[Contribution from the Chemical Laboratory of Middlebury College]

SOME OBSERVATIONS ON BENZOYLFORMIC ACID

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Received December 10, 1929 Published April 7, 1930

Benzoylformic acid was purified by repeated crystallization from carbon tetrachloride. The pure acid (snow-white) was stored in the dark over phosphorus pentoxide. It is very soluble in water; 1 cc. of a water solution saturated at 0° contains 0.92 ± 0.02 g. The density (d_4^0) of such a solution is 1.209 ± 0.003. The solubility of benzoylformic acid in 10 cc. of carbon tetrachloride is 0.04 g. at 0°; 0.1 at 15°; 0.4 at 35°; 0.8 at 40°; 1.1 at 43°; 1.9 at 45°; 3.3 at 47.5° and 7.9 g. at 52°. That the acid was pure was evidenced by sharp freezing point and correct titration values. The freezing point of the acid was found to be 64.85 ± 0.05° (corr.).[1]

Careful work on benzoylformic acid must be done in diffused light since the acid is light, sensitive both in the solid state and in water solution.[2] A $N/10$ water solution, exposed to direct sunlight, acquired a strong benzaldehyde odor in about ten minutes and within twenty minutes the solution (at first clear) had become cloudy. After two hours, small drops of oil were seen floating on the surface and after several days of exposure to light large reddish-brown drops of oil had settled on the bottom of the flask. A $N/10$ solution of acid which was kept in the dark remained clear and developed no benzaldehyde odor in twenty-four hours. The fall in acidity, due to exposure to light, was followed by titration. In one case there was a 19.4% decrease in acidity in the first two hours and an additional 8% during the next two hours. There was no loss in acidity when a similar solution was kept in the dark. That benzaldehyde was present in the rayed sample was evident from the odor; also, benzaldehyde phenylhydrazone was isolated and its identity established by a mixed melting point comparison with an authentic sample.

An attempt was made to devise a gravimetric method of analysis for benzoylformic acid. Its phenylhydrazone was precipitated in various acidities by means of phenylhydrazine hydrochloride and the yield determined. The best yield, 98.1 ± 0.2%, was obtained in the presence of a small excess of hydrochloric acid. With increase in acidity the yield gradually fell; in 20% hydrochloric acid the yield was 84.7%. On the other hand, any decrease in hydrochloric acid below the one equivalent corresponding to the phenylhydrazine resulted in a sticky product which could not be filtered. Precipitation does not occur in alkaline solution, the phenylhydrazone of benzoylformic acid being soluble even in sodium carbonate.

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[1] Glücksmann, *Monatsh.*, **11**, 249 (1890), reports the melting point as 65°; Claisen, *Ber.*, **10**, 431, 847 (1877), as 65–66°; Acree, *Am. Chem. J.*, **50**, 391 (1913), as 63–64°.

[2] Claisen [*Ber.*, **10**, 846 (1877); **12**, 627 (1879)] observed that the solid acid (and also the ammonium salt) became yellow on exposure to light.

Four derivatives of benzoylformic acid—semicarbazone, thiosemicarbazone, *p*-nitrophenylhydrazone and 2,4-dinitrophenylhydrazone—were prepared in the hope of obtaining a derivative more suitable for gravimetric estimation than the phenylhydrazone but the last named seemed to be the best.

Experimental Part

Preparation and Purification.—Methyl (n^{24}_{D} 1.5208) and ethyl benzoylformate (n^{23}_{D}, 1.5102)[3] were the starting materials for the preparation of the acid. The ester was hydrolyzed at room temperature with aqueous sodium hydroxide. The resulting alkaline solution was strongly acidified with sulfuric acid, cooled and finally extracted with ether several times. The ether extract was dried with anhydrous sodium sulfate and filtered. The ether was evaporated and the residual oil warmed in a vacuum at ≐60° for two hours. On standing overnight the oil solidified to a crystalline mass. The acid was crystallized seven times from carbon tetrachloride. The final product was freed from solvent by heating to incipient fusion in a current of dry air.

Carbon bisulfide was previously used[4] for crystallizing benzoylformic acid. Carbon tetrachloride, however, is more efficient in removing benzoic acid, which is the most probable impurity. This conclusion was reached after comparing the solubility curves of benzoylformic and benzoic acids in carbon bisulfide and carbon tetrachloride.

Benzoylformic acid has a slight odor. After handling this acid for several days one's fingers turn black and peel. The skin also turns black and peels when working with mandelic acid ($C_6H_5CHOHCOOH$), which is the starting material in the preparation of benzoylformic acid.

Solubility in Carbon Tetrachloride and in Water.—All solubilities in carbon tetrachloride except two were determined in a 20-cc. test-tube fitted with a cork which held a thermometer and which was nicked to allow a wire stirrer to be raised up and down. Ten cc. of solvent was placed in the tube and then weighed amounts of substance were added. Each addition was first brought into solution and then partially precipitated by cooling with rapid stirring. Finally, the tube was slowly warmed, with stirring, and the temperature noted at which the cloudiness (due to finely divided solid) disappeared. In the case of 0 and 52°, a 10-cc. portion of the saturated solution was evaporated and the solid weighed.

The solubility in water at 0° was determined by titrating a 1-cc. portion with *N*/10 sodium hydroxide. The density was measured according to Mulliken.[5] Scarcity of material prevented more accurate work. Concentrated solutions of benzoylformic acid in carbon tetrachloride and in water are yellow; dilute solutions are colorless.

Freezing Point.—The apparatus was essentially a small-scale Beckmann freezing point apparatus. It consisted of a 20-cc. test-tube equipped with a thermometer[6] and wire stirrer, the tube being jacketed with a slightly larger test-tube. Since benzoylformic acid is hygroscopic, entrance of moisture was prevented by blowing a gentle stream of dried air into the mouth of the inner test-tube. The cooling curve was plotted, temperature against time. After 0.5–1° supercooling, the temperature of the

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[3] Corson, Dodge, Harris and Hazen, "Organic Syntheses," John Wiley and Sons, Inc., New York, **1928,** Vol. 8, p. 68.

[4] Acree, *Am. Chem. J.*, **50,** 391 (1913).

[5] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, **1914,** Vol. I, p. 229.

[6] This thermometer was compared with one which had been calibrated by the U. S. Bureau of Standards.

freezing acid quickly rose to 64.85 ± 0.05° and remained constant until practically all the sample had solidified. In a typical run the liquid supercooled to 63.5° and then the temperature rose to the plateau where it remained for three minutes at 64.87° and four minutes at 64.83°. By this time the liquid was almost completely frozen and the temperature began to drop rapidly.

Titration.—The dissociation constant for benzoylformic acid at 25° as determined by Bader[7] by the conductivity method is 6×10^{-2}. According to Bjerrum's calculations of hydrolysis[8] a $N/10$ solution of the sodium salt of an acid of K_{A}, 6×10^{-2}, would have a P_{H} of 7.5. We titrated the purified acid ($N/10$ solution) with $N/10$ sodium hydroxide to an end-point of P_{H} 7.5 using phenol red as indicator and found the acid to be pure within 3 parts per 1000.

Anal. Calcd. for $C_8H_6O_3$: 0.2833 g. requires 15.31 cc. of 1.233 $N/10$ NaOH. Found: 15.35 cc.

Photochemical Decomposition.—We followed the decomposition of two samples of ± $N/10$ benzoylformic acid (tightly stoppered), one exposed to sunlight and the other kept in the dark. The procedure was to titrate 10-cc. samples with $N/10$ sodium hydroxide after various lengths of time.

Solution Exposed to Light			Solution Kept in the Dark		
Time	Hours	$N/10$ NaOH, cc.	Time	Hours	$N/10$ NaOH, cc.
11:35 A. M.	0	7.22	11:35 A. M.	0	7.23
1:35 P. M.	2	5.82	1:35 P. M.	2	7.23
2:35 P. M.	3	5.54	5:35 P. M.	6	7.24
3:35 P. M.	4	5.24	8:35 A. M.	21	7.25

The presence of benzaldehyde was proved by isolation of benzaldehyde phenylhydrazone. Since both benzaldehyde and benzoylformic acid precipitate phenylhydrazone when treated with phenylhydrazine reagent in the usual way, the normal procedure was modified so as to yield only benzaldehyde phenylhydrazone. This was easily accomplished by precipitating the hydrazone in the presence of a slight excess of sodium hydroxide. Under these conditions only the phenylhydrazone of benzaldehyde precipitated, the phenylhydrazone of benzoylformic acid remaining in solution as sodium salt.

In several cases another decomposition product was noticed, a very small quantity of a tan-colored, oily solid which floated on the top of the solution. The quantity was too small for identification. After drying on a clay plate and washing with petroleum ether, it melted from 90 to 110°. It bubbled a little when moistened with sodium carbonate solution but this acidity might have been due to adhering benzoylformic acid.

That benzoic acid was present was shown as follows. A rayed sample was extracted with ether and the ether, in turn, with sodium carbonate solution. The sodium carbonate was washed with ether and then acidified. The precipitated solid, after recrystallizing from water, was identified as benzoic acid. The amount was small and was very likely due to the air oxidation of the primary product, benzaldehyde. Presumably the decomposition brought about by light is $C_6H_5COCOOH \longrightarrow CO_2 + C_6H_5CHO$. Further work along this line is in progress in this Laboratory.

Gravimetric Estimation.—A method of analysis[9] for benzoylformic acid has been described in which the phenylhydrazone was precipitated with phenylhydrazine acetate

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[7] Bader, *Z. physik. Chem.*, **6**, 289 (1890).

[8] Taylor, "Treatise on Physical Chemistry," D. Van Nostrand Co., New York, **1929**, Vol. II, p. 828.

[9] Evans, *Am. Chem. J.*, **35**, 123 (1906).

solution. After standing for twenty-four hours, the product was dissolved in sodium carbonate solution and reprecipitated with dilute sulfuric acid; the hydrazone was finally crystallized from hot benzene.

We were interested in developing a simpler procedure. Using phenylhydrazine hydrochloride as reagent the resulting phenylhydrazone was of such purity that recrystallization was unnecessary. A 98.1 ± 0.2% yield was consistently obtained according to the following directions. To a water solution of benzoylformic acid (25 cc. contains 0.25 g. of acid) was added 25 cc. of hydrazine reagent containing 0.48 g. (100% excess) of recrystallized phenylhydrazine hydrochloride and 0.5–5.5 cc. of $N/5$ hydrochloric acid. The mixture immediately became cloudy and within a few seconds was semi-solid with the lemon-yellow precipitate of benzoylformic acid phenylhydrazone. After standing for ten minutes, the mixture was filtered through a fretted glass Gooch crucible. The Gooch was dried in a vacuum desiccator containing both phosphorus pentoxide and stick sodium hydroxide (the latter to absorb hydrochloric acid). The hydrazone cannot be heated in an oven, even at 100° without some decomposition. Also, when concentrated sulfuric acid is used in the vacuum desiccator, the hydrazone changes from butter-yellow to dark brown and becomes sticky. Using the above procedure the yields are consistent and therefore benzoylformic acid can be determined gravimetrically provided the factor 100/98.1 is employed.

Derivatives.—The method of preparation was the same in all cases. To a water solution of the acid was added a water solution (usually hot) of the hydrochloride of the reagent in question. The solid product quickly appeared. These products are soluble in the usual organic solvents and they are also moderately soluble in water. They decompose at the melting point and the melting point depends somewhat on the speed of heating. Of the four derivatives prepared only two—thiosemicarbazone and 2,4-dinitrophenylhydrazone—are new.

Benzoylformic Acid Thiosemicarbazone.—This substance crystallizes from acetic acid or water as a pale yellow solid. It melts at 188–189° (corr.) with decomposition.

Anal. Calcd. for $C_9H_9O_2N_3S$: C, 48.4; H, 4.0; S, 14.4. Found: C, 47.8; H. 4.2; S, 14.0.

Benzoylformic Acid 2,4-Dinitrophenylhydrazone.—The yellow product was crystallized from acetic acid. It melts at 196–197° (corr.) with decomposition.

Anal. Calcd. for $C_{14}H_{10}O_6N_4$: C, 50.9; H, 3.0. Found: C, 50.8, 51.0; H, 2.9, 2.8.

Summary

The solubility of benzoylformic acid in carbon tetrachloride at several temperatures and in water at 0° has been determined—also the density of the latter solution. The pure acid freezes at 64.85 ± 0.05°. A $N/10$ water solution of the acid decomposes slowly when exposed to sunlight. Benzoylformic acid phenylhydrazone may be used under certain conditions in the gravimetric estimation of the acid. Two new derivatives are described.

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