The Vapor Pressures and Some Thermodynamic Functions of B-trifluoro-, B-trichloro-, and B-tribromoborazine

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The vapor pressures of B-trifluoro-, B-trichloro-, and B-tribromoborazine ($X_3B_3N_3H_3$, where X = F, Cl, and Br) have been measured over several temperature ranges. The results are expressed in the form, $\log p_{(mm.)} = A - B/T$ (°K.). Average enthalpies and entropies of sublimation, vaporization, and fusion over the experimental temperature ranges are obtained. Results are compared with those known for analogous 1,3,5-trihalogenobenzenes. Thermal stability decreases in the order B-trifluoro-, B-trichloro-, and B-tribromoborazine.

VAPOR PRESSURE data for B-trichloroborazine has been obtained previously by Brown and Laubengayer (4). These data have been extended over a wider temperature range, and the vapor pressures of B-trifluoro- and B-tribromoborazine have been measured.

EXPERIMENTAL

Preparation. B-trichloro- and B-tribromoborazine were prepared by the hot tube method (4), reacting, respectively, boron trichloride with ammonium chloride, and boron tribromide with ammonium bromide. The ammonium salts were mixed with powdered asbestos as suggested by Hutto (9) to prevent caking. B-trifluoroborazine was prepared by transhalogenation of B-trichloroborazine with titanium tetrafluoride as recommended by Niedenzu (13).

Purification. Three independently prepared samples of B-trifluoroborazine were purified by double sublimation at room temperature. Anal. Calcd. for $F_3B_3N_3H_3$: B, 24.12; N, 31.25; F, 42.38. Found: B, 24.18; N, 31.20; F, 42.10 (as PbClF); B, 24.20; N, 31.22; F, 42.18; B, 24.17; N, 31.22; F, 42.13.

No evidence for any impurities was found by mass spectrometric analysis (11). Each of the samples was sublimed directly into the isoteniscope. A mass spectrum at the end of each run showed only a trace of hydrogen fluoride from slow decomposition. B-trifluoroborazine was sublimed from the isoteniscope leaving traces of unidentified, white, nonvolatile solids.

Two independently prepared samples of B-trichloroborazine were purified by double sublimation at room temperature [m.p. 83.6-84.2° C., 83.8-84.2° C. (4)]. Anal. Calcd. for $Cl_3B_3N_3H_3$: B, 17.64; N, 22.85; Cl, 57.86. Found: B, 17.72; N, 22.81; Cl, 57.70; B, 17.59; N, 22.90; Cl, 57.92.

Part of one of these samples and two parts of the other were sublimed directly into the isoteniscope. A mass spectrum at the end of each run showed hydrogen chloride and a trace of nitrogen from slow decomposition. B-trichloroborazine was sublimed from the isoteniscope leaving traces of unidentified, white, nonvolatile solids.

Two independently prepared samples of B-tribromoborazine were purified by double sublimation at 50° C. [m.p. 128.5-129.0° C., 128.6-129.0° C. (6)]. Anal. Calcd. for $Br_3B_3N_3H_3$: B, 10.22; N, 13.25; Br, 75.58. Found: B, 10.28; N, 13.21; Br, 75.47; B, 10.30; N, 13.23; Br, 75.39.

Part of one of these samples and two parts of the other were loaded into the isoteniscope in a nitrogen-filled drybox. A mass spectrum at the end of each run showed only hydrogen bromide and a trace of nitrogen from slow decomposition. B-tribromoborazine was sublimed from the isoteni-

scope leaving traces of unidentified, white, nonvolatile solids.

Measurements. A mercury isoteniscope, modified as suggested by Booth and Halbedel (3), was connected directly to a standard vacuum line manifold having an open-end mercury manometer. The isoteniscope was immersed in a water bath for data below 22° C. and in a paraffin oil bath for data above 22° C. Thermal equilibrium was ensured by continuous stirring, by holding the temperature constant for at least 1 hour before taking any given reading, and by running both heating and cooling curves. Temperatures were read on specific range calibrated thermometers, marked off in 0.05° C. intervals below 103° C. and in 1° C. intervals above 103° C. Pressures less than 95 mm. were read directly in the differential U-tube of the isoteniscope using a cathetometer having a 0.01-mm. vernier scale. Pressures greater than 95 mm. were read as the sum of the difference between two mercury columns on the open-end manometer having a 0.2-mm. vernier scale and the small difference in the nearly balanced U-tube of the isoteniscope.

Appropriate corrections were made for the vapor pressure of mercury (10). Residual pressures at room temperature due to thermal decomposition were checked after each reading and become measurable for B-trifluoroborazine above 100° C., for B-trichloroborazine above 84° C., and for B-tribromoborazine above 70° C. The volatile decomposition products of the three compunds are gases at room temperature as shown by mass spectral data in this work and in previous studies (11, 4, 18). It was assumed that these gases act as ideal gases. Appropriate corrections could then be applied to the total pressures above the decomposition temperatures so that tabulated values represent actual vapor pressures of the B-trihalogenoborazines. This assumption is reasonable for hydrogen chloride, hydrogen bromide and nitrogen, but is not a good assumption for hydrogen fluoride which is believed to associate into chain polymers even in the vapor phase (1) However, this would have a negligible effect on the accuracy of the data for B-trifluoroborazine since the correction for decomposition was only 0.1 mm. in 400 mm., or less than the experimental error. The maximum temperatures at which data for B-trichloro- and B-tribromoborazine were taken were those temperatures above which meaningful corrections for decomposition could no longer be made.

RESULTS

Typical results for vapor pressure as a function of temperature for B-trifluoro-, B-trichloro-, and B-tribromoborazine are given in Table I. Data from three runs for each of the

Table I. Vapor Pressure Data for B-trifluoro-, B-trichloro-, and B-tribromoborazine

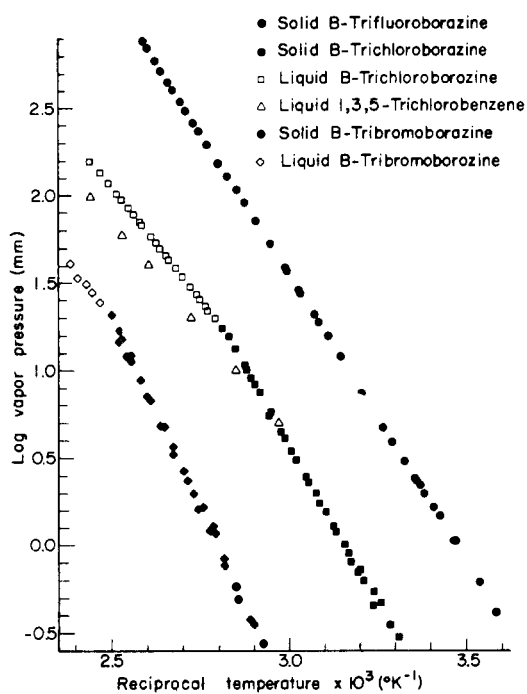| $F_3B_3N_3H_3$		$Cl_3B_3N_3H_3$		$Br_3B_3N_3H_3$	
$T, °C.$	$p,$ mm.	$T, °C.$	$p,$ mm.	$T, °C.$	$p,$ mm.
0.31	0.25				
9.82	0.60				
20.37	1.62				
30.59	3.85	29.35	0.29		
38.84	7.36	40.25	0.70		
50.86	18.7	50.80	1.70		
60.74	36.4	59.46	3.44		
70.53	69.9	69.54	7.36	69.10	0.27
80.23	126.7	80.13	15.2	82.02	0.76
90.40	230.4	90.49	25.3	90.72	1.61
100.23	399.7	99.40	37.8	100.67	3.29
110.3	696.4	109.1	57.2	109.9	6.72
112.2	760.0	121.7	93.0	121.7	15.1
		131.4	133.4	131.5	24.8
		136.0	154.7	142.0	34.0

Figure 1. Log of the vapor pressure vs. the reciprocal of the absolute temperature for B-trifluoro-, B-trichloro-, and B-tribromoborazine, and 1,3,5-trichlorobenzene

three B-trihalogenoborazines are summarized graphically in Figure 1 where log vapor pressure in plotted against reciprocal temperature. Data from Dow Chemical Co. files for 1,3,5-trichlorobenzene (17) are plotted for comparison. Least squares regression analyses of the sets of data on a digital computer (5) give, as shown in Table II, equations

B-trifluoroborazine is unique in not having any liquid phase at pressure less than 1 atm. The calculated sublimation point (112.2 ± 0.1° C.) is in agreement with the experimental value.

representing the data of the form $\log p_{(mm.)} = A - B/T$ (° K.), average values for the appropriate thermodynamic functions, and the error in each calculated value. For liquid B-tribromoborazine, the only case where the experimental error was determined to be greater then the computer-calculated statistical error, values in Table II represent the experimental error.

Hydrogen halides were the primary decomposition prod ucts in all cases. The observed evolution of hydrogen fluoride from the slow decomposition of B-trifluoroborazine at 110° C. differs from the case of high temperature pyrolysis at 200° to 600° C. where boron trifluoride has been reported as the primary halogen-containing product (11).

DISCUSSION

B-Trifluoroborazine, in showing no liquid phase at pressures less than 1 atm., differs from 1,3,5-trifluorobenzene, which has a normal liquid range [m.p. -5.5° C., b.p. 75.5° C. (7)]. Furthermore, no other borazines including N-trialkylated-B-trifluoroborazines prepared by Niedinzu, Beyer, and Jenne (14) show this characteristic. Sublimation points previously reported for B-trifluoroborazine [122° C. (13) and 118° C. (11)] are in error because these were observed by experiments in sealed tubes where there was no way to determine when the sample pressure equaled 760 mm.

The physical properties of B-trichloroborazine are much like those of 1,3,5-trichlorobenzene: m.p. 63.5° C., b.p. 208.4° C., $\log p_{(mm.)} = 7.98 ± 0.03 - 2450 ± 9/T$ (° K.) for the liquid, and $\Delta H_{vap.} = 11.21 ± 0.04$ kcal./mole (17). Likewise, the physical properties of B-tribromoborazine are like those of 1.3.5-tribromobenzene [m.p. 120° C., b.p. 271° C. (8)].

The observed decomposition temperatures indicate that the B-trihalogenoborazines are less stable thermally than their benzene analogs. The authors' decomposition temperature for B-trichloroborazine is in agreement with previous work by Massey and Park (12). Thermal stability, which at least for low temperature decomposition where the borazine ring remains intact, seems to be a function of the B-X bond strength and decreases from B-trifluoro- to B-tribromoborazine. This assumes that the B-X bond strength follows the same order as in BX_3 molecules where

Table II. Physical Constants for B-trifluoro-, B-trichloro-, and B-tribromoborazine

	$F_3B_3N_3N_3$	$Cl_3B_3N_3H_3$		$Br_3B_3N_3H_3$	
	Solid	Solid	Liquid	Solid	Liquid
M.p., ° C.	112.2, subl.	83.6 – 84.2		128.5 – 129.0	
B.p., ° C.[a]			185 ± 2		263 ± 42
A	11.43 ± 0.01	11.61 ± 0.06	8.54 ± 0.03	12.58 ± 0.08	7.46 ± 0.70
B	3294 ± 4	3683 ± 19	2592 ± 8	4502 ± 30	2453 ± 264
$\Delta H_{subl.}$[b]	15.07 ± 0.02	16.85 ± 0.09		20.6 ± 0.1	
$\Delta S_{subl.}$[c]	39.10 ± 0.05				
ΔH_{fusion}		5.0 ± 0.1		9.4 ± 1.4	
ΔS_{fusion}		14.0 ± 0.3		23 ± 3	
$\Delta H_{vap.}$			11.86 ± 0.04		11.2 ± 1.3
$\Delta S_{vap.}$			25.9 ± 0.1		21 ± 3
Triple point		81.9° C., 17.9 mm.		126.6° C., 20.8 mm.	

[a] Extrapolated. [b] All ΔH values in units of kcal. per mole. [c] All ΔS values in units of cal. per deg.-mole.

force constants decrease regularly from boron trifluoride to boron triiodide (2). Thus, one correctly predicts that B-triiodoborazine prepared by Nöth (16) is thermally unstable around room temperature (15).

ACKNOWLEDGMENT

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Electrical Conductivity of Concentrated Phosphoric Acid from 25° to 60° C.

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The electrical conductivity for concentrated phosphoric acid in the range 62.14 to 85.58% P_4O_{10} has been measured at 25°, 30°, 40°, 50°, and 60° C. The results differ from several previous conductivity measurements in the concentrated phosphoric acid region.

PHOSPHORIC ACID is an effective absorbent-electrolyte in water-vapor electrolysis cells (2). To carry out voltage analysis studies on such cells, reliable electrical conductivity data is needed.

Several reports on the electrical conductivity of concentrated phosphoric acid have appeared in the literature (5, 6, 7). However, in view of the variability of reported values, the electrical conductivity of concentrated phosphoric acid has been redetermined over a wide range of concentration at intervals from 25° to 60° C.

EXPERIMENTAL

Acid samples in the range 64.08 to 73.61 weight % phosphorus pentoxide were prepared by the thermal dehydration of analytical reagent grade "85%" phosphoric acid (62.14% phosphorus pentoxide by analysis in this laboratory) at about 150° C. Samples more concentrated than 73.61% P_4O_{10} were prepared by the slow addition of reagent grade P_4O_{10} to a thermally dehydrated acid sample containing approximately 70% P_4O_{10}. Since concentrated phosphoric acid attacks glass above 200° C., the sample vessel was placed in an ice bath during the addition of P_4O_{10} to prevent a large temperature rise. Samples prepared by the addition of P_4O_{10} were finally heated to 180° C. to hasten dissolution of the oxide. Samples ranged from a transparent, colorless liquid at the lower concentrations, to a straw yellow color at the higher concentrations.

A Washburn conductivity cell with platinized platinum electrodes, maintained at a constant temperature (±0.05° C.), was used in measuring the conductivity. The cell constant,

0.759 cm.⁻1, was determined at 25° C. by measuring the resistance of a 0.01N KCl solution. The conductivity values for 0.01N KCl used to calculate the cell constant were obtained from the data of Jones and Bradshaw (4). Resistance was measured with a General Radio 1650A impedance bridge at a frequency of 1000 c.p.s. No fewer than five measurements of the resistance were made, over varying time intervals, at each temperature for any given concentration. Bridge balance was determined by either an oscilloscope or the impedance bridge null detector. No difference in resistance, within experimental error, could be detected by using either the oscilloscope or the null detector. (The manufacturers estimate for the accuracy of the resistance reading is ±1%). The accuracy of the measurements was further checked by measuring the conductivity of 0.1N KCl at 0° and 25° C., and of 0.01N KCl at 0° C. These data were then compared with values found in the literature (4). The mean standard deviation between this work and the reported values for the conductivity of potassium chloride is ±0.4%.

Following the conductivity measurements, three samples of acid were taken for analysis. Samples were transferred with a glass syringe from the conductivity cell to glass stoppered weighing bottles and weighed immediately. The acid concentration was determined by titration with sodium hydroxide using an expanded scale pH meter to detect the first equivalence point.

RESULTS AND DISCUSSION

In Table I values for the specific conductivity of phosphoric acid (62.14 to 85.58 weight % phosphorus pentoxide)