A New Preparation of Potassium Dinitromethane and its Conversion to 2,2-Dinitro-1,3-propanediol[1,2]

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Dinitromethane or its potassium salt has been prepared by a number of previous investigators.[4]

The yield of potassium dinitromethane by earlier procedures is low and a shorter and more convenient synthesis has been developed utilizing nitromethane as a starting material. The following equations show the two-step synthesis which gives the desired product in a yield of 25% based on chloronitromethane.

$$\mathrm{CH_3NO_2} \xrightarrow[\mathrm{NaOH}]{\mathrm{Cl_2}} \mathrm{CH_2Cl(NO_2)} \tag{1}$$

$$\mathrm{CH_2ClNO_2} \xrightarrow[\mathrm{KNO_2}]{\mathrm{OH^-}} \mathrm{K^+CH^-(NO_2)_2} \tag{2}$$

The second step of the synthesis was carried out by the dropwise addition of the base to a cold (−5 to 0°) aqueous methanol solution of chloronitromethane and potassium nitrite. The crude potassium dinitromethane crystallized from the reaction mixture as it was formed.

When aqueous ethylene glycol was substituted for aqueous methanol the crude salt obtained was of higher purity. It was also found possible to prepare potassium dinitromethane under anhydrous conditions in methanol; however, the procedure is not recommended. In one such experiment a finely divided dark red powder was obtained which "fumed-off" with a flash when touched with a metal spatula.

The reaction is fairly rapid and most of the product is obtained in the first 30 minutes after the addition of the base. It is best carried out in the temperature range of −5 to 0°.

The amount of water present in the solvent has less influence on the yield of product than the reaction time or reaction temperature. It was found that the most consistent yields were obtained when the solvent contained 15 to 30 weight per cent. of water. Attempts to increase the yield by using twice the theoretical amount of potassium nitrite were unsuccessful. Substitution of bromonitromethane for chloronitromethane, did not influence the yield.

The crude product was purified by washing and recrystallization. It was identified: (1) by its explosion point, (2) by nitrogen analysis, (3) by conversion to potassium dinitroethanol,[5] which also analyzed satisfactorily for nitrogen. Further confirmation of the identity of the salt was obtained by converting it to the known ether-soluble dinitromethane. The salt was reformed by treatment with a methanol solution of potassium methoxide.

Potassium dinitromethane was converted, in one step, to 2,2-dinitro-1,3-propanediol by acidifying an aqueous mixture of the salt and formaldehyde, using a 10% excess of the latter. It does not give a positive test for the hydroxyl groups when tested with ceric nitrate reagent. On treatment with an equimolar amount of base the diol is decomposed to potassium dinitroethanol and formaldehyde. When the diol is heated with an excess of aqueous alkali the corresponding salt of dinitromethane is obtained. The alcohol is quite stable in acidic solution and even prolonged heating with fuming nitric acid at 60–70° has no effect. It yielded a distillable diacetate on treatment with acetyl chloride.

Experimental

Preparation of Potassium Dinitromethane.—To 96 g. (1.0 mole) of chloronitromethane[6] in 250 ml. of methanol at −5°, was added 100 g. (1.0 mole of 87% assay) of potassium nitrite dissolved in 133 ml. of water; then a solution of 66 g. (1.0 mole of 86% assay) of potassium hydroxide in 250 ml. of methanol was added dropwise, with stirring. The addition required 2 hours and the mixture was stirred for an additional 9 hours at −5°. The slurry was filtered and 151 g. of moist, crude salt was obtained. It was purified by mixing it with 200 ml. of water to dissolve the potassium chloride and potassium nitrite which were present as contaminants. After filtration and recrystallization from hot water 36.1 g. (25% yield) of potassium dinitromethane was obtained which exploded at 208°; literature values[4] 205 and 207°. The salt was converted to potassium dinitroethanol according to the directions of Duden.[5]

Anal. Calcd. for $\mathrm{C_2H_3N_2O_5K}$: N, 16.0. Found: N, 15.6.

Preparation of 2,2-Dinitro-1,3-propanediol and Its Diacetate.—To 50 ml. of water and 34 ml. of 40% formalin solution (0.45 mole of formaldehyde) was added 28.8 g. (0.20 mole) of potassium dinitromethane. The flask was cooled in an ice–water mixture, and 12 g. of acetic acid dissolved in 15 ml. of water was added dropwise, with stirring. After the addition, the mixture was stirred for 90 minutes without cooling. The solution was extracted with three 50-ml. portions of ether and the combined extracts were evaporated leaving a straw-colored oil which crystallized. Recrystallization from benzene gave 21.9 g. (66%) of long, white needles of 2,2-dinitro-1,3-propanediol, m.p. 142°. The diol was soluble in the common organic solvents such as acetone, ether, dioxane, alcohols and nitromethane as well as in water.

Anal. Calcd. for $\mathrm{C_3H_6N_2O_6}$: C, 21.8; H, 3.61; N, 16.86. Found: C, 22.3; H, 3.77; N, 16.92.

The diacetate ester was prepared by treating the diol with acetyl chloride at 10–15° for 2 hours. The ester was obtained as a clear liquid, b.p. 113–115° (1 mm.).

Anal. Calcd. for $\mathrm{C_7H_{10}N_2O_8}$: C, 33.6; N, 11.2; H, 4.0. Found: C, 33.55; N, 10.84; H, 4.02.

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(1) Abstracted from a thesis submitted to the Faculty of the Graduate School of Purdue University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) Financial support of this research was supplied by the United States Office of Naval Research.

(3) Aerojet Engineering Corporation, Azusa, Calif.

(4) G. Chancel, *Compt. rend.*, **86**, 1405 (1878); P. Duden, *Ber.*, **26**, 3003 (1893); R. A. Gotts and L. Hunter, *J. Chem. Soc.*, **125**, 445 (1924); P. Lipp, *Ann.*, **449**, 23 (1926); S. M. Losanitch, *Ber.*, **16**, 51 (1883); R. Scholl and A. Schmidt, *Ber.*, **35**, 4291 (1902); W. Wislicenus, *Ann.*, **460**, 282 (1928).

(5) P. Duden and G. Ponndorf, *Ber.*, **38**, 203 (1905).

(6) J. B. Tindall, U. S. Patent 2,309,806, February 2, 1943.

LAFAYETTE, IND. RECEIVED NOVEMBER 22, 1950

Heat Capacity of Crystalline Dextrose between 25 and 95°

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As part of a project sponsored at the National Bureau of Standards by the Corn Industries Research Foundation for the determination of the physical properties of raw materials, industrial products and pure substances of importance in the

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