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

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

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

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

(d) $B_2O_3(gls) + (3 + x)H_2O(l) = 2H_3BO_3(\text{satd. soln.})$ 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) $3/2O_2(g, 25°, 40\text{ atm.}) = 3/2O_2(g. 25°, \text{unit fugacity})$ $\Delta E_g = 0.09$ kcal.[6] Combining (c) and (g) gives

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

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(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

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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).