EXPERIMENTS WITH REGENERATED CELLULOSE

Ratio cellulose/sodium	Cell, g.	Sodium, g.	Time, min.	Atoms of H_2 per atom of sodium
1:0.250	1.8262	0.0648	...	1.000
1:0.496	0.8726	.0615	2	1.003
1:0.832	.4995	.0531	...	1.035
1:1.01	.4496	.0644	5	1.005
1:1.50	.2761	.0587	24	1.013
1:1.97	.1815	.0508	30	1.014
1:2.47	.1976	.0692	113	0.961
1:2.93	.1358	.0564	150	.925
1:excess	.2532	.2310	240	2.949[a]
			General average	0.990

[a] These values give the atoms of hydrogen replaced per $C_6H_{10}O_5$ group, the general average of which is 2.993 atoms.

Summary

1. The action of metallic sodium on cellulose in liquid ammonia has been studied.

2. One atom of sodium enters the molecule rapidly, whereas the second and third enter very slowly.

3. A maximum of three atoms of sodium per $C_6H_{10}O_5$ group enters the molecule.

4. The reaction corresponds in general to the ordinary alcoholate reaction, $ROH + Na = RONa + \frac{1}{2}H_2$.

5. It is concluded that cellulose acts as an alcohol in liquid ammonia and probably does so in its other reactions in other solvents.

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[JOINT CONTRIBUTION FROM THE FOOD RESEARCH DIVISION, BUREAU OF CHEMISTRY AND SOILS, AND MICROANALYTICAL LABORATORY, FOOD AND DRUG ADMINISTRATION, UNITED STATES DEPARTMENT OF AGRICULTURE]

THE IDENTIFICATION OF MESACONIC ACID[1]

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RECEIVED APRIL 9, 1931 PUBLISHED JUNE 8, 1931

During an investigation of the occurrence of organic acids in plant material, interest was aroused in the true melting point of mesaconic acid, and also in the preparation and physical and chemical properties of some new derivatives which might prove useful in its identification. Of the derivatives commonly used, the amide is the only one which previously has been reported, but since the hydrazide is the most easily prepared, when the ester is available, it has been the derivative most commonly used in this Laboratory for the identification of naturally occurring organic acids.

[1] Food Research Division Contribution No. 103.

Mesaconic acid and two of its derivatives, the hydrazide and *p*-nitrobenzyl mesaconate, being definitely crystalline, readily lend themselves to a microscopical study by the optical immersion method. The optical data given are of considerable importance in the rapid and accurate identification of small amounts of these substances. They have not been reported heretofore.

Experimental

Mesaconic Acid.—Mesaconic acid was prepared from citraconic anhydride by the method of Fittig.[2] Citric acid was distilled at atmospheric pressure and the oily layer obtained in the distillate was separated from the aqueous layer and redistilled; 40 g. of citraconic anhydride thus obtained was dissolved in 80 cc. of water containing 12 cc. of concentrated nitric acid, and the solution was boiled until fumes of nitrogen tetroxide appeared. When the solution had cooled, mesaconic acid crystallized out and was separated from the mother liquor by filtration. The acid was purified by recrystallization from water and was dried at 100°. It melted at 204.5° corrected. When sublimated in a Hortvet sublimator it showed no change in melting point. Mesaconic acid obtained from Kahlbaum melted at 204°. The melting point is variously stated in the literature to be from 200.5 to 208°, 202° being the most commonly accepted temperature.

The melting points were taken on two different types of melting point apparatus, including the electrically heated apparatus of Sando.[3] Anschütz and Wheeler total immersion thermometers with Bureau of Standards corrections were used. All determinations were by the capillary method and were taken slowly, as the compound does not show any decomposition at this temperature within the ordinary time of taking a melting point. It is concluded therefore that 204.5° represents the melting point of mesaconic acid more closely than any figure previously reported.

Optical Properties.—Mesaconic acid, sublimed, is colorless and rod-like in habit, usually occurring in laminated, fibrous masses. With crossed nicols (parallel polarized light), the rods show parallel extinction, and the elongation is positive or negative. The double refraction apparently is very strong. The minimum index of refraction (immersion method) is considerably less than $n = 1.445$. The acid is soluble in all the oily mixtures available. The maximum refractive index (γ) was found to be 1.740 (methylene iodide) but occurs infrequently. The most significant refractive index for the substance is that shown when the elongated crystals are oriented with their long axis parallel to the vibration plane of the lower nicol. In this position the rods frequently match a liquid with $n = 1.690$ (apparently the β-value). This liquid is most useful for determinative purposes since the intermediate value occurs so frequently and is always shown lengthwise on the rods. The liquid used for this purpose consisted of a mixture of monochloronaphthalene and methylene iodide in proportions to give the refractive index desired.

A sample of mesaconic acid obtained from Kahlbaum. and one prepared from citric acid showed the same optical constants as the sublimed material.

Diethyl Mesaconate.—Fifteen grams of mesaconic acid prepared as previously described was refluxed for eighteen hours on a steam-bath with 300 cc. of absolute alcohol containing 2% of dry hydrogen chloride. The alcohol was then distilled off and the ester was dissolved in ether and washed in a separatory funnel with dilute sodium hydroxide solution until the wash water remained alkaline, then dried with anhydrous

[2] R. Fittig, *Ann.*, **188**, 73 (1877).

[3] C. E. Sando, *Ind. Eng. Chem., Anal. Ed.*, **3**, 65 (1931).

sodium sulfate. The ether was distilled off and the ester distilled under reduced pressure. The diethyl mesaconate so obtained boiled at 93–95° under 10 mm. pressure. The boiling point under reduced pressure has not been previously reported.

Mesaconic Hydrazide.—The hydrazide of mesaconic acid was prepared from the ester as follows. One cc. of 42% hydrazine hydrate in water was added to a solution of 0.7 g. of the ester in 5 cc. of absolute alcohol. After standing overnight the hydrazide crystallized out in the form of clear, glassy rods. It was soluble in water and insoluble in alcohol. On recrystallization from dilute alcohol the hydrazide melted with decomposition at 217–218°, corrected.

Anal. Subs., 0.0982, 0.0969: CO_2, 0.1377, 0.1356; H_2O, 0.0550, 0.0560. Subs., 0.0438, 0.0435: N, 0.0157, 0.0157. Calcd. for $C_5H_{10}N_4O_2$: C, 37.96; H, 6.37; N, 35.43. Found: C, 38.25, 38.18; H, 6.27, 6.47; N, 35.85, 36.09.

Optical Properties.—When examined at a magnification of 15 diameters, mesaconic hydrazide, crystallized from dilute alcohol, is seen to consist of clear, glassy rods. For microscopical examination by the immersion method, the substance is pulverized into a fine powder, producing irregular fragments. When examined with crossed nicols (parallel polarized light), most of the fragments extinguish sharply and show colors of first and second order. Occasionally fragments occur which do not extinguish sharply, remaining essentially bright when the stage is rotated, and showing a partial biaxial interference figure with the optic axis up when the material is examined in convergent polarized light (crossed nicols). The refractive indices are: n_α 1.583; n_β 1.610; n_γ 1.680; all ± 0.003.

***p*-Nitrobenzyl Mesaconate.**—The *p*-nitrobenzyl ester of mesaconic acid was prepared by the method of Reid.[4] On recrystallization from dilute alcohol it melted sharply at 134° corrected.

Optical Properties.—*p*-Nitrobenzyl mesaconate crystallizes in rods and plates. With crossed nicols, the extinction is parallel and the elongation negative. The refractive indices are $n_\alpha = 1.610$, occurring frequently lengthwise on rods; $n_\beta = 1.627$, frequently shown crosswise on rods; $n_\gamma = 1.680$, also shown crosswise on rods but not as common as α and β; all ± 0.003. In identifying the substance by the optical immersion method, the α- and β-values are very useful.

Summary

The capillary melting point of mesaconic acid was found to be 204.5°. The ethyl ester boiled at 93–95° at 10 mm. The melting point of the hydrazide is 217–218°, and of the *p*-nitrobenzyl ester, 134°. Both the hydrazide and the *p*-nitrobenzyl ester were found to be satisfactory derivatives for the purpose of identification, but the hydrazide is the more easily prepared, if the ester is available. Optical crystallographic data for the acid and two of the derivatives are given.

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[4] E. E. Reid, THIS JOURNAL, **39**, 124 (1917)