[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Preparation and Properties of Anhydrous Acetic Acid

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Cryoscopic and solubility investigations with acetic acid as solvent require the preparation of anhydrous material of high purity in large quantities. The melting point must be highly reproducible without entailing undue labor.

The methods that have been employed may be summarized as follows: (1) repeated fractional crystallization,[1] followed by (a) distillation;[2] (b) drying with phosphorus pentoxide in the quantity calculated to react with the water present to form orthophosphoric acid and then distillation from the phosphorus pentoxide[3] (a small quantity of acetic anhydride is produced[3]); or (c) refluxing with the exact quantity of acetic anhydride required to convert the remaining water to acetic acid.[4] (2) Refluxing for one-half hour with two per cent. by weight of potassium permanganate and distilling from the residue.[5,6] We have found that such acid never melts above 16.55°. (3) Refluxing for ten hours with chromium trioxide[7] in an amount in excess of that calculated to react with the water present to convert it to chromic acid.[8]

The melting point is a good and frequently used criterion of purity but unfortunately only two laboratories[5,6] have reported how their thermometers were standardized, so that variations ranging from 16.4 to 16.60° may be due to inaccuracy in the temperature scale as well as to impurities.

We investigated methods (1a), (2) and (3). The first was very tedious when large quantities are needed. One fractional distillation with a good still yields acid of higher melting point than several recrystallizations. Potassium permanganate oxidized much of the acetic acid when applied to quantities of four liters or more. The chromic oxide method proved to be the most satisfactory.

Chromic Oxide Method.—Four liters of Niacet Chemical Company C. P. acetic acid (melting point 16.5°) was refluxed for about ten hours with an amount of chromium trioxide slightly in excess of that calculated to react with the water present to form chromic acid (about 1% by weight), assuming 16.60° to be the melting point of the pure

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(1) De Visser, *Rec. trav. chim.*, **12,** 101 (1893); m. p. 16.5965°.

(2) Conant and Werner, THIS JOURNAL, **52,** 4436 (1930); m. p. 16.4 to 16.6°; Hall and Voge, *ibid.*, **55**, 239 (1933); m. p. 16.63°, $\kappa = 3 \times 10^{-8}$ mhos at 25°.

(3) Orton, Edwards and King, *J. Chem. Soc.*, **99,** 1178, 1181 (1911); m. p. 16.4 to 16.51°.

(4) Kendall and Gross, THIS JOURNAL, **43,** 1426 (1921); m. p. 16.57 ± 0.05°; $\kappa = 2.4 \times 10^{-8}$ mhos at 25°.

(5) Bousfield and Lowry, *J. Chem. Soc.*, **99,** 1432 (1911); m. p. 16.60 ± 0.005°. Thermometer calibrated at Reichsanstalt and National Physical Laboratory.

(6) MacInnes and Shedlovsky, THIS JOURNAL, **54,** 1429 (1932); m. p. 16.54 ± 0.01°. Thermometer calibrated against resistance thermometer certified by Bureau of Standards; $\kappa = 1.4 \times 10^{-8}$ mhos at 25°.

(7) Hutchison and Chandlee, *ibid.*, **53**, 2881 (1931); m. p. 16.55°.

(8) Harned and Ehlers, *ibid.*, **54,** 1350 (1932); m. p. 16.55°.

acid and all the freezing point lowering to be due to water.[1] The acid was then distilled rapidly using an all-glass distilling apparatus protected by calcium chloride guards, followed by a careful fractionation with a two-foot Vigreaux column. After one liter had been distilled, the melting point of the distillate was 16.3°; it rose to 16.50–16.55° for the next liter, and to 16.57–16.60° for the remainder. Other workers[6,7,8] using this or the potassium permanganate method report a melting point of 16.55° for the second and third quarters of the distillate. One purification using two per cent. chromium trioxide yielded acid of the same purity but more of the low-boiling fraction, indicating that more water had been formed and hence more acid decomposed.

Triacetyl Borate Method.—Triacetyl borate[9] is an excellent dehydrating agent for purifying acetic acid which has apparently escaped attention. It reacts with water to yield acetic acid and insoluble boric acid which may be completely separated in the final distillation: $B(OCOCH_3)_3 + 3H_2O = 3CH_3COOH + B(OH)_3$.

Triacetyl borate was prepared according to the directions of Pictet and Geleznoff[10] by warming to 60° a mixture of boric acid (powdered) and acetic anhydride in the ratio of 1:5 parts by weight: $B(OH)_3 + 3(CH_3CO)_2O = B(OCOCH_3)_3 + 3CH_3COOH$. On cooling, most of the triacetyl borate precipitates and is removed on a suction filter. It is very hygroscopic.

The purified acetic acid was refluxed with the triacetyl borate in the all-glass apparatus and then carefully distilled. Two to four times the amount of triacetyl borate calculated to react with the water present was used. Acetic acid of the same melting point was always produced. If four liters of the acid was dried at one time, two and a half to three liters was collected with a variation of not over 0.02° in the melting point, that is, from 16.58–16.60°.

This value was determined with a thermometer calibrated against a copper–constantan thermocouple, standardized against the fixed points of 0°, 32.384 ($Na_2SO_4 \cdot 10 H_2O$) and a platinum resistance thermometer certified by the Bureau of Standards. The specific conductance (κ) of the acid was measured at the Rockefeller Institute with apparatus placed at our disposal by Dr. D. A. MacInnes, and yielded a value of 1.4×10^{-8} mhos at 25°.

Conclusions

Methods of purifying pure, anhydrous acetic acid in large quantities are discussed. Oxidation with chromium trioxide to remove impurities followed by dehydration with triacetyl borate was found to be the most satisfactory method.

The melting point of pure anhydrous acetic acid is $16.60 \pm 0.01°$ and the specific conductance is 1.4×10^{-8} mhos (25°).

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(9) Suggested by Dr. Donald MacGillavry of this Laboratory who has made a preliminary investigation.

(10) Pictet and Geleznoff, *Ber.*, **36**, 2219 (1903).