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 Using a metal container that had been sealed by a gold gasket after the air had been replaced by helium, 42 determinations were made with the empty container and 25 with the sample, with the furnace temperature varied in approximately 10° steps from 25 to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.

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

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

The authors wish to thank Dr. D. C. Ginnings for his help and advice in this work.

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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.

NATIONAL BUREAU OF STANDARDS
WASHINGTON, D. C.

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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).

treated with hydrobromic acid. An over-all yield of 19% was obtained for the bromo-acid. A considerable amount of a high boiling fraction which solidified upon cooling was also isolated. This material was identified as adipic acid by its melting point and neutral equivalent. Marvel and co-workers[3] prepared ε-bromocaproic acid in an over-all yield of approximately 40% by the treatment of δ-phenoxybutyl bromide with ethyl malonate and subsequent decomposition of the diethylphenoxybutyl malonate with hydrobromic acid.

Several unsuccessful attempts were made to isolate the ε-caprolactone from the oxidation step. The excess peroxide was destroyed by the addition of sodium bisulfite and the solution extracted with ether. The ether was evaporated and the residue subjected to vacuum distillation. A violent explosion occurred. This behavior did not parallel the results of Westerfeld who was able to isolate δ-valerolactone. Two subsequent experiments only served to confirm the original observation.

Experimental

To a solution of 600 ml. of 2 *N* NaOH was added alternately with continuous stirring, 114 g. of redistilled cyclohexanone with 300 ml. of 30% hydrogen peroxide (Merck Superoxol). The temperature of the oxidation mixture was held at 45°. Water was distilled from the reaction mixture under diminished pressure until a white pasty residue was formed.

The crude reaction product was treated with 100 ml. of 48% hydrobromic acid solution followed by the slow addition of 100 ml. of concd. sulfuric acid. After gentle refluxing for 3 hours the reaction mixture was diluted with one liter of water and extracted 5 times with ether. Upon evaporation of this ethereal extract 43.6 g. of ε-bromocaproic acid was obtained. It distilled completely at 142–143° (11 mm), m.p. 32.5°. The acid was recrystallized from petroleum ether. *Anal.* Calcd. for $C_6H_{11}O_2Br$: Br. 40.9. Found: Br, 40.3.

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(3) Marvel, *et al.*, This Journal, **46**, 2841 (1924); **49**, 1831 (1927).

DEPARTMENT OF CHEMISTRY
BUCKNELL UNIVERSITY
LEWISBURG, PENNA.

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Positive Halogens from Trifluoroacetyl Hypohalites[1]

BY ALBERT L. HENNE AND WILLIAM F. ZIMMER

CF_3COOBr and CF_3COOI are a source of positive bromine and iodine, respectively, as shown by the fact that they halogenate toluene in the ring in marked preference to or even to the exclusion of the side chain. They are conveniently made by adding the stoichiometric amount of bromine or iodine to a solution of silver trifluoroacetate in an organic solvent: (1) $CF_3CO_2Ag + X_2 \rightarrow AgX\downarrow + CF_3CO_2X$ and (2) $CF_3CO_2X + CH_3C_6H_5 \rightarrow CF_3CO_2H + CH_3C_6H_4X$. Discoloration is a convenient measure of the reaction progress. Trifluoroacetic acid is recoverable.

The positive character of the halogen in these hypohalites is similar to that of the bromine in perfluorinated N-bromosuccinimide $\overline{\text{CO(CF}_2)_n\text{CON}}\text{Br}$.[2] In both cases, the positive halogen "hangs" from a polarizable atom attached to one or two strongly electronegative perfluoroacetyl groups.

Other acyl hypohalites should, and do show a similar property, but to a smaller extent (CH_3CO_2Br) or in a less convenient form (CCl_3CO_2Br). The solubility of silver trifluoroacetate in organic solvent is of great practical help, and the resistance of the CF_3CO_2 ion to decarboxylation[3] minimizes the importance of the so called Hunsdiecker or Simonini reactions, with formation of CF_3X. Specifically,[4] the reaction $CF_3CO_2Ag + I_2 \rightarrow CO_2 + CF_3I + AgI$ does not occur appreciably below 100°.

A private communication[5] reports that "CF_3CO_2X halogenates benzenic derivatives such as phenol, aniline and benzoic acid in the expected positions." These experiments confirm the ability of X to act in a positive form, yet have no opportunity to show that it does so in preference to acting in atomic form.

Experimental

Iodination of Toluene.—CF_3CO_2Ag[4] (55 g. or 0.25 mole) dissolved in toluene (120 g.) was added dropwise to a slurry of iodine (63.5 g. or 0.25 mole) in toluene (125 g.). Reaction with heat evolution, silver iodide precipitation and formation of CF_3CO_2H fumes was instant. AgI was decanted. Trifluoroacetic acid and the excess of toluene were distilled off. Tolyl iodide (46 g. or 0.21 mole) $n^{20}D$ 1.6005 was then collected about 210°; this is an 84% yield. A small amount was oxidized with chromic acid to give iodobenzoic acid, which after one crystallization from benzene melted at 269–270°, correct for *p*-iodobenzoic acid.

Bromination of Toluene.—A solution of bromine (80 g. or 0.36 mole) in carbon tetrachloride was added to CF_3CO_2Ag (80 g. or 0.36 mole) and toluene (33.1 g. or 0.36 mole) in carbon tetrachloride. Stirring and cooling were maintained throughout the reaction. Working up was as above. Distillation gave tolyl bromide (45 g. or 73%) at 179–181°. A small amount of this was converted to its Grignard derivative and the latter carbonated to methylbenzoic acid; after one crystallization from water, a m.p of 176–178° was observed which denoted *p*-methylbenzoic acid.

Bromination of Methylnaphthalene.—Bromine (32 g. or 0.20 mole) was added in 90 minutes to an ether solution of β-methylnaphthalene (28.5 g. or 0.20 mole) and CF_3CO_2Ag (44.2 g. or 0.20 mole) with constant stirring and cooling in a water-bath. After filtration of AgBr, the filtrate was brown and could not be bleached by a bisulfite wash. Distillation at reduced pressure gave: β-methylnaphthalene, 4.8 g., b. 116–120° (16 mm.), intermediate, 1.3 g., b. 120–140° (16 mm.); α-bromo-β-methylnaphthalene, 26.7 g., b. 107–115° (1.0 to 1.5 mm.); higher boiling fraction, 1.3 g., b. 115–140° (1.0 to 1.5 mm.); residue, 5.4 g. The third fraction (26.7 g. or 0.121 mole) is a 60.5% conversion, or a 77.1% net yield when fraction 1 is taken into count. A small amount of this was converted to its Grignard derivative and carbonated; after one crystallization from benzene, the reaction product melted at 126–127°, denoting β-methyl-α-naphthoic acid.

Testing of Acetyl Hypoiodite.—Silver acetate was mechanically dispersed in an excess of toluene containing an equimolecular amount of iodine; the reaction was slow and required gentle heating to proceed to completion. During the working up, extensive decomposition was observed, with liberation of iodine. The yield of tolyl iodide was only 47.5%, mostly the para-isomer as shown by oxidation to low grade *p*-iodobenzoic acid.

Testing of Trichloroacetyl Hypoiodite.—Preparation of silver trichloroacetate proved inconvenient, light sensitive and beset with silver chloride formation. The reaction was then tried by placing CCl_3CO_2H in an excess of toluene, stirring with silver oxide until neutralized and adding an

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[1] A. L. Henne, Am. Chem. Soc., Chicago Meeting, Sept., 1950. Abstracts p. 10L.

[2] A. L. Henne and W. F. Zimmer, *ibid.*, p. 11L; and This Journal, **73**, 1103 (1951).

[3] I. Auerbach, F. Verhoek and A. Henne, *ibid*, **72**, 299 (1950).

[4] A. L. Henne and W. G. Finnegan, *ibid.*, **72**, 3806 (1950).

[5] R. N. Haszeldine, The University, Cambridge, England.