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Sublimation study of triphenyl boron and the bond-dissociation enthalpy of $B-C_6H_5^{a}$

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The sublimation pressures of triphenyl boron, $B(C_6H_5)_3$, in the temperature range 340 to 380 K have been determined from simultaneous measurements of the rate of mass effusion and torsional recoil. The measured vapor pressures expressed by the equations:

 $\log_{10}(p_{\rm K}/p'') = (9.52 \pm 0.07) - (5.326 \pm 0.026) \times 10^3 ({\rm K}/T) \\ \log_{10}(p_{\rm T}/p'') = (10.08 \pm 0.06) - (5.518 \pm 0.022) \times 10^3 ({\rm K}/T)$

where $p_{\rm K}$ and $p_{\rm r}$ are the pressures measured by the Knudsen effusion and torsional recoil techniques, respectively, and $p^{\circ} = 101.325$ kPa, confirm that triphenyl boron is a monomer in the vapor phase in the temperature range of the measurements. The mean standard molar enthalpy and entropy of sublimation ($p^{\circ} = 101.325$ kPa) derived from these equations are: $\Delta_{\rm sub}H_{\rm m}^{\circ}$ {B(C₆H₅)₃, cr, 360 K} = (103.8 \pm 2.5) kJ \cdot mol^{-1} and $\Delta_{\rm sub}S_{\rm m}^{\circ}$ {B(C₆H₅)₃, cr, 360 K} = (187.6 \pm 7.6) J \cdot K^{-1} \cdot mol^{-1}. The mean molar bond-dissociation enthalpy $\langle D \rangle$ (B-C₆H₅) is calculated to be (459 ± 11.6) kJ \cdot mol^{-1}.

1. Introduction

The molar enthalpy of sublimation of triphenyl boron was reported as (111.3 ± 1.3) kJ·mol⁻¹ by Greenwood *et al.*⁽¹⁾ from Knudsen-effusion measurements in connection with a study of structural differences between the triphenyl compounds of Group III elements. The absolute vapor pressures as a function of temperature were not included. Greenwood *et al.* accounted for the relatively low enthalpy of sublimation of triphenyl boron, as compared with phenyl derivatives of other members of group III, by lack of coplanarity of the three phenyl rings with the B–C skeleton of the molecule. In this paper, the sublimation pressures and associated thermochemical properties of triphenyl boron are reported. The sublimation pressures have been determined from simultaneous measurements of the rate of mass effusion (Knudsen-effusion) and of torsional recoil (torsion-effusion) in the temperature range 340 to 380 K. The combination of Knudsen-effusion and torsion-

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effusion in one experimental arrangement offers the opportunity to check the mutual consistency of the two methods and to ascertain the mode of sublimation.

2. Experimental

The apparatus which has been used in previous sublimation studies, is described elsewhere.^(2,3) Only details unique to the present study are mentioned. The Pyrex enclosure of the effusion cell is of 85 mm i.d. The sample was heated by a 30 cm long cylindrical heating mantle, which tightly fits the Pyrex enclosure. The pertinent parameters of the spectroscopic graphite effusion cell are listed in table 1. The torsional constants for the tungsten wire (0.038 mm in diameter and 35 cm long) used as the torsion fiber in experiments 1 and 2, are: 0.8838 and 0.8846 $\times 10^{-7}$ N·m, respectively.

Triphenyl boron was prepared from trimethylammonium tetraphenylborate: $\{(CH_3)_3NH\}^+\{B(C_6H_5)_4\}^-$.⁽⁴⁾ The latter was precipitated by treatment of an aqueous solution of sodium tetraphenylborate, NaB(C₆H₅)₄, with trimethylamine hydrochloride, $\{(CH_3)_3NH\}^+Cl^-$. After filtration and thorough washing with water, the precipitate was thoroughly dried *in vacuo*. A nitrogen-atmosphere dry box was used for all subsequent handling or transfer operations. With nitrogen flow at atmospheric pressure, trimethylammonium tetraphenylborate was decomposed by heating at 473 to 483 K. When the evolution of trimethylamine and benzene ceased, the system was evacuated to remove the remainder of these volatile products. The remaining product, triphenyl boron, after cooling to room temperature, was crystallized from hexene, and was further purified by sublimation under vacuum. A freshly prepared sample was used in each of the two experiments. The melting temperatures were between 408 and 416 K. The literature values are 411 to 413 K and 415 to 416 K.^(4, 5) The broad range for the fusion temperature is probably due to sample instability in the vicinity of the melting temperature.

The experimental procedure described elsewhere was followed.⁽⁶⁾ To avoid exposure to oxygen and moisture, the cell was loaded with approximately 0.7 g of $B(C_6H_5)_3$ and its orifices were sealed with fused naphthalene before it was transferred from the nitrogen-atmosphere dry box. Prior to recording the first point in an experiment, the sample was maintained under vacuum for at least 48 h, then heated gradually to 350 K for experiment 1, and to 375 K for experiment 2. At each

TABLE 1. Parameters of the effusion cell: radius r; area a; moment arm d; depth h

	Orifice 1	Orifice 2
$10^2 r/cm$	4.07 + 0.03	4.05 +0.05
$10^{3} a/cm^{2}$	5.20 ± 0.08	5.15 ± 0.13
10 <i>d</i> /cm	11.09 ± 0.01	10.91 ± 0.01
$10^{2}h/cm$	1.84 ± 0.03	1.84 ± 0.03
h/r	0.452 ± 0.018	0.454 ± 0.020
Clausing factor W	0.817 ± 0.006	0.816 ± 0.007
Pressure factor f	0.864 ± 0.005	0.864 ± 0.006

setting of the temperature controller the temperature and angular displacement produced by the recoil of the suspended cell were measured every 300 to 400 s and the results were averaged.

3. Results

CALCULATIONS

The saturated vapor pressures in equilibrium with solid triphenyl boron were calculated according to the familiar equations of Knudsen-effusion:⁽⁷⁾

$$p_{\rm K} = (m/t)(a_1w_1 + a_2w_2)^{-1}(2\pi R T/M)^{1/2}, \tag{1}$$

and torsion-effusion:(8)

$$p_{\tau} = (2 \Upsilon \Theta) (a_1 d_1 f_1 + a_2 d_2 f_2)^{-1}, \tag{2}$$

where $p_{\rm K}$ is the Knudsen pressure; p_{τ} is the torsion pressure; m/t is the rate of mass effusion of substance from the cell; Υ is the constant of the torsion filament; Θ is the displacement angle of the torsion pendulum due to the vapor effusing from the cell; a, d, w, and f are the area, moment arm, transmission probability,⁽⁹⁾ and recoil force factor,⁽¹⁰⁾ respectively of the effusion orifices 1 and 2; T is the temperature of the sample in the cell; and M is the molar mass of the effusing vapor. The molar mass $M\{B(C_6H_5)_3\} = 242.127 \text{ g} \cdot \text{mol}^{-1}$ was used in the calculation of the Knudsen pressure $p_{\rm K}$. The angular displacement Θ , was determined from measurement of the deflection of the light from a galvanometer lamp after reflection at the mirror of the torsion assembly. The deflection was measured on a scale mounted on the arc of a circle with radius R = 1 m with the mirror as the center. The measured deflection Dis related to Θ through the geometry of the optical lever system by $\Theta = D/2R$. Linear least-squares treatment of $p_{\rm K}$ and p_{τ} for the two experiments, individually and collectively, was performed to establish the equation:

$$\log_{10}(p/p^{1}) = A - B(K/T).$$
(3)

The standard molar enthalpy and entropy of sublimation were calculated from B and A, respectively.

The results of effusion measurements and the calculated pressures for two experiments are presented in table 2 and in figure 1. The linear least-squares analyses of the results are summarized in table 3. The cited errors are the standard deviations obtained in the least-squares analyses. Also listed in table 3 are the results of linear least-squares analyses of the combined points of the two experiments. The standard deviation of $\log_{10}(p/p^2)$ from the calculated values is 0.02 for both Knudsen- and torsion-effusion. The relative mean errors are 3 and 4 per cent for both Knudsen- and torsion-effusion from experiments 1 and 2, respectively.

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The molar enthalpy of formation of gaseous triphenyl boron and the mean molar bond-dissociation enthalpy $\langle D \rangle (B-C_6H_5)$ were calculated using the following thermodynamic quantities.

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TABLE 2.	Effusion res	ults for	triphenyl	boron: 1	n is the	mass; t is	s the	time of	of effusion	and $p_{\rm K}$	the	pressure	in the
	Knudsen e	experime	ents; D is 1	the displ	acement	and p_{τ} the	e pres	ssure in	n the torsic	on exper	imen	ts	

	Knudsen			Torsion			Knud	Torsion			
T/K	m/mg	t/s	$10^3 p_{\rm K}/{\rm kPa}$	D/cm	$10^{3} p_{\tau} / k Pa$	T/K	<i>m</i> /mg	1:8	$10^3 p_{\rm K}/{\rm kPa}$	D/cm	$-10^2 p_v/\mathrm{kPa}$
					Evnorime	 					
					Experime	int no. 1					
339.8	1.48	6000	0.0790	0.76	0.0748	365.9	6.83	2400	0.9452	10.01	0.9825
343.8	0.93	2700	0.1109	1.07	0.1047	369.9	4.95	1200	1.378	14.99	1.471
344.6	0.87	2400	0.1169	1.17	0.1147	370.7	2.65	600	1.477	16.10	1.581
345.2	0.70	1800	0.1255	1.27	0.1247	371.5	2.80	600	1.562	17.22	1.691
351.7	1.72	2400	0.2334	2.44	0.2394	372.6	3.18	600	1.776	19.46	1.910
352.3	0.90	1200	0.2444	2.59	0.2544	373.5	8.57	1500	1.917	21.39	2.100
350.2	2.50	3900	0.2083	2.18	0.2144	375.0	14.00	2100	2.242	24.43	2.399
354.0	1.50	1800	0.2722	2.95	0.2893	374.5	3.77	600	2.112	23.37	2.294
358.0	1.90	1500	0.4162	4.52	0.4439	376.9	11.68	1500	2.625	29.31	2.878
360.3	4.37	2700	0.5335	5.64	0.5536	377.5	14.37	1800	2.693	30.53	2.997
361.5	2.80	1500	0.6163	6.45	0.6334	341.9	0.25	900	0.0892	0.97	0.0948
365.3	3.28	1200	0.9071	9.75	0.9576	342.6	0.52	1800	0.0928	0.97	0.0948
368.6	3.27	900	1.211	12.95	1.272	343.3	0.98	3000	0.1051	1.07	0.1047
					F						
					Experime	nt no. 2					
368.7	7.72	2400	1.072	12.19	1.198	357.2	1.19	900	0.4339	4.52	0.4443
369.4	8.40	2400	1.168	13.31	1.308	357.9	1.60	1200	0.4380	4.67	0.4593
368.8	5.95	1800	1.102	12.50	1.228	357.2	2.29	1800	0.4175	4.39	0.4318
375.6	19.20	3000	2.153	25.55	2.511	364.3	4.36	1800	0.8028	8.69	0.8537
377.9	12.15	1500	2.734	32.00	3.145	372.0	1.41	300	1.574	17.81	1.750
380.4	12.23	1200	3.452	40.69	3.999	371.0	2.61	600	1.455	16.48	1.620
350.0	3.45	5100	0.2198	2.29	0.2247	364.0	2.02	900	0.7436	8.33	0.8187
360.2	1.49	900	0.5456	5.99	0.5891	363.7	7.20	3300	0.7225	8.03	0.7888



FIGURE 1. Vapor pressure of triphenyl boron from Knudsen-effusion and torsion-effusion measurements. Knudsen (dashed line): \triangle , experiment 1; \triangle , experiment 2. Torsion (solid line): \bigcirc , experiment 1; \bigcirc , experiment 2.

given are the bounds T_1 and T_2 of the temperature range and $\Delta_{sub}H_m^\circ$ and $\Delta_{sub}S_m$									
Expt.	Method	A	В	$\frac{T_1}{K}$	$\frac{T_2}{K}$	$\frac{\Delta_{\rm sub}H_{\rm m}^\circ}{\rm kJ\cdot mol^{-1}}$	$\frac{\Delta_{sub}S_m}{J\cdot K^{-1}\cdot mol^{-1}}$		
1	Knudsen	9.68±0.10	5381±37	340	378	103.0 ± 0.7	185.2 ± 2.0		
	Torsion	10.11 ± 0.09	5531 ± 33	340	378	105.9 <u>+</u> 0.6	193.6 <u>+</u> 1.8		
2	Knudsen	9.15 ± 0.25	5194 ± 93	350	380	99.4 <u>+</u> 1·8	175.2 ± 4.9		
	Torsion	9.95 ± 0.23	5472 ± 85	350	380	104.8 <u>+</u> 1.6	190.4 ± 4.4		
1, 2	Knudsen	9.52 ± 0.07	5326 ± 26	340	380	102.0 ± 0.5	182.2 ± 1.4		
	Torsion	10.08 + 0.06	5518 + 22	340	380	105.6 ± 0.4	192.9 ± 1.1		

TABLE 3. Sublimation results for triphenyl boron. The coefficients A and B are for the equation $\log_{10}(p/p^2) = A - B(K/T)$ where p is the vapor pressure and p^2 is the standard pressure (101.325 kPa); also given are the bounds T_1 and T_2 of the temperature range and $\Delta_{sub}H_m^\circ$ and $\Delta_{sub}S_m^\circ$

The standard molar enthalpy of the reaction:

$$B(C_6H_5)_3(cr) + 3H_2O_2(l) = 3C_6H_6O(cr) + H_3BO_3(cr),$$
(4)

at 298.15 K was reported by Pedley and Rylance⁽¹¹⁾ to be $\Delta H_m^{\circ} = -(1074.5 \pm 7.5)$ kJ·mol⁻¹.[†] This value when combined with the standard molar enthalpies of formation of H₂O₂(l), C₆H₆O(cr), and H₃BO₃(cr) gives the standard molar enthalpy of formation of crystalline triphenyl boron. Using the values: $\Delta_f H_m^{\circ}(H_2O_2, l, 298.15 \text{ K}) = -(187.8 \pm 0.0) \text{ kJ} \cdot \text{mol}^{-1}, {}^{(12)}\Delta_f H_m^{\circ}(H_3BO_3, \text{cr}, 298.15 \text{ K}) = -(1094.5 \pm 0.5) \text{ kJ} \cdot \text{mol}^{-1}, {}^{(12)}$ and $\Delta_f H_m^{\circ}(C_6H_6O, \text{cr}, 298.15 \text{ K}) = -(165.0 \pm 0.7) \text{ kJ} \cdot \text{mol}^{-1}, {}^{(12)}$ the calculated standard molar enthalpy of formation is $\Delta_f H_m^{\circ}(B(C_6H_5)_3, \text{cr}, 298.15 \text{ K}) = (48.4 \pm 7.8) \text{ kJ} \cdot \text{mol}^{-1}$.

The average standard molar enthalpy of sublimation at 360 K from table 3, when corrected to 298.15 K gives $\Delta_{sub}H_m^{\circ}\{B(C_6H_5)_3, cr, 298.15 \text{ K}\} = (107.0 \pm 2.5) \text{ kJ} \cdot \text{mol}^{-1}$. The standard molar enthalpy of formation of the vapor is $\Delta_f H_m^{\circ}\{B(C_6H_5)_3, g, 298.15 \text{ K}\} = (155.4 \pm 8.2) \text{ kJ} \cdot \text{mol}^{-1}$.

The mean molar boron-phenyl bond-dissociation enthalpy may be expressed by

$$\langle D \rangle (B - C_6 H_5) = \frac{1}{3} [\Delta_f H_m^{\circ}(B, g) + 3\Delta_f H_m^{\circ}(C_6 H_5, g) - \Delta_f H_m^{\circ} \{ B(C_6 H_5)_3, g \}].$$
(5)

Using $\Delta_{\rm f} H^{\circ}_{\rm m}({\rm C}_{6}{\rm H}_{5}, {\rm g}, 298.15 {\rm K}) = (324.3 \pm 10.5) {\rm kJ} \cdot {\rm mol}^{-1,(13)}$ and $\Delta_{\rm f} H^{\circ}_{\rm m}({\rm B}, {\rm g}, 298.15 {\rm K}) = (559.8 \pm 12.6) {\rm kJ} \cdot {\rm mol}^{-1,(14)}$ the mean molar bond-dissociation enthalpy is found to be: $\langle D \rangle ({\rm B} - {\rm C}_{6}{\rm H}_{5}) = (459 \pm 11.6) {\rm kJ} \cdot {\rm mol}^{-1}$.

4. Discussion

SUBLIMATION PRESSURES

The results presented in table 2 show that the torsion pressures p_{τ} are larger than the Knudsen pressures $p_{\rm K}$. The average $p_{\tau}/p_{\rm K}$ is about (1.06 ± 0.05) . This lack of agreement was observed in the vapor pressures of cadmium in a sublimation study using the same experimental setup where a $p_{\tau}/p_{\rm K}$ value of (1.04 ± 0.03) was obtained. The deviation of $p_{\tau}/p_{\rm K}$ from unity might be partly attributable to factors specific to

[†] Throughout this paper the standard pressure p° was taken as 101.325 kPa.

the experimental arrangement rather than to lack of information about the composition of the gaseous phase. Thus, the present results establish that $B(C_6H_5)_3$ vapor is a monomer. It is surmised that p_r is larger than p_{κ} because of the additional torque imparted by the effustate molecules that are preferentially reflected from the enclosure wall to the same side of the cell from which they originated. On the other hand, the mass effusion may be too low because some of the molecules outside the cell return through the orifices. These effects, partly dependent on the size of the surrounding enclosure of the effusion cell, appear to be larger for $p_{\rm K}$ than for $p_{\rm r}$ ^(15,16) The dependence on the size of the enclosure had been demonstrated with a decrease in $p_{\rm r}/p_{\rm K}$ from (1.17 ±0.05) to (1.04 ±0.03) using cell enclosures with inside diameters of 65 mm⁽¹⁷⁾ and 85 mm, respectively. In the absence of a definite criterion for deciding which of the two sets of measurements (Knudsen effusion and torsion effusion) from the two experiments is the more reliable, a linear least-squares treatment was applied to the combined points of each set. The resulting standard deviation of $\log_{10}(p_{\rm K}/p^{\circ})$ and of $\log_{10}(p_{\rm T}/p^{\circ})$ is 0.02. The mean relative errors in (p/p°) are 3.8 and 3.3 per cent, respectively. The close agreement between the linear leastsquares analyses of the combined points of each set with the results of the points of the corresponding determination from the two experiments, separately, suggests that both experiments are equally reliable. However, we do not intend to imply that the most reliable values of $\log_{10}(p/p^{\circ})$ and thermodynamic quantities derived therefrom are necessarily those obtained by this averaging method.

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Two values for the molar enthalpy of sublimation in the temperature range 340 to 380 K are obtained from the linear least-squares treatment of the combined points of each set of determinations. Although the presence of different systematic effects in the two methods is recognized we accept the average: $\Delta_{sub}H_m^{\circ}\{B(C_6H_5)_3, cr, 360 \text{ K}\}$ = (103.8±2.5) kJ·mol⁻¹. This value is lower than that reported by Greenwood et al.⁽¹⁾ The $\Delta_{sub}H_m^{\circ}\{B(C_6H_5)_3, cr, 298.15 \text{ K}\}$ based on the present results is consistent with a contribution to the molar enthalpy of sublimation of approximately 5.86 kJ·mol⁻¹ for nonplanar molecules.⁽²⁾ Greenwood et al. inferred that nonplanarity of the three phenyl rings with the B–C skeleton in $B(C_6H_5)_3$ is probably due to steric interference, which is almost non-existent in compounds with larger central atoms such as Ga and In.

The mean value of the standard molar entropy of sublimation is obtained by the same computation method used for the molar enthalpy of sublimation. The $\Delta_{sub}S_m^{\circ}\{B(C_6H_5)_3, cr, 360 \text{ K}\} = (187.6 \pm 7.6) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ is consistent with a contribution of $63 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ per phenyl group based on entropies of sublimation of tetraphenyl compounds of Group IV.⁽¹⁸⁾

The mean molar bond-dissociation enthalpy $\langle D \rangle (B-C_6H_5)$ is larger than $\langle D \rangle (M-C_6H_5)$ of the tetraphenyl compounds of Group IV,⁽¹⁸⁾ and the triphenyl compounds of Group V.⁽¹⁹⁾ Lack of sufficient thermodynamic results does not permit a check of a trend in $\langle D \rangle (M-C_6H_5)$ within the triphenyl compounds of Group III. It has been observed from the tetraphenyl compounds of Group IV⁽¹⁸⁾

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and the triphenyl compounds of Group $V^{(19)}$ that the change of $\langle D \rangle$ with M becomes progressively linear as M increases. Such a trend in Group III compounds is unlikely. The change of molecular structure from nonplanar in compounds of the light elements to planar in compounds of the heavier elements in the group may affect the bond strength.

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