potential of the positive iodine wave. Perusal of the half-wave potentials in Tables III and IV does not show any clear pattern. It is concluded that the half-wave potential is not grossly affected by the base strength of the amine with the series pyridine, 2-picoline, 2,6-lutidine. Rather the voltammetric behavior is influenced to a greater extent by the configuration of the amine.

Voltammetry of Dipyridine Iodine (I) Perchlorate.—It is difficult to interpret the observed voltammetric behavior of dipyridine iodine (I) perchlorate because the limiting currents are substantially smaller than would be expected. From the current constant for the over-all reaction, $I^- - e^- \rightarrow {}^1/_2\, I_2$, −4.91 μa. liter/mmole, one would estimate an over-all current constant of 9 to 10 μa. liter/mmole for the reaction[35]

$$[I(py)_2]^+ + 2e^- \longrightarrow I^- + 2\ py$$

The current constant for wave A is only 1.22 μa. liter/mmole. This low current constant can only be partly accounted for by a decreased diffusion coefficient. Cases of similar abnormally small current constants were found in the interhalogen and mixed polyhalide ion reduction.[19] No satisfactory explanation has been found.

The following electrode reactions are tentatively proposed to explain the current–voltage curve observed for dipyridine iodine (I) perchlorate.

$$\text{wave A}\quad 6I(py)_2^+ + 6e^- \longrightarrow 3I_2{\cdot}py_2$$
$$\text{wave B}\quad 3I_2{\cdot}py_2 + 2e^- \longrightarrow 2I_3^- + 2py$$
$$\text{wave C}\quad 2I_3^- + 2py + 4e^- \longrightarrow 6I^- + 2py$$

In view of the abnormally low current constant of wave A, the current constant for wave B, 0.7 μa. liter/mmole, seems qualitatively satisfactory for the reduction of iodine to triiodide ion (the observed current constant for the reduction of iodine to triiodide ion is 2.11 μa. liter/mmole).

It has not been possible to establish definitely the nature of the electrode reactions taking place in the electrochemical reduction of dipyridine iodine (I). The electrode reaction tentatively suggested for wave A probably involves an appreciable overvoltage because its half-wave potential is even slightly more negative than that for the reduction of iodine to triiodide ion. It would seem reasonable to suppose that it would require less energy to reduce an electronegative group like $[I(py)_2]^+$ than to reduce molecular iodine. This irreversibility is also found in the electrode reactions postulated for wave B and peak C.

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[35] The dependence of limiting current observed at a RPE on the diffusion coefficient ranges from 0.5 to 1.0 ($i_1 = kD^{0.5-1.0}$). From the limiting ionic conductances of the dipyridine iodine (I) ion and the iodide ion, 75 and 102.8, respectively, it is evident that even a direct proportionality between limiting current and diffusion coefficient gives a ratio of only 0.74 between the current constant for the iodide ion to iodine oxidation and the reduction of dipyridine iodine (I) to iodine.

[Contribution from the Department of Chemistry, Cornell University]

The Heat of Formation of Boric Oxide[1]

By Bernard H. Eckstein[2] and Ervin R. Van Artsdalen[2]

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The heat of formation of amorphous B_2O_3 is 304.6 kcal./mole as determined by burning crystalline boron in oxygen without the use of any organic initiator. This agrees well with the value of 302 kcal./mole found by Prosen using the decomposition of diborane as the experimental route.

Introduction

This paper describes the determination of the heat of formation of largely amorphous boric oxide by the direct union of elementary crystalline boron and oxygen without the use of any organic initiator. The heat of formation is defined as the enthalpy change for this reaction

$$2B(\text{cryst}) + 3/2\ O_2(g) = B_2O_3(\text{amorph})$$

The earlier determinations of this heat of formation are summarized in Table I. Note the wide divergence in the results obtained whenever organic initiators were used. The agreement between the 304.6 kcal./mole found in this study, using the most direct method of determining heats of formation, and the very careful work by Prosen, *et al.*, makes it seem very likely that the heat of formation of B_2O_3 is indeed *ca.* 302 kcal./mole.

Description of Apparatus

The actual combustions were carried out in a double valve type, self-sealing Parr Oxygen Bomb of 330-ml. capacity, made of Illium steel. This bomb was immersed in about 2600 g. of distilled water, weighed to 0.1 g., in a calorimeter consisting of three concentric cylindrical cans, all chrome plated and highly polished. There were an outer and an inner can and an interspersed aluminum radiation guard. All three elements were fastened at the top to a "Lucite"[12] ring. The bomb in the inner can was completely submerged but did not touch bottom, so that water could circulate freely about the bomb. The cover for the assembly consisted of a chrome-plated brass disc as the lower face, a monel metal plate as the upper face and a one inch block of "Lucite" as insulating material in between. The cover was pierced to permit access for the various leads to the bomb, the resistance thermometer, and a platinum resistance thermometer for calibration purposes. The pump type stirrer consisted of a shaft with four four-bladed propellers. The stirrer shaft was made in two sections joined by a section of "Lucite" to minimize heat losses. The pump housing served as support for a four-lead copper resistance thermometer. Because the calorimeter was completely submerged in a constant temperature bath a superstructure

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[1] The work here reported was carried out at the Department of Chemistry, Cornell University, during 1948 and 1949. It forms part of a Ph.D. thesis submitted to Cornell in February, 1953, by B. H. Eckstein.

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TABLE I

SUMMARY OF THE OLD VALUES OF THE HEAT OF FORMATION OF BORIC OXIDE

Investigator	Date	Heat, kcal./mole	Ref.	Method
Troost, *et al.*	1876	317.2	3	Involves heats of formation and hydrolysis of BCl_3 and heats of soln. of B_2O_3 and H_3BO_3
Berthelot	1878	279.9	4	Recalculation of 3
Roth and Boerger	1937	349 ± 3	5	Paraffin oil initiator for combustion
Robertson	1943	368	6	Cotton thread and naphthalene initiator, crude calorimeter, small samples
Todd and Miller	1945	335.8 ± 0.8	7	Mixed pellet with benzoic acid, using C_6H_5COOH:B ratio of 8:1
Eggersgluess, *et al.*	1948	281.1 ± 3.1	8	Lampblack initiator. Value revised informally to 300 kcal.[9]
Katz	1948	270 (minimum)	10	Separate pellets of about equal weight of B and C_6H_5COOH, former resting on latter
Prosen, *et al.*	1948	297.6 (cryst.) 302.0 (amorph.)	11	Decomposition of diborane in flow calorimeter

was mounted on the cover to keep out bath water, protect the leads, etc.

The entire calorimeter was suspended and submerged in a 40-liter water-bath maintained at 25.000 ± 0.002° with the use of a cooling coil, two heaters and a thermo-regulator activating a thyratron thermostatic control.

The resistance of the thermometer was measured on a Mueller bridge; a Leeds and Northrup No. 2285b, Type H-S galvanometer was used with an illuminated scale mounted on the opposite wall of the laboratory; the scale was read with a telescope. Since the bridge could be read to 5×10^{-5} ohm, and since 0.35 ohm corresponds to about 1°, the temperature intervals could be measured to better than 0.0002°.

The samples of benzoic acid and of boron were weighed on a sensitive analytical balance and the weights corrected to vacuum. Time readings were taken by using a component of a war surplus radar set, in which a tape was pulled past a pen which made a mark on the paper tape every second. The times of firing, taking readings, etc., could be recorded by sending in a signal with an ordinary telegraph key. By interpolating between the "second pips" the time of any given signal could be read accurately to 0.02 second.

Preparation of Reagents

Benzoic Acid.—Benzoic acid from National Bureau of Standards sample 39f was dried as needed in a 105° oven and stored in a desiccator until actually used.

Oxygen.—Commercial oxygen, claimed 99.5% pure, was used. Tests showed that no detectable amounts of oxides of nitrogen were formed, and passage of the oxygen over anhydrous copper sulfate failed to indicate the presence of appreciable amounts of water vapor.

Boron.—Boron was furnished by the Norton Company Research Laboratory at Niagara Falls, Ontario, through the kindness of Dr. Alexander Findlay. The method of preparing the element was not made known, but the Norton Company's analysis of the sample indicated that it consisted of at least 96.2% boron, 1.86% carbon, 0.72% boric oxide and 0.13% iron. The missing 1.1% was believed to be silicon and oxygen. The elements, except boron, were probably all present as compounds. An X-ray powder photograph showed the series of lines characteristic of a crystalline material.

The boron probably was purer than this analysis would indicate. Using standard tests no iron was detected. Chlorination studies showed no detectable amounts of B_2O_3. In a typical chlorination experiment 0.13 g. of boron was heated in a tube furnace under chlorine for over five hours at from 424 to 756°. There was a small visible residue in the combustion boat, but the amount was too small to be weighed on an analytical balance, that is, less than 0.1 mg.

Analytical Reagents.—Hydrochloric acid and sodium hydroxide to be used in the analysis for boric oxide were prepared according to standard analytical methods. The base, freed from carbonate, was standardized against "primary standard" potassium acid phthalate.

Procedure

Boron can be burned directly in oxygen by using very finely powdered boron and distributing it over a relatively large surface to allow free access of the oxygen. This differs from the general practice in which the material to be burned is formed into a compacted pellet. An oxygen pressure of 40 atmospheres was used. The sample was ignited by an iron fuse wire submerged in the form of a small spiral in the boron. In each run about 25 to 30% of the boron was burned, the exact amount being determined by analyzing for boric acid afterwards and checking by carefully weighing the initial amounts of boron and the boron residue. The initial boron sample usually weighed about 1 gram. Microscopic examination showed no evidence of the formation of any iron–boron compounds.

Investigators using initiators also burned no more than $^1/_4$ to $^1/_3$ of the boron sample. Some of the boric oxide sublimed off onto the walls, but the bulk of it formed a glass which coated the elemental boron, thus stopping the access of oxygen and the combustion. This glass was only slowly soluble but could be extracted by heating the residue in water at 50° for about 10 hours. In a separate test no detectable amount of boron was converted into boric oxide after being boiled in water for two days. The selection of a combustion vessel posed a problem because of the great reactivity of boron and boric oxide at high temperatures. Ultimately a crucible lid of pure fused Alundum was used. The vessel broke during the combustion, but the maximum error introduced in using a series of different lids (weighing 4.3 ± 0.3 g. each) is about 0.1 cal.

Analytical Procedure.—The standard method for determining boric oxide, involving 10% mannitol solution, was modified somewhat by Katz[9] to include the addition of solid mannitol when approaching the end-point of the titrations, and this method was used.

The extraction and analysis were carried out in boron-free glassware, and a small correction was derived from carrying out the procedure on blanks of distilled water.

Experimental Results

The calorimeter was calibrated with standard benzoic acid from the National Bureau of Standards, using the NBS calibration conditions. Small

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(3) L. Troost and P. Hautefeuille, *Ann. chim. phys.*, [5] **9**, 70 (1876).

(4) M. Berthelot, *ibid.*, **15**, 185 (1878).

(5) W. A. Roth and E. Boerger, *Ber.*, **70B**, 48 (1937).

(6) J. A. Robertson, "Heat of Combustion and Heat Capacity of Boron," Thesis, Cornell University, 1943.

(7) B. J. Todd and R. R. Miller, THIS JOURNAL, **68**, 530 (1946).

(8) W. Eggersgluess, A. G. Monroe and W. G. Parker, *Trans. Faraday Society*, **45**, 661 (1949).

(9) Personal communication, Parker to Van Artsdalen, at the 1951 ACS meeting in Cleveland, Ohio.

(10) C. Katz, "The Heat of Combustion of Boron," Thesis, Cornell University, 1949.

(11) E. J. Prosen, W. H. Johnson and F. A. Yenchius, National Bureau of Standards Technical Report on Project NA-onr-8-47 (1948).

(12) Trademark for du Pont acrylic resin.

corrections were then applied to allow for the increased amount of oxygen and the different heat capacities of the combustion vessel, leading to a water equivalent of the calorimeter of $593.3_8 \pm 0.3_8$ g. The procedure used in the combustions was to submerge the sealed calorimeter containing the bomb and about 2600 g. of water, the calorimeter contents being at about 23.7°. After submersion in the 25° thermostat for at least an hour before every run the calorimeter temperature was about 24° and the rate of temperature rise had been constant for at least 10 minutes. Then the charge was fired. The temperature readings were taken by presetting the bridge to a certain value and recording the time at which the temperature of the calorimeter passed this value by means of sharp peaks on the time tape. Readings were taken until the peak of the temperature was passed, and for about 10 minutes thereafter. The actual time–temperature curve was corrected for the various losses and lags to arrive at the "instantaneous" temperature rise by the method of White[13] and Dickinson.[14] However, following the Bureau of Standards practice, the time at which 60% of the observed temperature rise had taken place was chosen as the time to which the initial and final slopes were extrapolated. Corrections were applied for the heat of combustion of the iron fuse wires. The results obtained are shown in Table II. The average heat of formation is 304.6 ± 4.2 kcal./mole, which agrees well with the most recent value obtained by the National Bureau of Standards.[11] X-Ray diagrams showed the B_2O_3 to be non-crystalline.

TABLE II

HEAT OF FORMATION OF BORIC OXIDE

Original wt. of B., g.	Wt. of B burned, g.	% of B burned	Millimoles of B_2O_3 formed	T. rise, °C.	Mean T., °C.	Heat of formation, kcal./mole of B_2O_3 formed
0.59825	0.15585	26.05	7.202	0.6884	25.00	302.8
0.95835	.27602	28.80	12.755	1.2046	24.35	300.0
1.10820	.29197	26.35	13.492	1.3076	24.50	310.9

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[13] W. P. White, "The Modern Calorimeter," Chemical Catalog Company, New York, N. Y., 1928.

[14] H. C. Dickinson, *Sci. Papers Bur. Standards*, **11**, 189 (1914).