Part III

Heat of Formation of Boron Trichloride

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The heat of hydrolysis of BCl_3(liq.) was determined calorimetrically in a closed reaction vessel. The process was carried out adiabatically.

$$BCl_3(\text{liq.}) + 3\,H_2O + 590\,H_2O \rightarrow 3HCl + H_3BO_3 + 590\,H_2O$$

From this value and the heats of formation data of the products and water, the heat of formation of BCl_3(liq.) was calculated.

THE heat of hydrolysis of liquid BCl_3 was measured as part of a program to determine the heats of formation of the oxides and halides of boron. From these measurements and appropriate auxiliary data, the heat of formation of BCl_3(liq.) was calculated.

EXPERIMENTAL

Calorimeter. The heats of hydrolysis were measured in a modified Parr combustion calorimeter operated adiabatically. The reaction vessel consisted of a nickel alloy body, with a tantalum liner. A special lid was constructed through which passed a centered, gas-tight, moveable shaft. Two baffle plates were attached to the bottom section of the shaft which allowed the sample (contained in a glass vial) to be crushed while submerged in the water. The shaft and baffle plates were constructed of tantalum.

The lid to the calorimeter jacket was modified to allow the crushing shaft, thermistor tube, and heater tube to pass through to the calorimeter bucket contained within. Beckmann thermometers were used to monitor the bucket and jacket water temperatures. Improvements in water circulation were made by increasing the rate of stirring (small pulley used) and by placing a tube around the stirrer blades.

Temperature measurements were made by employing a GB32P8 Fenwal thermistor of 2 kilohms in one arm of a Wheatstone bridge network and powered by one mercury battery of 1.35 volts. The bridge was kept balanced by manipulating three 10-step decades totalling 111 ohms located in a second arm of the bridge. The output was amplified using a Leeds and Northrup microvolt amplifier 9835-A.

The sensitivity of the system was 6.8×10^{-5} °C. per 0.5 division on the amplifier meter. Operating under adiabatic conditions, the stirring energy was approximately 7×10^{-5} deg. min.$^{-1}$.

Calibration. The heater by which the calorimeter was electrically calibrated consisted of 15 inches of Cupron wire noninductively wound on a threaded nylon plug and immersed in mineral oil contained in a glass well. The total resistance of the heater was 23.96 ohms as determined from voltage drop measurements. Energy for the heater is supplied by a 12-volt storage battery. The timing of the heater was measured by a Model S-10 standard precision timer synchronized with the heater switch.

The reaction studied created a temperature rise of 0.5° C. Electrical calibrations were made, accordingly, over this temperature interval.

All experimental runs, including calibrations were initiated at a temperature of 25.00 ± 0.05° C. The results of the electrical calibration runs are 33.55 ± 0.02 cal. per ohm. The uncertainties listed throughout this work are twice the standard deviation.

Material. The boron trichloride was purchased from the Matheson Co., Inc. at a purity of 99.5% minimum. The material was further purified by low temperature vacuum distillation and fractionation just prior to preparing the sample in the liquid form in a glass ampoule. The distillation temperature was −23° C., and the collection was made at −78° C. No analysis of the purified material was made.

PROCEDURE

Two hundred milliliters of water was added to the reaction vessel. The boron trichloride (liquid) contained in a glass ampoule was immersed in the water and held in place by a baffle plate connected to the crushing rod. The lid was secured, and the vessel placed in the calorimeter bucket which contained 2000 ml. of water at 25° C. The jacket temperature was adjusted to a value close to 25° C. such that the heat loss (or gain) to the inner bucket was kept low (approximately 10^{-5} ° C. per min.). Upon reaching a steady state the reaction was initiated by turning down the crushing rod, thus breaking the sample containing ampoule. The jacket temperature was adjusted accordingly as the reaction progressed. All reactions were performed adiabatically. Final equilibrium was achieved in approximately 70 minutes. Temperature changes resulting from the reaction were approximately 0.5° C.

RESULTS

The following equation represents the reaction studied:

$$BCl_3 + 3\ H_2O + 590\ H_2O \rightarrow (3\ HCl + H_3BO_3)\cdot 590\ H_2O$$

$$\Delta H_{298} = -69.12 \pm 0.11 \text{ kcal./mole}$$

The heat of formation of BCL_3 (liq.) was then calculated, using the following auxiliary data:

$\Delta Hf\ H_3BO_3\cdot 590\ H_2O = -256.02 \pm 0.21$ kcal./mole

$\Delta Hf\ HCl\cdot 197\ H_2O = -39.695 \pm 0.02$ kcal./mole (*13*)

$\Delta Hf\ H_2O = -68.315 \pm 0.01$ kcal./mole (*9*)

The value of ΔHf for $H_3BO_3\cdot 590\ H_2O$ is based on Good's (*4*) determination of $\Delta Hf\ H_3BO_3$(c) and the heat of solution of H_3BO_3(c) done at National Research Corp. and reported separately (*2*).

The heat of formation of BCl_3(liq.) thus is calculated to be -101.04 ± 0.39 kcal. per mole.

DISCUSSION

A comparison of the results of this work with those appearing in the literature is presented in Table I for the hydrolysis of BCl_3(liq.), and in Table II for the heat of formation of BCl_3(liq.).

Although investigators of BCl_3(liq.) may agree in their hydrolysis studies at similar concentrations, the heat of formation value derived from the hydrolysis data will depend upon the chosen values for ΔHf of $HCl\cdot n\ H_2O$ and $H_3BO_3\cdot n\ H_2O$. In this work, the author attempted to use the most reliable data available.

In a comparison of the work of Skinner and Smith (*10*) with this work, the agreement in the hydrolysis study is excellent. A correction for concentration applied to either work to place the comparison on equal ground would not affect the hydrolysis value beyond the limits of uncertainty. However, Skinner and Smith report a value for the heat of formation of BCl_3(liq.) of −103.0 kcal. per mole, as compard with −101.04 kcal. per mole determined in this work. Had they used more recent $HCl\cdot n\ H_2O$ data (*1*), their ΔHf, BCl_3(liq.) value would be lowered by 0.18 kcal. per mole. Also, had they used the more recent $\Delta Hf\ H_3BO_3$(c) data of Good (*4*) with the dilution data of National Research Corp. (*2*) or Smisko and Mason (*11*), the calculated value for $\Delta Hf\ BCl_3$(liq.) would be lowered by an additional 1.31 kcal. per mole. The total correction would result in a value of −101.51 kcal. per mole for the ΔHf BCl_3(liq.). The agreement with this work would then be quite favorable.

The heat of formation data of Laubengayer and Sears (*8*) was calculated by Johnson (*6*) from the former investigators' hydrolysis data. No indication was given by Johnson as to the value of ΔHf for $H_3B_3\cdot 1000\ H_2O$ and $HCl\cdot 1000\ H_2O$ which was used in the calculation.

Table I. Comparison of Hydrolysis Results with Existing Data

$$BCl_3(\text{liq.}) + (3 + n)\ H_2O \rightarrow 3\ HCl + H_3BO_3 + n\ H_2O$$

Investigators	ΔH Hydrolysis, Kcal./Mole
Troost and Hautefeuille (*12*)	−80.0
Berthelot (*1*)	−68.2
Laubengayer and Sears (*8*)	−69.3
Kapustinskii and Samoilov (*7*)	−75.1
Skinner and Smith (*10*)	−69.2
Gunn and Green (*5*)	−68.68
This work	−69.12

Table II. Comparison of Values for the Heat of Formation of BCl_3 (Liq.)

Investigators	Method	ΔHf_{298}
Troost and Hautefeuille (*12*)	Direct	−103.3
Berthelot (*1*)	Hydrolysis	−103.2
Laubengayer and Sears (*8*)	Hydrolysis	−102.1
Lapustinskii and Samoilov (*7*)	Hydrolysis	−96.3
Skinner and Smith (*10*)	Hydrolysis	−103.0 ± 1
Johnson (*6*)	Direct	−102.7 ± 0.3
Gal'chenko (*3*)	Direct	−102.9 ± 0.6
This work	Hydrolysis	−101.04 ± 0.39

The use of Good's data (*4*) which was based on crystalline boron provides the pertinent auxiliary information required. Prior to his work, the heats of formation data for H_3BO_3 (aq.) were based on amorphous boron and an assumed heat of transition from crystalline boron. These new data would reduce the values in Table II for Laubengayer, Skinner, Johnson, and Gal'chenko to −101.1, −102.0, −101.7, and −101.9 kcal. per mole, respectively.

Having given consideration to the auxiliary data employed in the calculations of the heat of formation from hydrolysis studies, and by comparison to determinations by the direct chlorination method, the existing data for the heat of formation of BCl_3(liq.) appear now to be in good agreement.

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NOMENCLATURE

ΔH_{298} = heat of solution at constant pressure and at 298° K., kcal./mole
ΔHf_{298} = heat of formation at 298° K., kcal./mole
q = electrical energy supplied to the calorimeter, calories
E_s = voltage drop across standard resistor, volt
R_s = 0.500 ohm standard wire-wound resistor
t_{sec} = heating time, seconds
R = change in the resistance of the thermistor
ϵ = energy equivalent, calories/ohm

LITERATURE CITED

(1) Berthelot, M., *Ann. chim. phys.* (5) **15**, 185 (1878).
(2) Fasolino, L.G., J. Chem. Eng. Data **10**, 373 (1965).
(3) Gal'chenko, G.L., Timofeev, B.I., Skuratov, S.M., *Russ. J. Inorg. Chem.* **5**, No. 12, 1279 (1960).
(4) Good, W.D., Mansson, M., McCullough, J.P., Quarterly Technical Rept. No. **19**, November 4, 1963, Contract No. **C5059-9**, Bureau of Mines, Bartlesville, Okla.
(5) Gunn, S.R., Green, L.G., *J. Phys. Chem.* **64**, 61 (1960).

(6) Johnson, W.H., Miller, R.G., Prosen, E.J., *J. Res. Natl. Bur. Std.* **62**, No. 5, 213 (1959).
(7) Kapustinskii, A.F., Samoilov, O.Y., *Izv. Akad. Nauk SSSR Otd. Khim. Nauk* **1952**, p. 218.
(8) Laubengayer, A.W., Sears, D.S., *J. Am. Chem. Soc.* **67**, 164 (1945).
(9) *Natl. Bur. Std. U. S., Circ.* **500**, "Selected Values of Chemical Thermodynamic Properties," 1952.
(10) Skinner, H.A., Smith, N.B., *Trans. Faraday Soc.* **49**, 601 (1953).
(11) Smisko, J., Mason, L.S., *J. Am. Chem. Soc.* **72**, 3679 (1950).
(12) Troost, L., Hautefeuille, P., *Ann. chim. phys.* (5) **9**, 70 (1876).
(13) Wagman, D.D., NBS, private communication.

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Heats of Solution of Crystalline and Amorphous Boron Oxide and Boric Acid

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The heats of hydrolysis for $B_2O_3(c) + 348\ H_2O \rightarrow 2(H_3BO_3)\cdot 345\ H_2O$; B_2O_3 (amorphous) + $372\ H_2O \rightarrow 2(H_3BO_3)\cdot 369\ H_2O$, and $H_3BO_3(c) + 504\ H_2O \rightarrow H_3BO_3\cdot 504\ H_2O$ have been measured. From these data and accepting the value of -261.47 ± 0.2 kcal. per mole for the heat of formation of $H_3BO_3(c)$ as determined by Good and coworkers, the heats of formation for $H_3BO_3\cdot 504\ H_2O$, $B_2O_3(c)$, and B_2O_3 (amorphous) were calculated. The energy of transformation from crystalline to amorphous B_2O_3 was also calculated.

THE heats of solution of crystalline and amorphous B_2O_3 and H_3BO_3 in water were calorimetrically measured. From these data and other pertinent auxiliary data, the heats of formation of $H_3BO_3\cdot 504\ H_2O$, $B_2O_3(c)$, and B_2O_3(amorphous) were determined.

EXPERIMENTAL

Calorimeter. The heats of solution were measured in a silvered Dewar-type reaction vessel containing 200 ml. of water. The lid was constructed to allow passage of the stirrer, heater, thermistor tube, and sample ampoule crushing rod. The assembled reaction vessel was submerged in a stirred water bath of 17 liters. The experiments were performed adiabatically whereby the bath temperature was held by a heater-relay system, at ±0.008° of the bath and calorimeter temperature (~25° C.). The final temperature was 0.25° or 0.5° C. higher, depending on the reaction studied.

Temperature measurements were made by employing a GB32P8 Fenwal thermistor of 2 kilohms in one arm of a Wheatstone bridge network and powered by one mercury battery of 1.35 volts. The bridge is kept balanced by manipulation of three 10-step decades totaling 11 ohms located in a second arm of the bridge. The output is amplified utilizing a Leeds and Northrup microvolt amplifier 9835-A.

The sensitivity of the system is 2.5×10^{-5}° C., or 6×10^{-3} calorie. Operating under adiabatic conditions the thermal leak rate was approximately 0.003 to 0.045 calorie min.^{-1}.

Calibration. The calorimeter was electrically calibrated. The timing of the heating period was measured by a Model S-10 standard precision timer synchronized with the heater switch.

The reactions studied and the calibration runs created temperature increases of 0.25° and 0.5° C.

All experimental runs, including calibrations were initiated at a temperature between 25.0° and 25.1° C. The uncertainties listed throughout this work are twice the standard deviation.

Materials. The B_2O_3(amorphous) was from Fisher Scientific as 99.9+% pure; the $B_2O_3(c)$ was synthesized in this laboratory from seeded $H_3BO_3(c)$ which was obtained from U.S. Borax as 99.9+% pure.

The $H_3BO_3(c)$ and $B_2O_3(c)$ were identified by x-ray diffraction patterns. The boron compounds were spectrographically analyzed for 14 elements. The total impurities analyzed for in each were less than 300 p.p.m. No further analyses were made.

PROCEDURE

Two hundred milliliters of water were added to the Dewar reaction vessel. The sample contained in a glass ampoule was held in a submerged position by a three-pronged support. The Dewar was submerged in a stirred water bath maintained at 25.000±0.008° C. Upon initiating the reaction by breaking the sample ampoule, the bath temperature was simultaneously changed at the same rate as the solution temperature to effect an adiabatic measurement.

RESULTS

From the amounts of material used, the following equations represent the reactions studied and their heats of reaction.

	ΔH_{298}, Kcal./Mole	
$B_2O_3(c) + 3H_2O + 350\ H_2O \rightarrow$		
$2(H_2BO_3\cdot 175\ H_2O)$	-3.45 ± 0.03	(1)
$B_2O_3(\text{amorphous}) + 3H_2O + 369\ H_2O \rightarrow$		
$2(H_3BO_3\cdot 184\ H_2O)$	-7.78 ± 0.05	(2)
$H_3BO_3(c) + 504\ H_2O \rightarrow H_3BO_3\cdot 504\ H_2O$	$+5.45 \pm 0.01$	(3)

From the results of Equation 3, and accepting the value of Good and coworkers (*3*) for the heat of formation of