. >22 °C. Nitroform can be stored at -18 °C for months.

[1] a) P. Liang, *Organic Synthesis,* **1955**, *3*, 803-809; b) F. G. Borgardt, A. K. Seller, P. J. Nobel, *Org. Chem*, **1966**, *31*, 2806-2811; c) H. Shechter, H. L. Cates, *J. Org. Chem*, **1961**, *26*, 51-53.