Preparation and Properties of Acetic Acid-*d*[1]

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In connection with studies on the association of carboxylic acids, some acetic acid-*d* of high purity was prepared, and its m. p., density, and refractive index determined. The existing m. p. data are somewhat uncertain and apparently no values for the other constants have hitherto been reported.

Experimental

The heavy acid was prepared by hydrolyzing acetyl chloride with D_2O[2]: 18 ml. of 99.6% D_2O was added through a dropping funnel to 85 ml. of refractionated Merck reagent acetyl chloride (b. p. 50.08–50.13° at 750 mm.) in a Claisen flask. Phosphorus pentoxide tubes protected the apparatus from atmospheric moisture. Dry nitrogen was bubbled through the mixture during the reaction and the distillations to sweep out DCl and excess acetyl chloride. Two successive reduced pressure distillations were made without breaking the apparatus connections. The distillate was repeatedly fractionated through a 3-ft. glass Widmer still, and finally subjected to two fractional crystallizations. A product free of chloride resulted which froze at 14.93–15.05°. Titration showed 99.35% acetic acid, calculated as CH_3COOD.

The method of Orton and Bradfield[3] was tested on ordinary acetic acid. This method involves refluxing the acid with the calculated amount of acetic anhydride (assuming all impurity to be water), using CrO_3 as an oxidation catalyst. A sample of 98.54% CH_3COOH was raised to 99.8% (m. p. 16.35°) in this way. The same method was applied to the heavy acid. After refluxing, the final fractions were collected in ampoules and these were then sealed off from the still. The main fraction was about 17 ml. The m. p. was determined by solidifying the acid in the ampoule, and allowing it to warm up very slowly (0.1° per hour). Equilibrium was ensured by continuous shaking. A P. T. R. calibrated thermometer graduated in 0.02° was used to measure the temperature. The density was determined in a 2-g. pycnometer by Mr. Paul Gross, Jr. The refractive index was measured with a Zeiss Pulfrich refractometer on a residue which had become somewhat contaminated by handling (m. p. 15.04°; range, about 0.7°). Data obtained were

M. p. = 15.66 ± 0.05° (range—approx. 0.2°)
d^{30}_4 = 1.0527
d^{25}_4 = 1.0588
n^{20}_D = 1.37102

This entire procedure was checked by a complete run using ordinary water, and the same grade acetyl chloride as with the D_2O. This gave a final product melting at 16.55 ± 0.05° (range 0.2°) and titrating 99.82% acetic acid. The m. p. previous to the acetic anhydride–chromium trioxide treatment was 16.3°, and the titration value showed 99.78% acid.

Judging from the melting points of the ordinary acid obtained in the test run and in the test of Orton and Bradfield's method, the final heavy acid was probably better than 99.8%, of which about 99.0% was CH_3COOD. The m. p. reported by Lewis and Schutz[4] (13.3°) appears to be too low. That found here agrees well with the predictions of Angus, *et al.*,[5] and is slightly higher than the value obtained by Halford and Anderson[6] (15.4°). Since larger quantities of acid were prepared in this study, it is likely that the effect of impurities was not as serious as in previous work.

At 20°, the refractive index of acetic acid-*d* is 0.00080 lower than that for light acid. The presence of water as impurity would cause only a slight change in n. Thus, for 1% H_2O in light acid, the calculated decrease in n_D, assuming an ideal mixture, is 0.00035.

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(1) Original manuscript received December 17, 1940.

(2) Engler, *Z. physik. Chem.*, **B32**, 471 (1936).

(3) Orton and Bradfield, *J. Chem. Soc.*, 983 (1927).

(4) Lewis and Schutz, THIS JOURNAL, **56**, 493 (1934).

(5) Angus, Leckie and Wilson, *Proc. Roy. Soc.* (London), **A155**, 183 (1936).

(6) Halford and Anderson, THIS JOURNAL, **58**, 736 (1936).

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(*p*-Sulfamylphenylamino-)-pyrimidines[1]

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The chemotherapeutic success of sulfanilamide derivatives of organic heterocycles has led the authors to take a special interest in the corresponding amide derivatives of the pyrimidine bases.[2] It is possible that such derivatives of pyrimidine might represent an important class of chemotherapeutics, due to certain physiological

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(1) Researches on Pyrimidines, CLXXV.

(2) T. B. Johnson and G. de Sütö-Nagy, THIS JOURNAL, **63**, 261 (1941).