ditions previously shown to produce no fractionation.[5]

This indicates that the contribution of the cuprite oxygen to the density of the water formed from it is 5.5 p. p. m. less than that of atmospheric oxygen.

This is only 1 p. p. m. less than the difference between the density contributions of atmospheric and ordinary water oxygen[5] and indicates therefore that the isotopic composition of the cuprite oxygen is practically the same as that of ordinary water.

This probably indicates that the original copper sulfide deposit was altered by reaction with water and not with atmospheric oxygen.

(5) Hall and Johnston, THIS JOURNAL, 58, 1920–1922 (1936).

BOWLING GREEN STATE UNIVERSITY
BOWLING GREEN, OHIO
RECEIVED SEPTEMBER 6, 1940

The Freezing Points and Low Temperature Viscosities of Diacetone Alcohol–Acetone Mixtures[1a]

BY V. LANTZ

In determining the viscosities of diacetone alcohol and its mixtures with acetone at temperatures near the freezing points of the solutions, it was observed that the commercially pure diacetone alcohol used[1b] (d^{20}_4 0.9377, n^{20}_D 1.4235) had a freezing point considerably higher than the only published values that could be found. The published values are −55°[2] and −57 to −54°,[3] whereas the value found was −45°. A second sample of commercial "pure diacetone" from the same source (d^{20}_4 0.9375, n^{20}_D 1.4235) had a freezing point of −45.9°. A portion of the second sample was distilled at 50 mm. pressure using a 20 to 1 reflux ratio in a two-meter vacuum-jacketed column packed with glass helices. The 80% heart cut (d^{20}_4 0.9382, n^{20}_D 1.4232) had a freezing point of −44.0°. Similar results (−44.9°) have recently been obtained by W. C. B. Smithuysen of the Bataafsche Petroleum Maatschappij, Amsterdam.[4]

The freezing points of acetone–diacetone alcohol solutions, shown in Table I, indicate that from 15 to 20% of acetone, the most likely impurity in diacetone alcohol, would need to be present to lower the freezing point of diacetone alcohol to the previously published values. The especially purified acetone used to obtain the data in Table I had the following constants: d^{20}_4 0.7914, n^{20}_D 1.3587.

TABLE I

FREEZING POINT OF ACETONE–DIACETONE ALCOHOL SOLUTIONS

Acetone, by wt.	0	4.3	8.6	13.0	20.0
F. p., °C.	−44.0	−46.9	−50.4	−52.5	−55.5

Freezing points were determined by noting the break in a temperature–time curve obtained by slowly warming a mush of crystals and liquid in an air jacketed test-tube held at a nearly constant temperature above the freezing point of the solution. This method was found to be more satisfactory for determining initial freezing points than the use of cooling curves because the high viscosities of the solutions at their freezing points led to excessive under-cooling. Temperatures were measured with an iron–constantin thermocouple, calibrated against a platinum resistance thermometer.

Kinematic viscosities of diacetone alcohol and of a solution containing 12.8% by weight of acetone were measured at temperatures near their freezing points, using a Ubbelohde type viscometer.[5] Viscosities are shown in Table II.

TABLE II

LOW TEMPERATURE VISCOSITIES OF DIACETONE ALCOHOL AND OF A SOLUTION OF ACETONE IN DIACETONE

Diacetone alcohol		12.8% acetone 87.2% diacetone alcohol	
Temp., °C.	Viscosity centistokes	Temp., °C.	Viscosity centistokes
− 1.8	7.8	−33	15.0
− 2.7	8.1	−44	30.6
−15.0	15.3	−55.1	78.0[a]
−30.9	43.6		
−42.7	128		
−49.5	298[a]		

[a] Supercooled liquids

(1a) Original manuscript received July 19, 1939.

(1b) Supplied by Shell Chemical Company, San Francisco, California.

(2) T. H. Durrans, "Solvents," 4th ed., D. Van Nostrand Co., New York, N. Y., 1938, p. 112.

(3) "Handbook of Chemistry and Physics," 23rd ed., Chemical Rubber Publishing Company, Cleveland, Ohio, 1939, p. 750.

(4) Private communication.

(5) Ubbelohde, *Ind. Eng. Chem., Anal. Ed.*, 9, 85 (1937).

SHELL DEVELOPMENT CO.
EMERYVILLE, CALIFORNIA
RECEIVED SEPTEMBER 9, 1940

The Stable Form of Sucrose Octaacetate

BY R. P. LINSTEAD, A. RUTENBERG, W. G. DAUBEN AND W. L. EVANS[1]

In a recent preparation of sucrose octaacetate, a quantity of sucrose was heated in the usual way with sodium acetate and acetic anhydride. The only abnormal feature of the reaction was that the time of reacting was prolonged to twenty

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(1) After the authors became aware that work was being done simultaneously in the chemical laboratories of Harvard University and The Ohio State University on the stable form of sucrose octaacetate, they agreed to publish a joint paper on their results concerning this very important compound.

hours. A crystalline solid product was obtained in good yield, which, after one recrystallization from ether, formed bold prismatic needles, melting at 89°. The ordinary form of sucrose octaacetate known for more than fifty years has a melting point of about 69–70°.[2] It seemed probable that the new compound was a dimorphous modification of the octaacetate, or possible that some isomeric change or acetolysis had occurred.

The literature contains three descriptions of high melting forms of sucrose octaacetate. Pictet[3] observed the change of the usual form on standing into a "form II" of m. p. 75°. Frèrejacque[4] described the preparation of a "form III," m. p. 87°, by diluting an alcoholic solution of the usual form with water. Sandera[5] obtained a form of m. p. 83°. We believe that the product of the experiments which we now describe is a slightly purer version of Frèrejacque's "form III." We are led to publish this account of our work because our results supplement those of Frèrejacque, which we had overlooked when the work was carried out. We have not encountered Pictet's "form II."

It was first established that the compound of m. p. 89° was the octaacetate of a disaccharide, $C_{28}H_{38}O_{19}$, by elementary analysis and by the determination of acetyl values. The rotatory power of the new octaacetate was almost identical with that reported in the literature for the form of m. p. 69°. Hydrolysis of the material of m. p. 89° by Zemplén's method yielded sucrose with the correct melting point and rotatory power.

We have made a considerable number of preparations of sucrose octaacetate using a variety of experimental conditions, and have been quite unable to prepare the well-known form of m. p. about 69°. All our products have been more or less pure preparations of the 89° form. The usual precautions have been taken—different operators have performed the preparation and different rooms have been used—but without avail. We conclude that these laboratories are now seeded with the stable 89° form.

A sample of the 69° form was kindly supplied by Dr. Clifford Purves. When this was crystallized once from ether, either with or without conscious seeding with the 89° form, material melting at about 85° was obtained. Two commercial samples of sucrose octaacetate were also examined. One of these (Eastman Kodak Company) melted at 72–74° and after two crystallizations from ether was converted almost quantitatively into the 89° form. The second (Niacet Chemical Company) melted at 79–84° in the crude state and at 86° after one crystallization from ether.

These results leave no doubt that sucrose octaacetate is polymorphous and that the form of m. p. 89° is the most stable modification.

Experimental

Experiment 1.—The sucrose used had m. p. 183–184°, $[\alpha]^{22}_{\mathrm{D}}$ +66.6°, in water. A mixture of 150 g. of sucrose, 100 g. of anhydrous sodium acetate and 850 cc. of acetic anhydride was heated on the steam-bath for twenty hours. The product was poured onto 3 liters of ice water and left at 5° overnight. The hard solid so obtained was collected by filtration, washed with ice water and roughly dried in air. After one crystallization from 500 cc. of 95% alcohol (charcoal), 224 g. of **sucrose octaacetate** was obtained, m. p. 88–89°. The compound forms fine sheaves of glistening prismatic needles from dry ether or from alcohol, m. p. 89°. It is very soluble in benzene, insoluble in water and petroleum ether. It does not reduce Fehling solution even after prolonged boiling. For analysis the sample was dried to constant weight over alkali at 15 mm.

Anal. Calcd. for $C_{28}H_{38}O_{19}$: C, 49.56; H, 5.60. Found: C, 49.82, 49.82, 49.58, 49.33, 49.70, 49.74; H, 5.47, 5.83, 5.76, 5.59, 6.14, 5.60.

Acetyl Values. By hydrolysis with 0.1 *N* alcoholic potash for thirty minutes. Calcd. for $8(CH_3CO)$: CH_3CO, 50.72. Found: CH_3CO, 50.42, 50.55, 50.51.

Rotation. α, +2.99°; c, 2.566 in absolute alcohol; 2-dm. tube $[\alpha]^{25.4}_{\mathrm{D}}$ +58.5°. For the octaacetate of m. p. 69°, Georg found $[\alpha]^{28}_{\mathrm{D}}$ +57.8° in alcohol, c 2.733.[6]

Experiment 2.—Sucrose octaacetate was also obtained under the following experimental conditions which involve certain changes in concentration, temperature, time and technique from that given above. A mixture of 10 g. of sucrose, $[\alpha]^{22}_{\mathrm{D}}$ 66.7° (H_2O), m. p. 185–186°, 5 g. of anhydrous sodium acetate and 45 cc. of acetic anhydride was heated on a steam-bath for three hours and then let stand for thirty-six hours at room temperature. The mixture was again heated on a steam-bath and the hot solution poured slowly into 10 liters of *mechanically stirred* ice water. The reaction product separated as a white crystalline solid. The crude product was separated by filtration, washed well with cold water and dried in the open air (yield, 19 g. crude). It was then dissolved in hot 95% ethanol, decolorized with Carboraffin and allowed to crystallize (yield 17.3 g., 87.3%, m. p. 89°). Recrystallization from dry ether yielded the same white needles.

This experiment was repeated five times and the same results were obtained in each case. The use of potassium acetate for sodium acetate gave the same results.

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(2) Herzfeld, *Ber.*, **13**, 267 (1880); Koenigs and Knorr, *ibid.*, **34**, 4347 (1901); Hudson and Johnson, THIS JOURNAL, **37**, 2748 (1915); Brigl and Scheyer, *Z. physiol. Chem.*, **160**, 214 (1926); Pictet and Vogel, *Helv. Chim. Acta*, **11**, 436 (1928).

(3) Pictet, *ibid.*, **13**, 698 (1930).

(4) Frèrejacque, *Compt. rend.*, **203**, 731 (1936).

(5) Sandera, *Chem. Listy*, **33**, 139 (1939).

(6) Georg, *Helv. Chim. Acta*, **16**, 141 (1933).

Rotation. α, +0.95°; c, 0.795 in absolute chloroform; l, 2 dm.; $[\alpha]^{23}\text{D}$ +59.7°. This value is in close agreement with that reported by Hudson and Johnson,[3] $[+59.6]^{20}\text{D}$ ($CHCl_3$).

Anal. Calcd. for $C_{12}H_{14}O_{11}$: $(COCH_3)_8$ = acetyl,[7] 11.78 cc. of 0.1 N NaOH per 100 mg. of sample. Found: acetyl, 11.82, 11.81, 11.74 cc.

Crystallographic Analysis.—Lath-like crystals which show parallel extinction, but the character of the interference figures indicates monoclinic system of crystallization: optically negative, medium large optic angle, n_γ = 1.500 (±0.002), n_β = 1.488 (±0.002), n_α = 1.470 (±0.002).

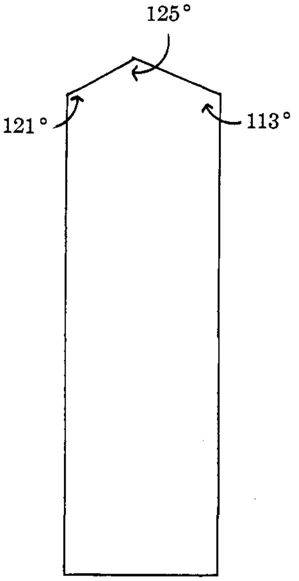

Fig. 1.—Characteristic crystal structure.

Experiment 3.—(Compare Koenigs and Knorr, ref. 2.) A mixture of 20 g. of sucrose, 40 g. of anhydrous sodium acetate and 120 cc. of acetic anhydride was heated to 110°, when reaction set in and heat was evolved. The mixture was kept at 125–135° for thirty minutes, allowed to cool to about 85°, and then diluted with 100 cc. of water. After the vigorous decomposition of the excess of the reagents, the product was poured onto ice. The sticky solid so formed was washed with fresh ice water from time to time until it was hard (4.5 hours). It was filtered and dried on a clay plate; yield, 30.5 g., m. p. (crude) 83–85°; 88–89° after one crystallization from ether.

Hydrolysis.—The octaacetate of m. p. 89° was hydrolyzed by sodium methoxide at room temperature following the method of Pictet and Vogel.[8] The white powder produced was dissolved in a little water and precipitated by the addition of a mixture of 5 parts of alcohol and 1 part of ether. The sucrose so obtained, after crystallization from 80% alcohol, had m. p. 183–184°, $[\alpha]^{23}\text{D}$ +66.5° in water.

Experiment 4.—In order to determine whether the sucrose octaacetate could be prepared by the method of acetylation which involves the use of pyridine and acetic anhydride, the following experiments were also carried out. A mixture of anhydrous sucrose (10 g.) and anhydrous pyridine (180 cc.) was shaken in a thermostat at 50° until solution of the sucrose was complete (sixteen hours). Acetic anhydride was added in 3-cc. portions (total, 45 cc.) and the temperature was not allowed to go above 52°. After remaining at 50° for about forty-eight hours the reaction mixture was poured into 10 liters of ice water and stirred vigorously for thirty minutes. The crude product was separated by filtration and the mother liquor allowed to stand at room temperature for twenty-four hours. From this clear water, upon standing, a second product was obtained in some quantity (7 g. air-dried). The acetate yielded beautiful needle-like crystals (m. p. 86°). Both products were crystallized from hot and cold ethanol and in all four cases the same sucrose octaacetate was obtained (combined yield 8.5 g., 43.7%, m. p. 89°). On repetition of this experiment at 0°, 3.5 g. of the pure sucrose octaacetate was obtained.

Experiment 5.—In this experiment the product was worked up as far as possible in the absence of free acetic acid. A mixture of 6 g. of sucrose, 4.5 g. of sodium acetate and 30 cc. of acetic anhydride was heated on the steam-bath under reflux for thirty minutes. The product was poured into a large bulk of ice and water and extracted twice with ether (total, 150 cc.). The combined ether extract was in turn extracted with successive quantities of aqueous sodium bicarbonate solution until free from acid. It was then washed with water and dried over sodium sulfate. Removal of the ether left an oil which soon solidified. The solid melted at 86° alone and at 87–89° on admixture with the 89° form.

Experiment 6.—(In this the product was worked up at high acidity.) Sucrose octaacetate (4 g., m. p. 89°) was dissolved in a mixture of 3 parts of acetic anhydride and 1 part of acetic acid. The mixture was heated to boiling and poured into 100 cc. of water. After standing overnight, the hard cake was filtered off. It melted at 86–87° in the crude state.

The lowest melting samples of octaacetate which could be obtained were made by ether extraction as under (5) above, followed by evaporation and rubbing of the resulting oil with alcohol. Products melting initially at about 79–80° were so obtained. On crystallization these gave the form of m. p. 89°.

Attempted Conversion of the 89° Form.—(i) The form of m. p. 89° was melted under high vacuum. On cooling the product set to a clear glass. Crystallization of this from hot water, ether and alcohol gave products melting severally at 82–83°, 81–83° and 89°. (ii) On crystallization of the 89° form from dilute or glacial acetic acids, products were obtained melting at about 86°. Recrystallization of these from alcohol or ether raised the m. p. to 89°. (iii) A solution of the 89° form in ether was seeded with the 69° form. The resulting crystals melted at 85°. These experiments indicate a slight tendency for the high melting form to revert to a lower melting modification.

Conversion of the 69° into the 89° Form.—(i) A sample of the octaacetate kindly provided by Dr. C. B. Purves melted at 69°. After two crystallizations from pure ether the m. p. was raised to 88°; mixed m. p. with the 89° form, 88–89°. A similar result was obtained when the ethereal

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(7) A. Kunz and C. S. Hudson, This Journal, **48**, 1978 (1926).

(8) Pictet and Vogel, *Helv. Chim. Acta*, **11**, 441 (1928).

solution was seeded with the 89° form. (ii) A sample of commercial sucrose octaacetate had m. p. 72–74°. One crystallization from ether gave material of m. p. 86–87°. Crystallization from alcohol, acetic acid, water and chloroform gave in all cases products melting between 80° and 88°, and after further crystallization at 89°. (iii) In quantitative conversions, 7.4 g. of the octaacetate, m. p. 72–74°, yielded 7.1 g. of m. p. 88° after two crystallizations from ether. In another experiment 5.6 g. of the low melting octaacetate was dissolved in ether. The solution was filtered, seeded with the 89° octaacetate and the solvent removed; 5.6 g. of product was obtained, m. p. 87–88°. (iv) On one occasion a product melting at 72° was obtained by the use of the procedure employed in experiment 2. At the end of two days, the specimen had changed to the high melting compound (89°). Many attempts were made to repeat this experiment but the high melting compound was always obtained.

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COLUMBUS, OHIO
CAMBRIDGE, MASS.

RECEIVED JUNE 19, 1940

Hydrogen Bonds Involving the C–H←F Link. XII[1]

BY C. S. MARVEL, M. J. COPLEY[2] AND E. GINSBERG

Although strong F–H←F bonds are present in the solid, liquid, and vapor phases of hydrogen fluoride, almost no evidence has been presented heretofore to indicate that a fluorine atom attached to a carbon atom is capable of acting as a donor atom for hydrogen bond formation. Zellhoefer, Copley, and Marvel[3] noted that the substitution of fluorine for chlorine in chloroform and in methylene chloride decreases the ratio of their observed to "ideal" (calculated from Raoult's law) solubilities at 3° in donor solvents. This effect is illustrated by the data[3] given in Table I when dimethyl ether of tetraethylene glycol is used as the solvent. The solubilities of the halogenated hydrocarbons were determined at partial pressures corresponding to their vapor pressure at 3°.

TABLE I

SOLUBILITY OF HALOGENATED HYDROCARBON IN TETRAETHYLENEGLYCOL DIMETHYL ETHER AT 3°

	Mole fraction Obsd.	Mole fraction Ideal	Ratio Obsd./Ideal
$CHCl_3$	0.625	0.283	2.20
$CHCl_2F$	.706	.381	1.85
$CHClF_2$	.740	.449	1.65
CH_2Cl_2	.600	.311	1.93
CH_2ClF	.647	.398	1.62

The decrease in the ratio may be explained by assuming that the smaller negative deviations observed with the fluorine derivatives are caused by weak C–H←F bonds between fluorinated hydrocarbon molecules. Unfortunately, fluoroform, for which the effect might be expected to be a maximum, is difficult to obtain and was not available.

It occurred to the authors that further evidence might be discovered by making a comparison of the heats of mixing with donor liquids of the vinylogs[4] $C_6H_5CF_3$ and $C_6H_5CCl_3$, respectively, of CHF_3 and $CHCl_3$. One would predict that the para hydrogens of the vinylogs are sufficiently activated to form hydrogen bonds with donor nitrogen or oxygen atoms. If the fluorine atoms have donor properties, some association through C–H←F bonds should be present in $C_6H_5CF_3$. The breaking of these bonds to form more stable C–H←N or O bonds on mixing with a donor liquid would lead to a smaller heat of mixing for $C_6H_5CF_3$ than for $C_6H_5CCl_3$. (This prediction contains the assumption that a chlorine atom does not bond or that at most it has a smaller donor capacity than a fluorine atom.)

The method followed in making these measurements has been described in a previous publication.[5] The data are tabulated in Table II.

TABLE II

HEATS OF MIXING IN CALORIES PER MOLE OF SOLUTION AT 3° FOR EQUIMOLAR MIXTURES

	Benzotrifluoride	Benzotrichloride
N,N-Dimethylacetamide	125	305
Dimethylcyclohexylamine	120	410
Ethyl phosphate	135	160
Ethyl ether	140	123
Acetone	40	40

The maxima in the heat of mixing curves occurred at approximately equimolar mixtures. A pronounced effect in the expected direction was observed with each of the nitrogen compounds but the results with the oxygen compounds are not conclusive. Apparently the para hydrogens of the ring are not sufficiently activated to form C–H←O bonds of any greater strength than the C–H←F bonds already present in the

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(1) For the eleventh communication in this series see Marvel, Copley and Ginsberg, THIS JOURNAL, **62**, 3109 (1940).

(2) Present address: Eastern Regional Research Laboratory, U. S. Department of Agriculture, Chestnut Hill Station, Philadelphia, Pennsylvania.

(3) Zellhoefer, Copley and Marvel, THIS JOURNAL, **60**, 1337 (1938).

(4) Fuson, *Chem. Rev.*, **16**, 1 (1935).

(5) Zellhoefer and Copley, THIS JOURNAL, **60**, 1343 (1938).