The Heat of Formation of Boric Oxide

By B. J. Todd* and R. R. Miller

Bichowsky and Rossini[1] give for the heat of formation of boric oxide(gls) 279.9 kcal. per mole at 18° obtained from measurement of the heat of formation of boron trichloride(g) by Troost and Hautefeuille,[2] corrected according to Berthelot,[3] and from Berthelot's measurement of the heat of hydrolysis of boron trichloride(g).[3] Roth and Borger[4] give for the heat of formation of boric oxide(gls) 349 ± 3 kcal. per mole at 18° from data obtained by burning boron(s) in compressed oxygen, utilizing the heat of combustion of a known amount of paraffin oil to start the boron oxidation. We find the heat of formation of boric oxide under standard conditions to be 335.8 ± 0.8 kcal. per mole at 25°.

In this study, use was made of a Parr isothermal bomb calorimeter. The volume of the bomb empty was 350 ml. The water jacket surrounding the calorimeter was kept at 25.00 ± 0.01°. The temperature rise of the calorimeter was measured by means of a Beckmann thermometer calibrated at the Bureau of Standards. The heat transfer between jacket and calorimeter was calculated by Dickinson's[5] method, and the general procedure used for a calorimetric experiment was that specified in the A. S. T. M. Standard D-271-43 for coal. The calorimeter was calibrated by use of benzoic acid, standard sample No. 39f, according to the conditions described on its certificate from the Bureau of Standards. Six calibration experiments gave for the energy equivalent of the calorimeter 2413.0 ± 2.7 cal. per degree at a mean temperature of 25°, defining one calorie equal to 4.1833 international joules. Twelve blank calorimetric expts. gave for the energy correction used in firing the charge 22.0 ± 2.7 cal.

The spectroscopically pure boron used was prepared under the direction of Dr. H. I. Schlesinger at the University of Chicago by the thermal decomposition of diborane. A mixture of boron (approx. 0.1 g.) and benzoic acid (approx. 0.75 g.) was pelleted and burned in pure oxygen at an initial pressure of 40 atm. at 25°. A nickel–chromium crucible was used in Run I; a quartz crucible, in Run II. The weight of benzoic acid converted to carbon dioxide and to carbon was calculated from the initial weight of benzoic acid in the pellet and the weight of carbon dioxide formed in the combustion as determined by absorption with ascarite. The weight of boron oxidized was determined by titration with 0.1 *N* sodium hydroxide in the presence of mannitol under carbon dioxide-free conditions.

Calculation of ΔE for the reaction $2B(s) + 3/2O_2(g, 40\ atm.) = B_2O_3(gls)$ at 25° was based on the bomb reaction represented by the equations

(a) $C_6H_5COOH(s) + 15/2O_2(g, 40\ atm.) = 7CO_2(g) + 0.00045H_2O(g) + 2.99955H_2O(l)$ $\Delta E_a = -772.2$ kcal.

(b) $C_6H_5COOH(s) + 1/2O_2(g, 40\ atm.) = 7C(s) + 3H_2O(l)$ $\Delta E_b = -118.0$ kcal.

(c) $2B(s) + 3/2O_2(g, 40\ atm.) = B_2O_3(gls)$

(d) $B_2O_3(gls) + (3 + x)H_2O(l) = 2H_3BO_3$(satd. soln.) At 18°, according to Roth and Borger,[4] $\Delta E_d = -10.8$ kcal., if the boric oxide has been in contact with water for 15 min. This appears to be the least precise part of the calculations.

(e) Heat of ignition (electrical energy + combustion of 0.011 g. No. 38 B. and S. gage iron wire) equals 22 cal.

(f) Nitric acid formation was found to be negligible when the bomb was adequately flushed out with oxygen prior to filling.

The experimental results follow, where q_x refers to the heat evolved in reaction (x).

	Run I	Run II
G. $C_6H_5COOH \rightarrow CO_2 + H_2O$	0.7804	0.7394
G. $C_6H_5COOH \rightarrow C + H_2O$	.0000	.0050
G. B reacted	$.0413_2$	$.0494_4$
G. B_2O_3 formed	$.133_0$	$.159_1$
Total kcal. evolved	5.617	5.489
q_a	4.934	4.675
q_b	0.000	0.005
q_d	.020	.024
q_e	.022	.022
q_c	.641	.763
ΔE_c	$-335._6$	$-334._0$

Mean $\Delta E_c = -334._8$

For the reaction

(g) $3/2O_2(g, 25°, 40\ atm.) = 3/2O_2(g. 25°$, unit fugacity) $\Delta E_g = 0.09$ kcal.[6] Combining (c) and (g) gives

(h) $2B(s) + 3/2O_2(g, 25°$, unit fugacity) $= B_2O_3(gls)$ $\Delta E_h = -334._9$ kcal.

To change to ΔH for this reaction, use is made of

$$\Delta H = \Delta E + RT\Delta n$$

Then for (h), $\Delta H = -335._8 \pm 0.8$ kcal.

The correction to convert ΔH_h at 25° to ΔH_h at 18° is negligible compared with the experimental error.

Naval Research Laboratory
Office of Research and Inventions
Washington 20, D. C.

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* Present address: Corning Glass Works, Corning, N. Y.

[1] Bichowsky and Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936.

[2] Troost and Hautefeuille, *Ann. chim. phys.*, [5] **9**, 70–77 (1876); *Compt. rend.*, **70**, 252–255 (1870).

[3] Berthelot, *Ann. chim. phys.*, [5] **15**, 185–220 (1878); "Thermochimie," Gauthier-Villars, Paris, 1897.

[4] Roth and Borger, *Ber.*, **70B**, 48–54 (1937).

[5] Dickinson, *Bull. of Bur. of Standards*, **11**, 189 (1915).

(6) Rossini and Frandsen, *J. Research Natl. Bur. Standards*, **9**, 733 (1932).

Effect of Hydrocarbon Bacteria on Racemic Mixtures of Hydrocarbons

By John Turkevich and Lejaren Arthur Hiller, Jr.

In a previous communication[1] was described the isolation and study of a *Bacterium aliphaticum.* This organism will metabolize in simple inorganic media numerous aliphatic hydrocarbons from pentane to paraffin oil. The washed cells will also oxidize glucose and other sugars, as well as the hydrocarbons, through a cyanide-sensitive respiratory system. There is no evidence of an anaerobic metabolism. It is the purpose of this investigation to determine whether *Bacterium*

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(1) F. H. Johnson, W. T. Goodale and J. Turkevich, *J. Cellular Comp. Physiol.*, **19**, 163–172 (1942).

aliphaticum will preferentially attack the *d* or *l* form of a racemic hydrocarbon mixture.

Materials and Methods

The original pure culture of *Bacterium aliphaticum* was isolated with the aid of petroleum ether enrichment from the soil obtained at the base of a gasolene pump on a farm. The culture used in this investigation was obtained from a stock culture maintained on Söhngen's inorganic medium (0.05% ammonium chloride, 0.05% potassium hydrogen phosphate, a trace of calcium chloride) and on 5% petroleum ether (maximum boiling point 120°).

One of the hydrocarbons used was 3-methylheptane obtained from the American Petroleum Institute Ohio State University Manifest P-61 and was characterized by $n^{20}\text{D}$ 1.3998. The other hydrocarbon, 3-methylhexane, was obtained through the courtesy of Dr. J. O. Smith of the Research Laboratory of the Tidewater Associates Company. It was characterized by $n^{20}\text{D}$ 1.3884. Both of these hydrocarbons showed no rotation.

The optical activity was determined on a Franz Schmidt Research Polarimeter whose accuracy was +0.01°. A two-decimeter semi-micro polarimeter tube was used.

Two hundred milliliters of the nutrient solution and ten milliliters of the substrate hydrocarbon were placed in an 8-oz. prescription bottle and the thickness of the hydrocarbon layer was measured to a thirty-second of an inch. This mixture was then inoculated by means of a platinum loop with a stock culture growing on petroleum ether. All standard precautions were observed to prevent contamination. The prescription bottles were closed with screw caps and allowed to stand at room temperatures. Two or three days after inoculation a cloudiness appeared and this became more and more dense with time indicating ready metabolism of the hydrocarbons. A blank showed no growth. After three weeks the level of the hydrocarbon dropped to half its original value and the cultures were treated as follows: The hydrocarbon layer was separated from the aqueous layer by means of a separatory funnel and dried over anhydrous calcium chloride. The optical activity was found to be zero in the case of either of the two hydrocarbons. Another portion of the hydrocarbon layer was washed six times with concentrated sulfuric acid and subsequently six times with saturated magnesium sulfate solution. It was then twice washed with distilled water and dried over anhydrous magnesium sulfate. The optical activity was again found to be zero in both cases. The aqueous layer was centrifuged to precipitate the bacterial suspension, and the supernatant liquid was measured in the polarimeter. The optical activity was again zero in both cases. After these measurements the hydrocarbons were again used as substrate for the growth of *bacterium aliphaticum*. After three weeks the same procedure as above was used on the residual hydrocarbon which represented one-third of the volume of the original sample. The optical activity in both cases, that of 3-methylhexane and 3-methylheptane, was again zero.

Discussion.—It has been abundantly established since Pasteur's discovery that certain organisms especially molds, yeasts and bacteria metabolize preferentially one of the two optical antipodes of a racemic mixture.[2]

The results of the present investigation show that the *bacterium aliphaticum* does not attack preferentially one of the two optical isomers of 3-methylhexane and of 3-methylheptane. P. A. Levene and R. E. Marker[3] report an observed rotation of $[\alpha]_D$ +1.64° and a maximum rotation of $[\alpha]_D$ 9.67° for 3-methylhexane while we observe less than 0.01°. It, therefore, follows that if there is a preferential action in the rate of attack of the *bacterium aliphaticum* it is less than one part in two thousand. This result is not surprising in view of the variety of substrates that this organism can metabolize, *e. g.*, aliphatic hydrocarbons and sugars. It is further consistent with the results of F. H. Johnson and H. W. Schwarz[4] who found that this bacterium metabolized both *d* and *l* arabinose though no attempt was made to determine whether the rate of metabolism was the same.

It is, however, unfortunate that there is no preferential action on optical antipodes, for if there were, it would offer a method of obtaining a wide variety of optically active hydrocarbons for the study of the mechanism of hydrocarbon reactions.

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[2] *Cf.* H. Scheibler in J. Houben's "Die Methoden der organischen Chemie," Vol. 2, Part 2, Leipzig, 1925, p. 1087; R. L. Shriner, R. Adams and C. S. Marvel in Gilman's "Organic Chemistry," **1**, 263 (1943).

[3] Levene and Marker, *J. Biol. Chem.*, **95**, 13 (1932).

[4] F. H. Johnson and H. W. Schwarz, *J. Bact.*, **47**, 373 (1944).

FRICK CHEMICAL LABORATORY
PRINCETON UNIVERSITY
PRINCETON, N. J.

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Addition of Secondary Amines to Dibromopropanol

BY FRANK C. WHITMORE, HARRY S. MOSHER, DAVID P. SPALDING, ROBERT B. TAYLOR, GEORGE W. MOERSCH AND WILLIAM H. YANKO

We reported[1] that 2,3-dibromopropanol (I) reacts with secondary amines such as piperidine, diethylamine or morpholine to give the metathetical product (II).

$$\underset{\text{(I)}}{\text{HOCH}_2\text{CHBrCH}_2\text{Br}} + \text{HNR}_2 \longrightarrow \underset{\text{(II)}}{\text{HOCH}_2\text{CH(NR}_2\text{)CH}_2\text{NR}_2}$$

On the suggestion of Dr. P. H. Williams, of the Shell Development Company, Emeryville, California, we have re-investigated these products, and have found in at least one case, *i. e.*, piperidine, that the symmetrical compound

$$\text{R}_2\text{NCH}_2\text{CHOHCH}_2\text{NR}_2 \quad \text{(III)}$$

is formed as well.

Thus, when piperidine was treated with 2,3-dibromopropanol and the product distilled from a Claisen flask, the first portion of the amine fraction gave a picrate, m. p. 190–191°, which showed no depression of the melting point when mixed with the picrate from the reaction product of piperidine and epichlorohydrin. This must be the symmetrical 1,3-dipiperidino-2-hydroxypropane (III). The last fraction from the distillation gave a picrate melting at 174–175° and showed the same melting point when mixed with the picrate from the product of the Bouveault–Blanc reduction of ethyl 2,3-dipiperidionpropionate. This must be the picrate of the metathetical reaction product, 2,3-dipiperidino-

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[1] Whitmore, *et al.*, THIS JOURNAL, **67**, 664 (1945).