2975 (1), 3040 (2) cm.$^{-1}$. A summary of the entropy calculation is given in Table VIII. The best value for the barrier to internal rotation is seen to be 3450 cal./mole.

This work adds to the evidence from thermodynamic measurements and other sources[10] that rotation about single carbon–carbon bonds is restricted considerably. Although the method used in this work is the most accurate now available for the determination of the magnitude of the barrier, the possible experimental error is always rather high, being probably in no case less than ±200–300 cal./mole. This is because the quantity of interest, *i. e.*, the contribution of the internal rotation to the entropy, is the small difference between two essentially experimental quantities each burdened with its own errors. It should also be remembered that the height of the barriers is of significance only in connection with the potential function assumed for the rotation. The tables used[8] assume a potential $\varphi = (V/2)(1 - \cos 3X)$; this is used largely because of the mathematical simplification introduced and its correctness has no conclusive support, either theoretical or experimental. Other assumptions as to the potential would give different barrier heights. For example Charlesby[11] has shown that for ethane the assumption of a rectangular barrier 1700 cal./mole high and 1.35 radians wide also gives a fit with available data. The cosine potential is more reasonable, however, and is quite satisfactory for comparing different molecules.

We believe that the values for ethane, 1,1,1-trichloroethane, and 1,1,1-trifluoroethane of 2700–3000, 2700, and 3450 cal./mole, respectively, do not differ enough to allow any reliable ordering as to magnitude, although the higher value of 1,1,1-trifluoroethane is probably significant. However, the important fact that the values are so nearly the same, should stimulate work on a fundamental theory of hindered rotation. Until such a theory is developed, a serious gap exists in our knowledge of simple molecular structures.

We wish to thank Mr. William Shand and Dr. R. A. Spurr for the use of their unpublished electron diffraction data for 1,1,1-trifluoroethane and Professor Alexander Goetz for supplying us with liquid hydrogen.

Summary

1. The heat capacity, heats of transition, fusion and vaporization, and vapor pressure of 1,1,1-trifluoroethane have been measured in the temperature range 13–226°K. From these data the calorimetric entropy has been calculated.

2. The Raman spectrum data have been reconsidered and slightly revised. From this and other molecular data, the entropy of the compound has been calculated statistically. Comparison of the calculated and observed entropies indicates a barrier of 3450 ± 400 cal./mole hindering the internal rotation of the molecules.

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[10] For an excellent review see G. Glockler, *Rev. Mod. Phys.*, **15**, 145 (1943).

[11] A. Charlesby, *Proc. Phys. Soc.* (London), **54**, 471 (1942).

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, THE UPJOHN COMPANY]

Concerning Racemic α-Hydroxy-β,β-dimethyl-γ-butyrolactone (Pantolactone)[1a]

BY JARED H. FORD

Glaser[1b] reported that he obtained pantolactone by vacuum distillation in the form of a transparent crystalline mass, m. p. 55°, that appeared under the microscope as clumps of prismatic needles. Stiller and co-workers[2] obtained a glassy product on vacuum distillation which on recrystallization from ether–petroleum ether gave clusters of fine colorless needles, m. p. 56–58°. Reichstein and Grüssner[3] and Carter and Ney[4] also obtained glassy products, but they reported melting points of 75–78° and 75–80°, respectively.

In the present investigation racemic pantolactone was obtained by vacuum distillation as a colorless transparent solid which became translucent at 80° and which melted at 89.8–91.0°. The melting point was not changed by recrystallization from a benzene–cyclohexane mixture. The melting point of 89.8–91.0° is practically the same as that reported for optically active pantolactone.[4a] On comparison, (−)-pantolactone ($[\alpha]^{25}_{D}$ −49.2° in water; $C = 2\%$) was found to melt at 89.9–91.1°, and a mixture of approximately equal parts of racemic and (−)-forms was found to melt at 89.8–91.0°. Thus it appears that the *d* and *l* forms of this compound form a racemic solid solution which, when partly melted, has the same composition in the liquid and solid phases.[5] The 56° melting form reported by previous investigators[1,2] is probably a racemic compound.

[1a] This name has been suggested by Barnett and Robinson [*Biochem. J.*, **36**, 357 (1942)] for α-hydroxy-β,β-dimethyl-γ-butyrolactone, the lactone half of pantothenic acid.

[1b] Glaser, *Monatsh.*, **25**, 46 (1904).

[2] Stiller, Harris, Finkelstein, Keresztesy and Folkers, THIS JOURNAL, **62**, 1785 (1940).

[3] Reichstein and Grüssner, *Helv. Chim. Acta*, **23**, 650 (1940).

[4] Carter and Ney, THIS JOURNAL, **63**, 312 (1941).

[4a] Stiller and co-workers[2] have reported a melting point of 90–91° for synthetic (−)-pantolactone and 91–92° for the (−)-pantolactone that they isolated from natural pantothenic acid.

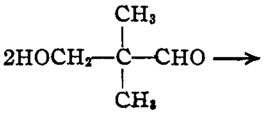
[5] Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1938, Vol. I, p. 182.

The racemic pantolactone, m. p. 89.8–91.0°, described in this communication, was prepared from α,α-dimethyl-β-hydroxypropionaldehyde[6] that had been recrystallized once from ethyl acetate and once from 95% ethanol. The cyanohydrin reaction was carried out with calcium chloride and sodium cyanide[3,4], and the resulting cyanohydrin was hydrolyzed with hydrochloric acid.[1,2] When the synthesis was carried out with crude α,α-dimethyl-β-hydroxypropionaldehyde as reported by Carter and Ney,[4] the melting point of the resulting pantolactone was in good agreement with the value reported by these investigators (75–80°) and by Reichstein and Grüssner[3] (75–78°). Fractional distillation of the impure material, using a 2-ft. column packed with Raschig rings, gave a product melting at 85–88°.

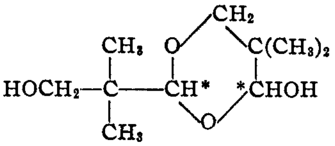
In order to obtain pure racemic pantolactone it is essential that the intermediate aldol, α,α-dimethyl-β-hydroxypropionaldehyde, be free from certain impurities, but the melting point was found to be a poor criterion of its purity. It usually melts over a range of 2 to 5 degrees. Melting points from 79–82° to 100–103° have been obtained on samples that were recrystallized several times from alcohol. Furthermore, some samples of crude aldol were found to have melting points within this range. The recrystallized samples differ from the crude ones in that they are substantially odorless and give clear solutions when dissolved in 10 parts of hot water.

Since three recrystallized samples having melting points of 79–82°, 82–84° and 100–103°, respectively, were found to give high yields of pure racemic pantolactone, it is believed that they were substantially pure. Melting points of 89–90°[6] and 96–97°[2] have been previously reported for this compound.

Wessely[6] has determined the molecular weight of crystalline α,α-dimethyl-β-hydroxypropionaldehyde and found it to be dimeric. By analogy with the structure proposed by Späth and Schmid[7] for the dimer of aldol it appears likely that the dimer of α,α-dimethyl-β-hydroxypropionaldehyde has the following structure



$$2HOCH_2-C(CH_3)_2-CHO \longrightarrow$$



Since this structure contains two different asymmetric carbon atoms, the compound should exist in two racemic modifications. This affords a logical explanation of the fact that samples having different melting points may give equally good yields of pantolactone. The above structure requires only the splitting of hemiacetal linkages to convert the dimeric into the monomeric form.

The author wishes to thank Messrs. Harold Emerson and William Struck of these Laboratories who carried out the analyses.

Experimental

α,α-Dimethyl-β-hydroxypropionaldehyde.—The proportions of reactants were the same as those described by Wessely,[6] but the temperature was held at approximately 25° by means of an ice-bath. A mechanical stirrer was used. After being recrystallized once from ethyl acetate and once from 95% ethanol, the product melted at 78–81°. The yield of crude aldol was 80%. Each recrystallization caused a loss of about 50% in the yield.

Pantolactone.—To a mechanically stirred mixture of 128.8 g. of α,α-dimethyl-β-hydroxypropionaldehyde (passed through a 12-mesh sieve), 400 g. of chopped ice, and 400 g. of water was added a solution of 111.0 g. of calcium chloride dihydrate (Mallinckrodt) in 100 ml. of water. A solution of 71.0 g. of sodium cyanide in 125 ml. of water was then added rapidly, and the stirring was continued for one hour. Concentrated hydrochloric acid (500 ml.) was then added, and the resulting clear solution was heated for eighteen hours on the steam-bath. The lactone was separated from the aqueous solution by continuous extraction with chloroform. The chloroform was removed, and the residue was vacuum distilled, using an ordinary Claisen flask. The lactone boiled at 117–121° (10 mm.) and was a sticky, wax-like semi-transparent solid, melting at 89.6–91.0°. The yield was 155.5 g. (95%). On redistillation a middle fraction (b. p. 120–121° (11 mm.)) was obtained which melted at 89.8–91.0°.[8]

Anal. Calcd. for $C_6H_{10}O_3$: C, 55.35; H, 7.75; sap. eq., 130.1. Found: C, 55.39; H, 8.05; sap. eq., 130.4, 130.4.

The saponification equivalent was determined by dissolving the sample in an excess of normal alkali, warming to 80° for fifteen minutes, cooling to 0° and titrating with normal acid at 0 to 5°.

Summary

1. Racemic pantolactone has been obtained as a solid solution which has the same melting point as the optically active forms.

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[6] Wessely, *Monatsh.*, **21**, 216 (1900).

[7] Späth and Schmid, *Ber.*, **74B**, 859 (1941).

[8] All melting points were corrected. Those on the lactone were taken in sealed tubes as the compound is very hygroscopic.