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ARL TECHNICAL REPORT 60-276

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THE PROPERTIES OF BORON COMPOUNDS

Compiled by
Estal D. West

National Bureau of Standards

MAY 1960

AERONAUTICAL RESEARCH LABORATORIES
AIR FORCE RESEARCH DIVISION

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AERONAUTICAL RESEARCH LABORATORIES
AIR FORCE RESEARCH DIVISION
AIR FORCE RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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FOREWORD

This report describes work done at the National Bureau of Standards, Washington, D. C., under Contract AF 33(616)-58-17, Task 70321 "Research in Boron Chemistry", Project 3048 "Aviation Fuels".

The Air Force scientist responsible for this Task is Karl Scheller of the Chemistry Research Laboratory, Aeronautical Research Laboratories, Air Force Research Division.

ABSTRACT

Three crystalline forms of metaboric acid exist: HBO_2(C,I), HBO_2(C,II), and HBO_2(C,III). Methods of preparing and identifying these three crystals and crystals of orthoboric acid H_3BO_3 are described. The heats of formation of the three forms of metaboric acid relative to that of orthoboric acid have been determined by measuring heats of solution of each of the four crystals in water and in sodium hydroxide solution. Taking the heat of formation of orthoboric acid as $\Delta Hf^\circ(25^\circ C) = -262.16 \pm 0.32$ kcal/mole, the heats of formation of the various forms of metaboric acid were found to be:

HBO_2(C,I), $\Delta Hf(25^\circ C) = -192.56 \pm 0.40$ kcal/mole

HBO_2(C,II), $\Delta Hf(25^\circ C) = -190.6 \pm 0.5$ kcal/mole

HBO_2(C,III), $\Delta Hf(25^\circ C) = -190.0 \pm 1.0$ kcal/mole

The value for HBO_2(C,III) may be somewhat high since it is felt that some orthoboric acid impurity was present in the sample. Further experiments are planned on HBO_2(C,II) and HBO_2(C,III).

Decomposition pressure measurements were made on the system $H_3BO_3(C) = H_2O(g) + HBO_2$(C,I), where the metaboric acid HBO_2 was in the form of HBO_2(C,I), HBO_2(C,II), or HBO_2(C,III). The results on crystals II and III confirm the data obtained by previous investigators. No previous data existed on crystal I, the most stable form of metaboric acid. From these measurements, heats of formation, free energies of formation, and entropies are derived.

The present status is reported of the compilation of thermodynamic properties of boron compounds, the measurement of the heat capacity of boric oxide, and the high temperature oscillating cup viscometer.

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I. Heats of Formation of the Metaboric Acids

by

Marthada V. Kilday and Edward J. Prosen

Introduction

Three crystalline forms of metaboric acid exist: HBO_2 (C, I), HBO_2 (C, II), and HBO_2 (C, III). Methods of preparing and identifying these three crystals and crystals of orthoboric acid H_3BO_3 are described. The heats of formation of the three forms of metaboric acid relative to that of orthoboric acid have been determined by measuring heats of solution of each of the four crystals in water and in sodium hydroxide solution. Taking the heat of formation of orthoboric acid as $\Delta Hf^\circ(25^\circ C) = -262.16 \pm 0.32$ kcal/mole, the heats of formation of the various forms of metaboric acid were found to be:

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The value for HBO_2 (C, III) may be somewhat high since it is felt that some orthoboric acid impurity was present in the sample. Further experiments are planned on HBO_2 (C,II) and HBO_2 (C,III).

Preparation of Samples

The methods of preparation of samples described here were developed by consideration of the experiences described by F. C. Kracek, G. W. Morey, and H. E. Merwin, Am. J. Sci. 35A, 143 (1938) and by H. Tazaki, J. Sci. Hiroshima Univ. 10, 37, 55, 63, 109, 113 (1939), and by other thermodynamic and mechanism considerations developed in the study of the decomposition pressures of boric acid.

H_3BO_3 (C). Orthoboric acid, analytical grade reagent, was recrystallized three times from aqueous solution and air-dried at room temperature. It was stored in a desiccator containing a saturated solution of calcium bromide which maintains a relative humidity of about 20 percent at room temperature. This orthoboric acid was used as starting material for the preparation of the metaboric acids.

HBO_2 (C,III). The orthorhombic form of metaboric acid was obtained by dehydration of orthoboric acid in flat, open dishes at 65°C. The samples were weighed every 2 or 3 days and reached the theoretical weight of metaboric acid in about 3 weeks. The theoretical weight was not an exact check on the thoroughness of dehydration since orthoboric acid volatilizes to an appreciable extent even at 65°C. The sample was stored in a glass-stoppered bottle over magnesium perchlorate drying agent.

HBO_2 (C,II). The monoclinic form of metaboric acid was prepared by dehydration of wet orthoboric acid in glass-stoppered bottles at 120°C. The glass-stoppers impeded the escape of water vapor. The formation of (C,II) was apparent from the form of globules or tree-like structures. Generally 3 or 4 weeks was required for complete dehydration of the orthoboric acid to metaboric acid (C, II). Extended heating beyond this time was undesirable because greater contamination with crystal I developed. These samples were also stored in glass-stoppered bottles over magnesium perchlorate.

HBO_2 (C,I). The most stable form of metaboric acid, crystal I, was obtained by two methods. The first method was the dehydration of air-dried orthoboric acid in glass-stoppered bottles at 120° to 130°C for 4 or 5 weeks. Most of the crystals were approximately 1 mm in "diameter". The disadvantage of this method is that sometimes crystal II forms and other times crystal I forms, depending apparently on the fit of the stopper and upon the development of a seed of crystal I. A second method was also used which is more certain to produce crystal I but usually smaller crystals, less than 0.5 mm "diameter", were formed. However, our largest crystal thus far (approximately 3 mm "diameter") was formed by this method. In this method 5 g of air-dried H_3BO_3(C), 15 g of HBO_2 (C,III), and a few seed crystals of HBO_2 (C,I) were sealed, after brief evacuation, in 100 ml glass ampoules. These were put in an oven at 180°C. Sometimes the melt developed "cloudiness", indicating crystal formation in a day or two, but other times a week was required before crystal formation was obvious. Three to six weeks was allowed to permit aggregation, but extended heating was no guarantee of large crystal formation. Our largest crystal was obtained in only 3 weeks, while other ampoules contained no crystals larger than 0.5 mm after 6 weeks. The ampoules were cooled and broken open and the crystal I obtained by washing away the orthoboric acid and metaboric acid crystals II and III (if present) with water. The final samples were stored in glass stoppered bottles over magnesium perchlorate.

Identification, Purification, and Analysis

The methods of preparing H_3BO_3(C) and HBO_2(C,III) yielded products pure enough for use without further processing.

The HBO_2(C,I) product was, in both methods, contaminated with crystal III and crystal II both of which are much more soluble in water than crystal I. After the crude washing with water, the sample was allowed to stand in methanol for several hours with frequent stirring. Each sample was washed in methanol several times. Methanol was used in these washings instead of water because it evaporated more readily when drying the crystals and it did not show any evidence of etching the crystal surfaces upon long exposure as did water.

The HBO_2(C,II) product contained some crystal I, and crystal III, and some H_3BO_3(C). The crystal III and H_3BO_3(C) were removed by washing with carbon tetrachloride (water-free spectroscopic grade) in which crystal II is only very slightly soluble. Some of the crystal I was removed by flotation in ethylene bromide. The crystal II floated and crystal I sank (see densities below). This did not remove all of crystal I due to air bubble effects and also to occlusion of crystal I by crystal II. Later results indicate that perhaps 5 percent crystal I remained in the crystal II.

The following table lists liquids which were found convenient for quick identification of the crystal forms by flotation:

TABLE I

Substance	Density g/cc
H_3BO_3 (C)	1.44
Carbon Tetrachloride	1.60
HBO_2 (C,III)	1.78
Ethyl Iodide	1.92
HBO_2 (C,II)	2.04
Ethylene Bromide	2.17
HBO_2 (C,I)	2.49

In addition to the above liquids, solutions of methylene iodide and toluene were also used as flotation liquids for further identification. The purified products were also identified by X-ray diffraction, refractive index, and densities by use of a pycnometer.

Quantitative analyses of the products were performed on weighed samples by solution in water and titration with sodium hydroxide in the presence of mannitol using a pH meter. In all cases the results indicated 99.5 percent of theoretical or better. This, of course, could not distinguish between crystal forms. X-ray analysis indicated only that the product was predominantly the nominal form within possibly 5 percent. We feel that the method of preparation and processing of the samples is reasonable assurance of high purity with respect to crystal form, except in the cases of HBO_2 (C,II) and HBO_2 (C,III).

An indication of the extent of crystal I contamination in HBO_2 (C,II) was found by analysis of the final calorimetric solutions when the samples were dissolved in water at 25°C. Under these conditions very little crystal I dissolves, so the solutions were filtered and the solid residue dissolved by boiling in water, then titrated. In four experiments 4.66, 6.14, 5.65 and 6.49 percent of crystal I contaminant were found. The final calorimetric results were corrected for these amounts of impurity. In the case of the solution experiments in sodium hydroxide smaller amounts of crystal I residue were found. In correcting the results of these experiments it was assumed that the samples originally contained an average of 6 percent of crystal I and that the part of this not found in the residue had dissolved and contributed to the heat of solution.

In the case of HBO_2 (C,III) the results of the calorimetric experiments indicated a trend and it is felt that not enough attention was paid to excluding moisture from the samples during the filling of the calorimetric bulbs. Crystal III absorbs water readily if the partial pressure of water is above the decomposition pressure of the system H_3BO_3 (C) = HBO_2(C,III) + H_2O(g). The results therefore presented here are perhaps in error due to contamination with H_3BO_3(C). No suitable correction can be made at this time. It is planned to run further experiments on both crystal II and crystal III.

Calorimetric Experiments

The solution calorimeter used was a glass, vacuum-jacketed vessel of 500 ml capacity submerged in a constant-temperature water bath. The calorimeter was equipped with a glass stirrer, a sample holder with a rod for crushing the glass bulb containing the sample, a platinum thermometer, and an electrical heater. The system was calibrated by measuring the electrical energy used in producing a given temperature rise in the system.

Conditions had to be found in which $HBO_2(C,I)$, the most difficultly soluble sample, would dissolve in reasonable time in the calorimeter. It was found that if crystal I was crushed to pass a #200 standard sieve, the sample would dissolve in 2N sodium hydroxide at 40°C in a period of 20 or 30 minutes. These are harsh conditions but after more than 25 such experiments, no etching of any of the glass surfaces is visible. We have now completed 5 or 6 experiments in each of 10 series of experiments. Four series (H_3BO_3, HBO_2 crystal I, II, III) were run in 2N NaOH at 40°C. Three series (H_3BO_3, HBO_2 crystal II, III) were run in 2N NaOH at 25°C. Three series (H_3BO_3, HBO_2 crystal II, III) were run in water at 25°C.

For $HBO_2(C,I)$, samples of 0.3 to 0.5 g were placed in weighed spherical glass ampoules, heated to 100°C for about 1/2 hour to drive off adsorbed moisture, cooled in a desiccator, then sealed off under vacuum, and weighed.

Ampoules of $HBO_2(C,II)$ were filled in a dry box, sealed under vacuum, and weighed.

Ampoules of $HBO_2(C,III)$ were filled in air (a dry box will be used on later experiments since these samples apparently were partially contaminated by water forming some $H_3BO_3(C)$), heated for about an hour at 90°C (this, later experience showed, was insufficient to drive off any appreciable amount of water picked up), cooled in a desiccator, sealed off under vacuum and weighed.

Ampoules of 0.5 to 18 g orthoboric acid were filled in air, sealed off under vacuum, and weighed.

The results of the calorimetric experiments are given in the table below listing ΔH at the temperature of reaction (40°C or 25°C) in kcal/mole.

TABLE II

Heats of Reaction

Solvent / Sample	2N NaOH at 40°C	2N NaOH at 25°C	Water at 25°C
	kcal/mole	kcal/mole	kcal/mole
HBO_2 (C,I)	-6.558 ±0.010	---	---
HBO_2 (C,II)	-8.51 ±0.04	-8.81 ±0.06	+1.66 ±0.03
HBO_3 (C,III)	-8.85 ±0.14	-9.16 ±0.10	+0.99 ±0.08
H_3BO_3 (C)	-5.129 ±0.003	-5.60 ±0.03	+5.27 ±0.05

As a first approximation we can assume that the final solutions obtained with the metaboric acids are the same as that obtained with orthoboric acid. Taking the heat of formation of orthoboric acid as ΔHf° (25°C) = -262.16 ±0.32 kcal/mole and the heat of formation of water as ΔHf° (25°C) = -68.317 ±0.010 kcal/mole, the heats of formation of the metaboric acids derived from the corresponding experiments given in the previous table are given below. The values taken at 40°C were corrected to 25°C by applying correction of -0.15 kcal/mole to the heats of formation.

TABLE III
Heats of Formation

Solvent / Sample	2N NaOH at 40°C	2N NaOH at 25°C	Water at 25°C
	kcal/mole (corrected to 25°C)	kcal/mole	kcal/mole
HBO_2 (C,I)	-192.56	---	---
HBO_2 (C,II)	-190.61	-190.63	-190.23
HBO_2 (C,III)	-190.27	-190.28	-189.56

Since these data are preliminary, no correction is applied for the fact that in the sodium hydroxide experiments the extra mole of water in the case of orthoboric acid ends up in a strong alkaline solution rather than in pure water. This correction is small and would lie well within the estimated uncertainties of the heats of formation obtained at this stage.

From the above data the heats of formation of the metaboric acids (Based on orthoboric acid, ΔHf = -262.16 ±0.32 kcal/mole) are taken as:

	ΔHf (25°C) kcal/mole
HBO_2 (C,I)	-192.56 ±0.40
HBO_2 (C,II)	-190.6 ±0.5
HBO_2 (C,III)	-190.0 ±1.0

The uncertainties are estimates and they include the uncertainty of ±0.32 kcal/mole in the heat of formation of orthoboric acid. The value for HBO_2 (C,I) is considered reliable since we feel the sample was sufficiently pure. The sample of HBO_2 (C,II) contained some crystal I but this effect has been corrected for, at least approximately. The value for HBO_2 (C,III) must be considered as only an approximate value since it is felt that the sample contained some orthoboric acid which would make the value too high and for which no correction was made. Thus this value could perhaps be 1.0 kcal too high. That is, the heat of formation may be -189.0 kcal rather than -190.0 kcal. Further experiments are planned on crystal II and III. Also an attempt will be made to find out why the values obtained in water solution are lower than the values obtained in sodium hydroxide solution.

Previous investigators have measured the heats of solution of metaboric acid. However, these were done before Kracek, Morey, and Merwin (Am. J. Sci. 35A, 143 (1938)) showed that there were three crystalline forms, hence it is not clear which forms the previous measurements refer to. M. von Stackelberg, F. Quatram, and J. Dressel, Z. elektrochem. 43, 14 (1937) measured the heat of solution of a metaboric acid and orthoboric acid in water. Their results give $\Delta Hf = -189.1$ kcal/mole for the metaboric acid. Presumably this was crystal III. W. A. Roth, E. Börger, an d A. Bertram Ber. 70B, 48, 971 (1937), Z. Naturforsch, 1, 574 (1946), measured the heat of solution of a metaboric acid and orthoboric acid in sodium hydroxide solution. Their results yield $\Delta Hf = -190.9$ kcal/mole. Presumably this was crystal II. In view of the uncertainty in crystal forms, no great confidence can be put in this previous data. Some work on the heats of solution of

HBO_2 (C,II) and HBO_2 (C,III) in water is now in progress at Moscow State University as reported by N.D. Sokolova, S. M. Skuratov, A. M. Shemonaeva, and V. M. Yuldasheva, in Bulletin of Chemical Thermodynamics, IUPAC (1960). As yet this work is unpublished. There have been no previous heat-of-solution measurements on HBO_2(C,I).

HBO_2 (C,II) and HBO_2 (C,III) in water is now in progress at Moscow State University as reported by N.D. Sokolova, S. M. Skuratov, A. M. Shemonaeva, and V. M. Yuldasheva, in Bulletin of Chemical Thermodynamics, IUPAC (1960). As yet this work is unpublished. There have been no previous heat-of-solution measurements on HBO_2(C,I).

II. Decomposition Pressures of Boric Acid

by

Edward J. Prosen

Introduction

Decomposition pressure measurements were made on the system $H_3BO_3(C) = H_2O(g) + HBO_2(C,X)$, where the metaboric acid HBO_2 was in the form of $HBO_2(C,I)$, $HBO_2(C,II)$, or $HBO_2(C,III)$. The results on crystals II and III confirm the data obtained by previous investigators. No previous data existed on crystal I, the most stable form of metaboric acid. From these measurements, heats of formation, free energies of formation, and entropies are derived.

Apparatus

The apparatus for measurement of the decomposition pressures of orthoboric acid consisted of a Pyrex glass bulb approximately 2 cm diameter and 5 cm long. To this was sealed a U-tube mercury manometer of 7 mm inside diameter. A mixture of the appropriate metaboric acid and orthoboric acid was introduced into the bulb and the system evacuated and then sealed off. In all but a few of the preliminary experiments on $HBO_2(C,II)$, the mercury manometer was of the closed-end type and pressures up to about 200 mm Hg could be read. The whole apparatus was immersed in a constant-temperature bath consisting of square pyrex glass jar containing silicone oil as the bath fluid, a mercury thermoregulator, a stirrer and thermometer. In the case of the preliminary experiments on HBO_2(C,II) where it was desired to go to pressures greater than 200 mm Hg, the manometer was connected to a dead-gas volume to which a manometer at room temperature was connected. Pressures up to 1000 mm Hg could be read. In this case the manometer in the bath connected to the sample bulb was used as a null indicator. Pressures were read to the nearest 0.05 mm by sighting on the mercury meniscus with a Gaertner Scientific Company cathetometer.

Measurements of Decomposition Pressures

Measurements of the decomposition pressure of H_3BO_3(C) to form H_2O(g) and HBO_2(C,X) where the HBO_2 is in the form of crystal II or crystal III have previously been made by L. F. Gilbert and M. Levi, J. Chem. Soc. **1929**, 527; A. Lescoeur, Ann. Chim. phys. [6] 19, 35 (1890); S. Bezzi, Gass. chim. ital. **65**, 766 (1935); H. Menzel, H. Schulz, and H. Deckert, Z. anorg. u. allgem. Chem. **220**, 49 (1934); A Thiel and H. Siebeneck, Z. anorg. u. allgem. Chem. **220**, 236 (1934); and H. Tazaki, J. Sci. Hiroshima Univ. Ser. A **10**, 37, 55, 63, 109, 113 (1939). The identification of crystal forms is given by F. C. Kracek, G. W. Morey, and H. E. Merwin, Am. J. Sci **35A**, 143 (1938).

We made preliminary decomposition pressure measurements on these two systems to verify the previous results. Our measurements on the equilibrium $H_3BO_3(C) = H_2O(g) + HBO_2(C,III)$ extended from 35°C to 100°C covering pressures from about 1 to 60 mm Hg. On the equilibrium $H_3BO_3(C) = H_2O(g) + HBO_2(C,II)$ our measurements extended from 35°C to 148°C covering pressures from about 2 to 900 mm Hg. Our equilibrium pressure measurements essentially confirm the results of the previous authors (when interpreted correctly as to crystal form). Consideration of all these data yiels the following decomposition pressure equations (p in mm Hg, T in °K):

$$H_3BO_3(C) = H_2O(g) + HBO_2(C,III)$$

$$\log p = 10.787 - (3352/T)$$

$$(308° - 421°K)$$

$$H_3BO_3(C) = H_2O(g) + HBO_2(C,II)$$

$$\log p = 10.099 - (2996/T)$$

$$(308° - 421°K)$$

In the paper by Tazaki, J. Sci. Hiroshima Univ. 10, 37 (1939) on $HBO_2(C,II)$, he stated that he could not obtain equilibrium pressures at temperatures below 100°C. We had no difficulty obtaining these pressures as would be expected since crystal II is more stable than crystal III. Also, as would be expected, if the bulb is filled mostly with H_3BO_3 with only a few crystals of $HBO_2(C,III)$ it is difficult to remain on the crystal III curve above 100°C since crystal III is transformed readily into crystal II under these conditions. However, if the bulb is filled with half H_3BO_3 and half $HBO_2(C,III)$, one can make measurements on the crystal III curve for long periods of time since the transformation to crystal II is rather slow and the pressures will not rise to the crystal II curve until all of crystal III has completely disappeared. The same is true of the crystal II to crystal I transformation. Once the transformation to the more stable form has taken place completely, there is no way to get back to the unstable form since at these temperatures and pressures the order of stability remains crystal I, II, III, with crystal I the most stable. The rate of transformation and rate of pressure equilibrium depends, no doubt, on the formation of nuclei, temperature, surface area, and other factors which are in process of being studied more completely.

For study of the equilibrium $H_3BO_3(C) = H_2O(g) + HBO_2(C,I)$, the bulb was filled with half $H_3BO_3(C)$ and half $HBO_2(C,I)$. The closed-end Hg manometer system was used and, after evacuation and sealing, the whole apparatus was immersed in the silicone oil bath. The length of the Hg manometer was sufficient, in this case, to read pressures up to about 140 mm. The temperature of the bath was raised (from room temperature) to 93°C. The manometer then showed an equilibrium pressure of about 45 mm, indicating that crystal III was present. This could have formed during the heating from room temperature since crystal III forms most readily on dehydration of H_3BO_3. After remaining a few hours at 45 mm, the pressure slowly began to rise and after about 18 hours, leveled off at about 90 mm pressure, indicating that crystall II was now present (in addition to crystal I) but that no crystal III remained. After a few more hours the pressure slowly began to rise to the crystal I equilibrium pressure. Since this pressure would clearly be higher than 140 mm, the temperature was lowered to 79°C and observations taken until near-equilibrium was attained. At the present time, pressure measurements have been made at 39°, 67°, and 79°C. It was found that several weeks may be necessary to approach within 1 mm of equilibrium. A study of the mechanism and rate of approach to equilibrium is being made.

The present measurements yield the following approximate decomposition pressure equation (p in mm, T in °K):

$$H_3BO_3(C) = H_2O(g) + HBO_2(C,I)$$

$$\log p = 9.441 - (2579/T)$$

$$(312^\circ - 352^\circ K)$$

Results Derived

In the table below are summarized the results of previous investigators on the decomposition pressures involving $HBO_2(C,III)$ and $HBO_2(C,II)$ and of the present investigation involving $HBO_2(C,I)$.

$$H_3BO_3(C) = H_2O(g) + HBO_2(C,X)$$

$$\log p = A - (B/T)$$

	A	B	Range, °K
$HBO_2(C,I)$	9.441	2579	312 to 352
$HBO_2(C,II)$	10.099	2996	308 to 421
$HBO_2(C,III)$	10.787	3352	308 to 421

From these values, we may derive the heat, free energy, and entropy changes for the reaction. These ΔH values would strictly apply to the mean temperature of the measurements, but the accuracy of the data do not warrant making a temperature coefficient correction. For the present purposes they will be taken to apply at 25°C.

$$H_3BO_3(C) = H_2O(g) + HBO_2(C,X)$$

Product	ΔH_{298} kcal/mole	ΔF_{298} kcal/mole	ΔS_{298} cal/deg mole
$HBO_2(C,I)$	11.80	2.85	30.0
$HBO_2(C,II)$	13.71	3.86	33.0
$HBO_2(C,III)$	15.34	4.55	36.2

Combining these data with the heats and free energies of formation and the entropies of water and of orthoboric acid, the following table is obtained:

Substance	ΔHf°_{298} kcal/mole	ΔFf°_{298} kcal/mole	S°_{298} cal/deg mole
$H_2O(g)$	- 57.798	- 54.636	45.106
$H_3BO_3(C)$	-262.16	-232.19	21.23
$HBO_2(C,I)$	-192.56	-174.70	6.14
$HBO_2(C,II)$	-190.65	-173.69	9.15
$HBO_2(C,III)$	-189.02	-173.00	12.30

The heats of formation of $HBO_2(C,I)$ and of $HBO_2(C,II)$ are in excellent agreement with the heats of formation derived from our heat-of-solution experiments. Until more heat-of-solution measurements are made on $HBO_2(C,III)$, the value given here for its heat of formation is considered more reliable.