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

By H. Feuer, G. B. Bachman and J. P. Kispersky[3]

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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(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.

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Heat Capacity of Crystalline Dextrose between 25 and 95°

By Thomas B. Douglas, Anne F. Ball and John L. Torgesen[1]

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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(1) Research Associate, Corn Industries Research Foundation.

corn milling industry, the relative enthalpy of pure crystalline α-dextrose was measured over a temperature range, 25 to 95°, in which this sugar was expected to be completely stable. The heat capacity was calculated from the enthalpy data.

Experimental

The dextrose used was Standard Sample material[2] issued by this Bureau. It had been recrystallized twice from water, the last recrystallization being carried out at 55° to yield the anhydrous form. In order to reduce the moisture content to a minimum, it was dried for 6 hours in a vacuum oven between 60 and 70° and at 2 mm. pressure and then stored in a vacuum desiccator. It is believed that this treatment yielded a sample whose ash and moisture content did not exceed 0.003 and 0.01%, respectively.

The apparatus and method for measuring enthalpy have been described in detail elsewhere.[3] Briefly, a sample that had been heated in a furnace to a temperature measured by a platinum resistance thermometer was dropped into an electrically calibrated ice calorimeter. This measured the heat delivered in cooling the sample to 0°. The enthalpy change of the container itself was accounted for by "blank" experiments. Using a metal container that had been sealed by a gold gasket after the air had been replaced by helium, 42 determinations were made with the empty container and 25 with the sample, with the furnace temperature varied in approximately 10° steps from 25 to 95°.[4] At a given temperature the probable error of the mean value of the enthalpy of dextrose computed from these observed heats was ±0.02 cal./g. on the average. These probable errors at the respective temperatures evidenced no definite trend with temperature.

The mean observed values of the enthalpy of dextrose, in excess of that at 0°, were: (25°) 6.953, (35°) 9.918, (45°) 12.947, (55°) 16.136, (65°) 19.328, (75°) 22.656, (85°) 26.048 and (95°) 29.684 cal./g.[5] By the method of least squares there were fitted to the mean observed enthalpy values at these temperatures quadratic equations for the empty container and container with sample, with an average deviation of 0.1%. The difference between these two equations led to the following equation for the heat capacity of dextrose, in cal./g.-deg. at $t°$

$$C_p = 0.2665 + 0.000955t \ (t = 25 \text{ to } 95°) \qquad (1)$$

One check on the general accuracy of the method was obtained by making several measurements, using the same apparatus, of the enthalpy change of water between 0 and 25°. The mean value obtained, which itself had a probable error of ±0.12%, was 0.05% lower than a more precise value obtained with an adiabatic calorimeter.[6]

Slightly higher values than those given by equation (1) for dextrose were obtained by Parks and Thomas,[7] who reported

$$C_p = 0.270 + 0.00092t \ (t = -10 \text{ to } +60°) \qquad (2)$$

Nelson and Newton,[8] using a calorimeter with an isothermal jacket at 60°, gave the following equation

$$C_p = 0.265 + 0.000975t \ (t = 0 \text{ to } 60°) \qquad (3)$$

This equation gives heat capacities at 47.5, 25 and 10° that are lower by 0.2, 0.3 and 0.5%, respectively, than those given by equation (1). They checked the accuracy of their procedure by making measurements at these temperatures on water, obtaining average heat capacities that were lower by 0.2, 0.5 and 0.6% at these respective temperatures than the values of the precise work[6] referred to above. If their results for dextrose are corrected by these latter figures to account for what may be supposed to be a systematic error in their method, their values become higher by 0.0, 0.2 and 0.1%, respectively, than those of equation (1).

Huffman and Fox[9] have accurately determined the heat of combustion of dextrose. After the recalculation of their values with the use of more recent values for the heat of combustion of benzoic acid and the heats of formation of water and of carbon dioxide,[10] their data gave for the standard heat and free energy of formation (ΔH_f^0 and ΔF_f^0) of dextrose at 25° the values −304.37 and −217.34 kcal., respectively. The available heat capacity data reliably determine the variation of these quantities between 25 and 95°. Using the above values, equation (1) for dextrose, and equations accurately fitting in this temperature range the heat capacities of carbon (graphite), hydrogen and oxygen as recently tabulated[11] at this Bureau, the following equations were derived in kcal./mole at T, °K.

$$\Delta H_f^0 = -288.60 - 0.06825T + 6.840(10^{-5})T^2 - 448/T \quad (T = 298 \text{ to } 368°\text{K.})$$

$$\Delta F_f^0 = -288.60 + 0.15715T \log_{10} T - 6.840(10^{-5})T^2 - 224/T - 0.12695T \quad (T = 298 \text{ to } 368°\text{K.})$$

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[2] F. J. Bates and Associates, "Polarimetry, Saccharimetry and the Sugars," N. B. S. Circular C440, U. S. Government Printing Office, Washington, D. C., 1942; R. F. Jackson, *Bull. Bur. Standards*, **13**, 633 (1916).

[3] D. C. Ginnings, T. B. Douglas and A. F. Ball, *J. Research Natl. Bur. Standards*, **45**, 23 (1950).

[4] According to previous reports, no appreciable decomposition of the dextrose is to be expected in this temperature range. See, *e.g.*, G. S. Parks, H. M. Huffman and F. R. Cattoir, *J. Phys. Chem.*, **32**, 1366 (1928).

[5] 1 cal. = 4.1840 absolute joules.

[6] N. S. Osborne, H. F. Stimson and D. C. Ginnings, *J. Research Natl. Bur. Standards*, **23**, 197 (1939).

[7] G. S. Parks and S. B. Thomas, THIS JOURNAL, **56**, 1423 (1934).

[8] E. W. Nelson and S. B. Newton, *ibid.*, **63**, 2178 (1941).

[9] H. M. Huffman and S. W. Fox, *ibid.*, **60**, 1400 (1938).

[10] R. S. Jessup, *J. Research Natl. Bur. Standards*, **36**, 421 (1946); D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer and F. D. Rossini, *ibid.*, **34**, 143 (1945); E. J. Prosen, R. S. Jessup and F. D. Rossini, *ibid.*, **33**, 447 (1944).

[11] F. G. Brickwedde, M. Moskow and J. G. Aston, *ibid.*, **37**, 263 (1946); H. W. Woolley, R. B. Scott and F. G. Brickwedde, *ibid.*, **41**, 379 (1948); H. W. Woolley, *ibid.*, **40**, 163 (1948); "Thermal Properties of Gases," NBS-NACA Tables 7.10 and 9.10, U. S. Government Printing Office, Washington, D. C., 1949.

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A Synthesis of ϵ-Bromocaproic Acid

BY HAROLD W. HEINE AND HOWARD JONES

The methods, recently described by Westerfeld[1] for the oxidation of cyclopentanone to δ-valerolactone and by Fling, Minard and Fox[2] for the transformation of the intermediate alkaline oxidation mixture to δ-bromovaleric acid, have been extended to the preparation of ϵ-bromocaproic acid.

Cyclohexanone was oxidized with hydrogen peroxide and the reaction mixture subsequently

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[1] Westerfeld, *J. Biol. Chem.*, **143**, 177 (1942).

[2] Fling, Minard and Fox, THIS JOURNAL, **69**, 2466 (1947).