**Summary.**—The results of standard analytical determinations on coconut shells agree well with those recorded by Fleck and colleagues except for the higher value found for cellulose.

It is proposed to investigate further the nature of the association of xylan and cellulose in coconut shells.

COCONUT RESEARCH SCHEME OF CEYLON
LUNUWILA, CEYLON
RECEIVED JANUARY 4, 1938

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## The Preparation of Diacetone Sugars

BY H. VAN GRUNENBERG, C. BREDT AND WERNER FREUDENBERG

The use of concentrated sulfuric acid as catalyst and dehydrant for acetonizations of carbohydrates has found general acceptance. Several disadvantages of this method are well known; while high (4–5%) concentration of sulfuric acid[1] brings about rapid condensation of acetone, less catalyst leaves considerable quantities of sugar undissolved and favors formation of monoacetone derivatives instead of diacetone sugars. Furthermore, the neutralization of sulfuric acid with anhydrous solid carbonate is time consuming. Other catalysts, zinc chloride,[2] copper sulfate[3] or phosphoric anhydride,[4] among others, have been suggested; much lower yields however have been obtained as compared to the sulfuric acid method.

In studying the acetonization of *l*-sorbose we have obtained by using zinc chloride in combination with a mixture of ortho- and metaphosphoric acids very satisfactory results and have developed the method given below which seems to be generally applicable to the preparation of diacetone sugars and superior to older methods in yield, speed and simplicity. The application of this process to the commercial preparation of diacetonesorbose (ascorbic acid synthesis) has been considered.

The following yields of diacetone sugars were obtained: *l*-sorbose 85%, *d*-arabinose 90%, *d*-galactose 78%, *d*-mannose 92% and *d*-glucose 75%. In all cases the products isolated were practically pure as checked by analysis and rotation. The yields are based on crystallized or distilled products. Due possibly to the acidic acetonization medium the same diacetone products are obtained which are formed by the use of sulfuric acid as catalyst.

**Procedure.**—One hundred grams of the very finely powdered sugar is suspended in two liters of dry acetone to which is added in rapid succession 120 g. of fused zinc chloride (sticks) and a homogeneous mixture of 20 g. of phosphorus pentoxide and 40 g. of phosphoric acid (85%). The whole is shaken mechanically until solution is complete, which lasts about two hours. Then, in order to bring the reaction to completion the solution is allowed to stand overnight at room temperature. The mixture is then made alkaline by adding an aqueous suspension of sodium carbonate, the precipitate of zinc carbonate is filtered, washed with acetone, and the combined filtrate and washings are distilled *in vacuo* until most of the acetone is removed.

The resulting aqueous residue is extracted with three 150-cc. portions of benzene or ether, which, after removal of the solvent *in vacuo*, leaves the diacetone product in practically pure form.

Acknowledgment is made to the Works Progress Administration of the City of New York for assistance rendered under Project 465-97-3-120.

DEPARTMENT OF CHEMISTRY
FORDHAM UNIVERSITY
NEW YORK, N. Y.
RECEIVED MAY 5, 1938

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(1) Bell, *J. Chem. Soc.*, 1874 (1935); Ohle, *Ber.*, **71**, 562 (1938); Reichstein and Grüssner, *Helv. Chim. Acta*, **17**, 311 (1934).

(2) Fisher, *Ber.*, **60**, 485 (1927).

(3) Ohle and Koller, *ibid.*, **57**, 1566 (1924).

(4) Smith and Lindberg, *ibid.*, **64**, 505 (1931).

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## Thermal Data on Organic Compounds. XVIII. The Heat Capacity and Entropy of *t*-Butylethylene

BY WM. D. KENNEDY, C. HOWARD SHOMATE AND GEORGE S. PARKS

The combination of constancy of freezing point and constancy of boiling point serves as an excellent criterion of the purity of a chemical compound. This criterion has been used frequently by Kistiakowsky[1] and his collaborators in their extremely accurate determinations of the heats of organic reactions. Recently in the case of *t*-butylethylene,[1b] however, they failed to find a constant freezing point by their methods, although otherwise they had every reason to believe in the extreme purity of the material; and accordingly they invited us to study the fusion behavior of a sample of their material by our calorimetric method.

We have now measured the heat capacities of this olefin between 80 and 298°K. From the temperature change during the fusion of the crys-

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(1) (a) Kistiakowsky, Ruhoff, Smith and Vaughan, THIS JOURNAL, **58**, 137, 146 (1936); (b) Dolliver, Gresham, Kistiakowsky and Vaughan, *ibid.*, **59**, 831 (1937); (c) Dolliver, Gresham, Kistiakowsky, Smith and Vaughan, *ibid.*, **60**, 440 (1938).

talline material we have estimated the purity of the sample as, at least, 99.8 mole per cent. The heat of fusion, however, is unusually small for such a type of compound and this fact readily accounts for the difficulty encountered by the Harvard investigators in their freezing point tests.

Furthermore, it should be noted that this compound exists in two crystalline forms at low temperatures with a transition point at 124.9°K. In magnitude the heat of transition (12.35 cal. per g.) is almost four times that of the heat of fusion of the Crystals II.

## Experimental Results

In principle, the method of Nernst was employed with an aneroid calorimeter in determining the "true" specific heats and the transition and fusion data. The apparatus and details of experimental procedure have been fully described in other places.[2] In view of the accuracy of the various measurements involved, the error in the experimental values obtained here is probably less than 0.7% at all temperatures.

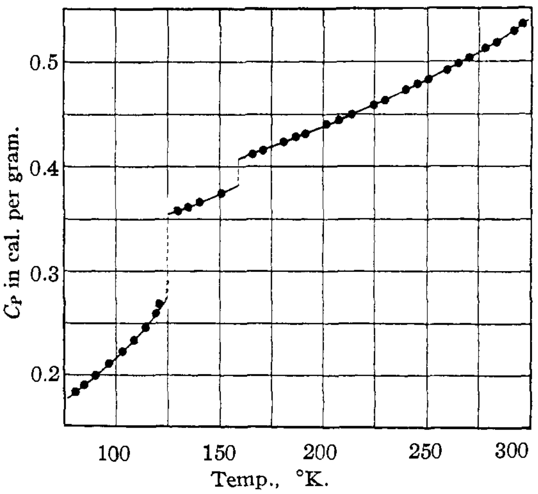

Fig. 1.—The specific heat curve for *t*-butylethylene.

These heat capacity data, expressed in terms of the defined calorie (equivalent to 4.1833 international joules) and with all weights reduced to a vacuum basis, appear in Tables I and II. The specific heat values are also represented graphically in Fig. 1, in which it is noteworthy that premelting and other effects of impurities are practically negligible.

TABLE I

SPECIFIC HEATS IN CALORIES PER GRAM OF *t*-BUTYLETHYLENE

| *T*, °K. | $C_p$ | *T*, °K. | $C_p$ | *T*, °K. | $C_p$ |
|---|---|---|---|---|---|
| | | Crystals I | | | |
| 80.8 | 0.1828 | 97.2 | 0.2107 | 113.6 | 0.2458 |
| 85.6 | .1903 | 102.8 | .2221 | 118.8 | .2595 |
| 90.9 | .1990 | 108.4 | .2333 | 121.1 | .2689 |
| | | Crystals II | | | |
| 129.5 | 0.3569 | 140.2 | 0.3655 | 151.3 | 0.3750 |
| 134.4 | 0.3608 | | | | |
| | | Liquid | | | |
| 165.9 | 0.4104 | 213.6 | 0.4492 | 265.3 | 0.4972 |
| 171.2 | .4138 | 224.7 | .4581 | 270.8 | .5027 |
| 181.2 | .4226 | 230.3 | .4624 | 277.8 | .5119 |
| 186.8 | .4275 | 240.4 | .4719 | 283.4 | .5182 |
| 191.7 | .4294 | 246.0 | .4780 | 291.4 | .5287 |
| 201.5 | .4397 | 251.3 | .4817 | 295.9 | .5348 |
| 207.3 | .4445 | 260.2 | .4912 | | |

TABLE II

TRANSITION AND FUSION DATA

| Process | *T*, °K. | $\Delta H$ determination (cal. per g.) I | II | Mean |
|---|---|---|---|---|
| Transition | 124.9 | 12.34 | 12.35 | 12.35 |
| Fusion | 158.4 | 3.11 | 3.11 | 3.11 |

## Entropy Data

Using the heat capacity data contained in the preceding section in conjunction with the third law of thermodynamics, we have calculated the entropy of liquid *t*-butylethylene at 298.1°K. The detailed entropy increments are given in Table III. In this calculation we have employed the extrapolation method (with "class I" constants) of Kelley, Parks and Huffman[3] for estimating the entropy increase for the low temperature crystals from 0 to 80°K. The various increments from 80 to 298.1°K. were obtained by the usual methods directly from the experimental data. The result for the molal entropy at 298.1°K. is thus found to be 61.3 cal. per degree. This

TABLE III

THE ENTROPY OF *t*-BUTYLETHYLENE

| | |
|---|---|
| Crystals I (0–80°) extrapolated | 11.39 |
| Crystals I (80–124.9°) graphical | 8.26 |
| Transition $\left(\frac{12.35 \times 84.092}{124.9}\right)$ | 8.32 |
| Crystals II (124.9–158.4°) graphical | 7.32 |
| Fusion $\left(\frac{3.11 \times 84.092}{158.4}\right)$ | 1.65 |
| Liquid (158.4–298.1°) graphical | 24.35 |
| $S^\circ_{298}$ for the liquid state in cal. per degree | 61.3 |

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(2) Parks, THIS JOURNAL, **47**, 338 (1925); also Parks and Kelley, *J. Phys. Chem.*, **30**, 47 (1926).

(3) Kelley, Parks and Huffman, *ibid.*, **33**, 1802 (1929). As recently indicated in the paper of Parks, Shomate, Kennedy and Crawford [*J. Chem. Phys.*, **5**, 359 (1937)], the "class II" constants, designed originally for cyclic compounds, may yet prove more accurate in the extrapolation of the entropies of all hydrocarbons, both aliphatic and cyclic. Until this point is definitely proved, however, it seems to us preferable to continue to employ the class I constants for aliphatic hydrocarbons, as in the past.

value is probably reliable to within 1.0 e. u. in an absolute sense and to 0.5 e. u. for comparative purposes.

The molal entropy of the corresponding paraffin, 2,2-dimethylbutane, has been reported recently by Stull[4] as 64.4 (±1.8) e. u. Thus the paraffin–olefin difference here is apparently 3.1 e. u., which is a somewhat greater effect than that (2.2 e. u.) found by Parks, Todd and Shomate[5] in the case of 2,4,4-trimethylpentane and 2,4,4-trimethylpentene-1.

### Free Energy of Dehydrogenation of 2,2-Dimethylbutane

The data are now available for the estimation of the free energy change in the dehydrogenation process

$$t\text{-butylethane (l)} \longrightarrow t\text{-butylethylene (l)} + H_2\ (g)$$

For the gas-phase reaction Kistiakowsky and coworkers[1b] have found $\Delta H_{355} = 30{,}340\ (\pm 60)$ cal. Reducing this value by 250 cal. for the temperature change from 355 to 298°K. and assuming that the heats of vaporization of the paraffin and olefin are practically the same, we now find $\Delta H_{298} = 30{,}090\ (\pm 200)$ cal. In the preceding section we found the entropy difference between the liquid paraffin and olefin to be 3.1 e. u. and in view of the similarities in the extrapolations we now estimate the probable error in this figure as under 1.5 e. u. Accordingly, taking 31.23 e. u.[6] for the molal entropy of hydrogen, we have $\Delta S_{298} = 28.1\ (\pm 1.5)$ e. u. Hence, $\Delta F^\circ_{298} = 30{,}090 - (298.1)(28.1) = 21{,}700\ (\pm 500)$ cal. for the process in question.

This result is in good agreement with the figure 21,000 (±400) cal. reported by Parks, Todd and Shomate[5] for several other cases involving the dehydrogenation of paraffins to yield monosubstituted ethylenes.

[4] Stull, THIS JOURNAL, **59**, 2727 (1937).

[5] Parks, Todd and Shomate, *ibid.*, **58**, 2505 (1936).

[6] Giauque, *ibid.*, **52**, 4825 (1930).

DEPARTMENT OF CHEMISTRY
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RECEIVED APRIL 8, 1938

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## A Semi-Micro Sublimation Apparatus

BY C. M. MARBERG[1]

In the course of some work on the isolation and identification of lipoids undertaken in this Laboratory, it became necessary to submit certain fractions to high-vacuum sublimation. The theory, technique, and several designs of apparatus for this procedure are contained in an article by Hickman and Sandford.[2] The apparatus of Werner,[3] which utilizes a ground joint and a water-cooled condenser is useful only with minute quantities of material, which are condensed on a cover glass. When used with larger quantities of material, omitting the cover-glass, the sublimate may become contaminated with grease upon withdrawal of the condenser, due to accidentally touching the ground joint. Finally, when sealed to the high-vacuum line, it is necessary to break the apparatus loose after each time it is used. Carothers and Hill[4] devised a molecular still which overcame the possibility of contamination of the distillate with grease, by using a large, flat-ground joint. Their apparatus was improved by Strain and Allen[5] who simplified the heating arrangement, sealed the water-cooled condenser into the upper dome, and added a ground joint by means of which the apparatus could be attached to the high-vacuum line. Since we desired to cool our condenser below temperatures possible with water or circulating fluid, none of this apparatus, which utilizes water-cooled condensers, was suitable for our work.

The apparatus devised for our work,[6] shown in the accompanying diagram, has the advantages that (1) low temperatures may be used for the condensing surface, since the condenser may be cooled with carbon dioxide, liquid ammonia, or liquid air, (2) the ground joints, including the stopcock, are all interchangeable, and (3) the section carrying the stopcock can be sealed to the high-vacuum line (we use a mercury pump backed by a Cenco Hyvac) and may be left in place, since it does not come into contact with either the crude material or the sublimate.

A solution of the crude substance is placed in the unattached lower vessel, the design of which may be modified to suit the particular experiment and the solvent is evaporated on a water-bath or *in vacuo*, leaving the crude material in a ring in the bottom of the container. Then, after placing a light ring of grease along the upper edge of the

[1] The Otho S. A. Sprague Memorial Institute and the Department of Pathology, The University of Chicago.

[2] K. C. D. Hickman and C. R. Sandford, *J. Phys. Chem.*, **34**, 637 (1930).

[3] Othmar Werner, *Mikrochemie*, **1**, 33 (1923).

[4] W. H. Carothers and J. W. Hill, THIS JOURNAL, **54**, 1557 (1932).

[5] W. H. Strain and W. M. Allen, *Ind. Eng. Chem., Anal. Ed.*, **7**, 443 (1935).

[6] The Scientific Glass Apparatus Co., of Bloomfield, N. J., have satisfactorily made it for us.