Determination of the Molar Limits of the Reaction of Boric Acid with an Amine: Boric Acid-*n*-Octylamine Reaction (7 to 1 Mole Ratio).—*n*-Octylamine (6.45 g., 0.05 mole) was added to a slurry of 22.3 g. (0.36 mole) of boric acid in a mixture of 10 ml. of water and 100 ml. of benzene. The mixture was stirred at 50° for 30 min. and then heated to reflux (70°). Refluxing was continued until 12–13 ml. of water had been removed by azeotropic distillation. Acetonitrile (100 ml.) was added and the solid product (23.4 g.) collected on a filter. Infrared analysis and X-ray powder diffraction indicated that the product was a mixture of *n*-octylammonium pentaborate and boric acid. This result shows that the reaction stops at the spiropentaborate even in the presence of excess boric acid.

Acknowledgments.—The authors wish to express their appreciation to Dr. M. J. S. Dewar, Dr. A. A. Schleppnik, and Dr. M. C. Freerks for helpful suggestions and comments; to Dr. E. D. Pierron and Mr. H. Yepez for the X-ray analyses and interpretations; and to Mr. J. L. O'Sullivan and Mr. O. S. Kring for the elemental analyses.

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Thermodynamic Properties of Dichloroborane

BY LAHMER LYNDS AND C. DAVID BASS

Received March 23, 1964

The disproportionation reaction for $HBCl_2$, $6HBCl_2 \rightleftharpoons 4BCl_3 + B_2H_6$, was followed spectrophotometrically in the infrared region and an equilibrium constant (K_p (298°K.) = 532 ± 15 atm.$^{-1}$) was obtained. Statistical thermodynamic functions in the range 298–1200°K. were computed from fundamental frequencies and molecular constants of $HBCl_2$. Experimental results and statistical calculations were combined and the change of zero-point energy, $\Delta E°_0$, was calculated to be −18.62 ± 0.02 kcal./mole. The molar free energy and heat of formation at 298°K. for $HBCl_2$ were calculated to be −56.68 ± 0.05 and −60.37 ± 0.05 kcal., respectively.

Introduction

A vibrational analysis of the dihaloboranes made possible the observation and assignment of fundamental frequencies for the isotopic species $HB^{11}Cl_2$, $HB^{10}Cl_2$, $DB^{11}Cl_2$, and $DB^{10}Cl_2$. The frequencies were computed by utilizing the Green's function and matrix partitioning techniques applied to molecular systems[1] without invoking a force constant model.[2] The vibrational spectrum of these molecules consists of six fundamentals, which are all infrared and Raman active for both a planar (C_{2v}) and nonplanar (C_s) model. Although there is no evidence to eliminate the latter, we shall make the reasonable assumption that the molecules are planar.[3] This form allows the maximum opportunity for π-orbital interactions, which act to stabilize the planar structure of BX_3 molecules, when X contains lone-pair electrons. Coupled with the recent determination of the rotational constants and molecular geometry of $HBCl_2$ and $DBCl_2$,[3] it was possible to obtain the thermodynamic functions for $HB^{11}Cl_2$ from statistical calculations. The disproportionation reaction for dichloroborane

$$6HBCl_2 \rightleftharpoons 4BCl_3 + B_2H_6 \qquad (1)$$

was followed spectrophotometrically utilizing well-characterized and noninterfering infrared bands of the reaction partners. From the experimentally derived equilibrium constant and statistical computations, some additional thermodynamic properties of dichloroborane and equilibrium constants at various temperatures for reaction 1 were calculated.

Experimental

Dichloroborane was prepared by reducing BCl_3 with hydrogen in the presence of magnesium maintained at 350° in a stainless-steel tube.[3,4] The stainless-steel reactor was sealed into a vacuum system having a facility for low temperature separations. Dichloroborane was separated from reactants (H_2, BCl_3) and other products (HCl) by repeated distillations through series of traps maintained at −125, −135, and −196°. After numerous passes, the fraction retained in the −135° trap was introduced into a 10-cm. infrared cell fitted with NaCl windows. The cell was monitored continuously during the first hour of disproportionation and periodically for 336 hr. Since the cell temperature (25°) and volume remained constant during the disproportionation, optical densities of certain preselected bands were directly related to the partial pressures of the reaction constituents. From Beer's law and total pressure measurements the partial pressures of each constituent could be calculated. Details of this technique have been reported previously.[5] Total cell pressures in the range 20–25 mm. were convenient to work with in this case and avoided complications from pressure broadening and nonideal behavior.

Results

At room temperature, dichloroborane disproportionated to form BCl_3 and B_2H_6 according to the stiochiometry given in eq. 1. After 30 min. at 25°, the reaction appeared to be approximately 50% complete; after 168 hr. further changes were not observed and equilibrium appeared to be attained. Monochlorodiborane and other possible products were not observed. Final measurements were made on systems which had been

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[1] R. E. DeWames and T. Wolfram, *J. Chem. Phys.*, **40**, 853 (1964).

[2] C. D. Bass, L. Lynds, T. Wolfram, and R. E. DeWames, *ibid.*, **40**, 3611 (1964).

[3] L. Lynds and C. D. Bass, *ibid.*, **40**, 1590 (1964).

[4] L. Lynds and D. R. Stern, *J. Am. Chem. Soc.*, **81**, 5006 (1959).

[5] H. G. Nadeau and D. M. Oaks, *Anal. Chem.*, **32**, 1480 (1960).

in contact for 330-336 hr. The equilibrium constant for reaction 1 is related to the reaction constituents according to the mass action expression

$$K_p = \frac{[P_{BCl_3}]^4[P_{B_2H_6}]}{[P_{HBCl_2}]^6} \qquad (2)$$

The average K_p (298°K.) from several runs was calculated to be 532 ± 15 atm.$^{-1}$. The ambient temperature of the infrared beam did not appear to perturb the equilibrium distribution during the course of 1-hr. exposure.

Calculations

Molecular parameters[3] and fundamental vibrational frequencies[2] for $HBCl_2$ and $DBCl_2$ used in the statistical calculations are presented in Table I.

TABLE I

FUNDAMENTAL FREQUENCIES[a] AND MOLECULAR CONSTANTS FOR $HBCl_2$ AND $DBCl_2$[2,3]

Symmetry type	Mode		$HB^{11}Cl_2$	$HB^{10}Cl_2$	$DB^{11}Cl_2$	$DB^{10}Cl_2$
A_1	ν_1	Obsd.	740	762		
		Calcd.			714	735
A_1	ν_2	Obsd.	2617	2617	1969	1969
		Calcd.				
A_1	ν_3	Obsd.				
		Calcd.	287	289	285	288
B_1	ν_4	Obsd.	1089	1100	1005	1050
		Calcd.				
B_1	ν_5	Obsd.	891			
		Calcd.		860	640	641
B_2	ν_6	Obsd.	784	795	645	661
		Calcd.				
A, cm.$^{-1}$			1.556		1.179	
B, cm.$^{-1}$			0.103		0.103	
C, cm.$^{-1}$			0.097		0.095	
∠ClBCl				119.7 ± 3°		

[a] Frequencies are in cm.$^{-1}$. Band centers were estimated from positions of the observed vibration–rotation envelopes.

The thermodynamic functions which we have calculated in the temperature range 298 to 1200°K. for $HB^{11}Cl_2$ are compiled in Table II. All statistical calculations were based on a perfect gas model in which the coupling between vibration and rotation was ignored as well as the contribution from nuclear spins. For the vibrational contributions, a rigid harmonic-oscillator approximation was used. The ν_3 (A_1) fundamental of $HB^{11}Cl_2$ was outside the range of our equipment and the calculated value was used in computing the vibrational contributions to the thermodynamic functions. There is evidence that the value is a good approximation based on our vibrational analysis of mixed boron halides[6] compared to published experimental results.[7] The equilibrium constant from eq. 2 can be represented by[8]

$$-R \ln K_p = \frac{\Delta G^\circ}{T} = \frac{\Delta E^\circ_0}{T} + 4\left(\frac{G^\circ - E^\circ_0}{T}\right)_{BCl_3} + \left(\frac{G^\circ - E^\circ_0}{T}\right)_{B_2H_6} - 6\left(\frac{G^\circ - E^\circ_0}{T}\right)_{HBCl_2} \qquad (3)$$

where ΔG° is the standard molar Gibbs free energy change and ΔE°_0 is the change in energy of formation at 0°K. for the reaction. The standard state was taken to be the ideal gas at 1 atm. The change of the energy of formation at 0°K., ΔE°_0, for reaction 1 was calculated to be −18.62 ± 0.02 kcal. by comparing the opposite sides of eq. 3. Thermodynamic functions for BCl_3 and B_2H_6 were taken from the literature.[9] It was then possible to compute the equilibrium constant (eq. 2) at other temperatures assuming ΔH did not vary appreciably with temperature over the range considered. The molar free energy of formation and heat of formation at 298°K. for $HBCl_2$ were calculated to be −56.68 ± 0.05 and −60.37 ± 0.05 kcal., respectively, from eq. 1 using published thermodynamic data[10] for BCl_3 and B_2H_6. Results of other thermodynamic calculations are summarized in Table III.

TABLE II

THERMODYNAMIC FUNCTIONS[a] OF $HB^{11}Cl_2$

T, °K.	C_p°	S°	$-\frac{G^\circ - E^\circ_0}{T}$	$\frac{H^\circ - E^\circ_0}{T}$
298	11.879	64.088	54.668	9.420
400	13.515	67.823	57.559	10.264
500	14.699	70.972	59.933	11.039
600	15.573	73.732	62.007	11.725
700	16.242	76.184	63.859	12.325
800	16.772	78.389	65.540	12.849
900	17.200	80.389	67.080	13.309
1000	17.552	82.219	68.503	13.716
1100	17.843	83.906	69.829	14.077
1200	18.088	85.470	71.067	14.403

[a] Cal./deg. mole.

TABLE III

THERMODYNAMIC DATA

	K_p, atm.$^{-1}$	ΔG°, kcal./mole[a]	ΔH°, kcal./mole[a]	ΔS°, cal./mole deg.[b]
298	532	−3.72	−19.18	−51.90
400	0.159	1.46	−18.97	−51.06
500	1.21×10^{-3}	6.67	−18.80	−50.94
800	1.14×10^{-6}	21.76	−18.04	−49.75
1000	1.22×10^{-7}	31.63	−17.36	−49.01

[a] ±0.02 kcal./mole. [b] ±0.01 cal./mole deg.

Discussion

Errors introduced by intermingling thermodynamic functions of $HB^{11}Cl_2$ with data derived from BCl_3 and B_2H_6 possessing the naturally occurring isotopic distribution of boron were considered to be negligible compared to the uncertainty in measurement of the equilibrium constant. The variation of the equilibrium constant with temperature indicates that the stability of $HBCl_2$ with respect to disproportionation is favored with increasing temperature. It supports the fact that $HBCl_2$ may be formed in flow systems at elevated tempera-

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(9) W. H. Evans, E. J. Prosen, and D. D. Wagman, "Thermodynamic and Transport Properties of Gases, Liquids and Solids," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 226 ff.

(10) National Bureau of Standards, "Selected Values of Chemical Thermodynamic Properties," Circular 500, Feb. 1, 1952.

tures in relatively high yields[11] with the occurrence of only small quantities of B_2H_6. Although there is evidence that reaction 1 may proceed by a more devious course under different circumstances,[12] the relatively slow rate of disproportionation at room temperature presents an interesting candidate for a kinetic study which could be followed spectrophotometrically.

Acknowledgment.—The authors are indebted to Dr. Milton Blander for helpful discussions concerning thermodynamic topics in this paper.

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The Fluorosulfuric Acid Solvent System. I. Electrical Conductivities, Transport Numbers, and Densities[1]

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Received September 18, 1963

The results of measurements of the conductivities and transport numbers of solutions of some alkali and alkaline earth metal fluorosulfates in fluorosulfuric acid are reported. It is concluded that the fluorosulfate ion conducts mainly by a proton-transfer process. Conductometric studies of a number of other bases are reported. Dissociation constants are calculated for several weak bases. Densities of solutions of a number of solutes have been measured.

Introduction

Fluorosulfuric acid ionizes as a weak acid in dilute solution in the very weakly basic solvent sulfuric acid.[2a]

$$HSO_3F + H_2SO_4 = H_3SO_4^+ + SO_3F^-$$

This behavior suggests that pure liquid fluorosulfuric acid might be a still more acidic and less basic medium than 100% sulfuric acid.

Since there has only been one previous study of fluorosulfuric acid as a solvent system,[2b] a study has been conducted in this laboratory which has given the results reported in this and subsequent papers of this series.

A comparison of some of the physical properties of fluorosulfuric acid with those of sulfuric acid shows that, in addition to its greater acidity, fluorosulfuric acid has a lower boiling point (162.7° *vs.* 290–317° for H_2SO_4), a lower viscosity than sulfuric acid (1.56 *vs.* 24.54 cp. at 25°), and a very low freezing point (−89.0° *vs.* 10.37° for H_2SO_4). The density is 1.7264 g./cc. at 25° compared with 1.8267 g./cc. for H_2SO_4.

Experimental

Purification and Conductivity of Fluorosulfuric Acid.—Commerical fluorosulfuric acid (Allied Chemical Co.) was purified by double distillation at atmospheric pressure in a completely enclosed all-glass apparatus, which had been carefully dried by flaming under a stream of dry air. In the second distillation a constant-boiling fraction was collected directly in the conductivity cell. This acid generally had a conductivity in the range 1.09 to 1.4×10^{-4} ohm^{-1} cm.$^{-1}$. The conductivity of any given sample did not increase by more than 0.5% during twelve or more hours standing. It was not possible to reduce the conductivity of the acid by further distillation to less than 1.085×10^{-4} ohm^{-1} cm.$^{-1}$. This is the lowest conductivity that we have observed for the acid. The twice-distilled acid had a boiling point of 162.7 ± 0.1°, in excellent agreement with the value reported originally by Thorpe and Kirman.[3] The small variations in the conductivity of different samples of the acid may be attributed to the presence of very small and variable amounts of impurities, such as water. As there is probably a very slight decomposition of the acid into HF and SO_3 even at room temperature which may become appreciable at the boiling point of the acid, and as there may be some fractionation in the distillation, there may be small variable amounts of free SO_3 or HF in the distilled acid. Woolf[2b] also found a variation in the conductivity of different samples of the acid, but the lowest conductivity that he reported was 2.2×10^{-4} ohm^{-1} cm.$^{-1}$. He purified the acid by trap to trap distillation under reduced pressure. This could have given a distillate which contained more free HF than that present in the acid purified by distillation at atmospheric pressure. Hydrogen fluoride is a weak base in the fluorosulfuric acid solvent system and this could account for the high conductivity of the acid prepared by Woolf.

Conductivity Measurements.—The design of the cell used in measuring the conductivities of solutions in fluorosulfuric acid was similar to that used previously for sulfuric acid solutions[4] except that it contained three electrodes and had cell constants of approximately 2 and 40. Thus, a wide range of electrolyte concentrations could be covered by successive additions of electrolyte to the solution in the cell. The capacity of the cell was approximately 200 ml. The electrodes were plated with platinum black.[5]

In the early stages of this work the cells were calibrated using aqueous potassium chloride solution.[6a] Although this method is very accurate it was later found more convenient to calibrate the cells by measuring the resistance of minimum-conducting sulfuric acid.[6b] All measurements were made in an oil thermostat at 25 ± 0.002°.

Solid solutes were added to the cell by means of a weight buret with a wide-bore tap. After each addition of solute the cell was shaken well to ensure good mixing and placed in the thermostat.

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