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The Standard Heat of Formation of Boron Phosphide

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Although there is considerable current interest in boron phosphide because of its potential semiconductor properties (*cf.* other group III phosphides), literature values for $\Delta H_f{}^\circ{}_{298}[\mathrm{BP(c)}]$ vary between −20 and −115 kcal mol^{-1}. This note reports a new value for this datum, obtained indirectly. In view of the wide divergence in literature data, the available sources are briefly discussed.

Using a flow technique, Stone, *et al.*,[1] have determined the equilibrium constant at eight temperatures between 1193 and 1843°K for

$$\mathrm{BCl_3(g)} + {}^3/_2\mathrm{H_2(g)} + {}^1/_4\mathrm{P_4(g)} \rightleftharpoons \mathrm{BP(cubic)} + 3\mathrm{HCl(g)}$$

With an estimated heat capacity for BP, these workers derived for $\mathrm{B}(\beta\ \mathrm{rhom}) + \mathrm{P}(\alpha\ \mathrm{white}) = \mathrm{BP(cubic)}$, $\Delta H^\circ{}_{298} = -19.9$ kcal mol^{-1}. The likely error is ± 4 kcal mol^{-1}.

By a similar technique, Medvedeva, *et al.*,[2] have studied the equilibrium

$$2\mathrm{H_2(g)} + 4\mathrm{BBr(g)} + \mathrm{P_4(g)} \rightleftharpoons 4\mathrm{BP(c)} + 4\mathrm{HBr}$$

at one temperature, 1473°K. Estimating $S^\circ[\mathrm{BP(c)}]$ from the isoelectronic SiC and AlN, they derived $\Delta H_f{}^\circ{}_{1473}[\mathrm{BP(c)}] = -99.6 \pm 0.3$ kcal mol^{-1}. Using Stone's estimate for $C_p[\mathrm{BP(c)}]$ and other heat capacities from ref 3, $\Delta H_f{}^\circ{}_{298}[\mathrm{BP(c)}] = -91.4$ kcal mol^{-1}.

Kischio[4] has studied the following two reactions in a combustion calorimeter: $\mathrm{BP(c)} + 4\mathrm{Cl_2(g)} = \mathrm{PCl_5 \cdot BCl_3(c)}$ and $\mathrm{B(am.)} + 4\mathrm{Cl_2(g)} + \mathrm{P(violet)} = \mathrm{PCl_5 \cdot BCl_3(c)}$. No experimental details were given and he derived for $\mathrm{B(am.)} + \mathrm{P(violet)} = \mathrm{BP(c)}$, $\Delta H^\circ{}_{295} = -29 \pm 2$ kcal mol^{-1}. Correcting to $\mathrm{B}(\beta\ \mathrm{rhom})$ and $\mathrm{P}(\alpha\ \mathrm{white})$, $\Delta H_f{}^\circ{}_{295}[\mathrm{BP(c)}] = -28 \pm 2$ kcal mol^{-1}.

In the presence of benzoic acid as promoter, Thevenot[5] found that the combustion of BP under 40 atm of oxygen was almost quantitative: for $\mathrm{BP(c)} + 2\mathrm{O_2(g)} = \mathrm{BPO_4(c)}$, $\Delta H^\circ{}_{298} = -224.9 \pm 4.7$ kcal mol^{-1}. Using Paule's figure,[6] $\Delta H_f{}^\circ[\mathrm{BPO_4(c)}] = -339 \pm 10$ kcal mol^{-1}, Thevenot derived for $\mathrm{B(c)} + \mathrm{P(red)} = \mathrm{BP(c)}$, $\Delta H^\circ{}_{298} = -114.1 \pm 14.7$ kcal mol [-112.3 ± 14.7 kcal mol^{-1} with reference to $\mathrm{P}(\alpha\ \mathrm{white})$].

Using an adapted bomb calorimeter, Gal'chencko[7] combusted BP(c) in 7 atm of chlorine and obtained for $\mathrm{BP(c)} + 4\mathrm{Cl_2(g)} = \mathrm{PCl_5 \cdot BCl_3(c)}$, $\Delta H^\circ{}_{298} = -192.25 \pm 0.20$ kcal mol^{-1}. Using this datum and $\Delta H_f{}^\circ[\mathrm{PCl_5 \cdot BCl_3(c)}]$, reported below, we derive $\Delta H_f{}^\circ{}_{298}[\mathrm{BP(c)}]$.

Experimental Section

The complex $\mathrm{PCl_5 \cdot BCl_3}$ was prepared according to Holmes.[8] *Anal.* Calcd for $\mathrm{BCl_8P}$: B, 3.32; Cl, 87.2. Found: B, 3.4; Cl, 87.3. The calorimeter and its standardization have been previously described.[9] All results are reported in terms of the thermochemical calorie (≡4.1840 abs. J).

Results

$\mathrm{PCl_5 \cdot BCl_3(c)}$ hydrolyzed rapidly and quantitatively, but without undue violence, to phosphoric, boric, and hydrochloric acids: $\Delta H_f{}^\circ[\mathrm{PCl_5.BCl_3(c)}] = \Delta H_f{}^\circ[\mathrm{H_3PO_4},\ n\mathrm{H_2O}] + 8\Delta H_f{}^\circ[\mathrm{HCl},\ (n/_8)\mathrm{H_2O}] + \Delta H_f{}^\circ[\mathrm{H_3BO_3},\ n\mathrm{H_2O}] - 7\Delta H_f{}^\circ[\mathrm{H_2O(l)}] - \Delta H_{\mathrm{obsd}}$. See Table I for the parameters in this equation.

TABLE I

Temp, °C	n^a	$-\Delta H_{\mathrm{obsd}}$, kcal mol^{-1}	$-\Delta H_f{}^\circ{}_{298}$, kcal mol^{-1}
24.9	26,290	155.3	−251.15
25.0	25,555	155.3	−251.1
24.9	14,985	154.1	−252.2
25.1	15,354	153.4	−252.9
24.8	30,105	155.4	−251.1
24.9	39,271	155.2	−251.3
24.5	19,867	155.0	−251.4
24.6	20,151	156.1	−250.3

[a] *n* is the mole ratio of water to adduct.

Ignoring the heats of mixing of the products and using ancillary data from ref 10, we derive $\Delta H_f{}^\circ{}_{298}[\mathrm{PCl_5 \cdot BCl_3(c)}] = -251.4 \pm 0.8$ kcal mol^{-1}; hence, $\Delta H_f{}^\circ{}_{298}[\mathrm{BP(c)}] = -59.15 \pm 0.8$ kcal mol^{-1}, where the uncertainty interval is twice the standard deviation of the mean.

For this figure to be valid it must be verified that the $\mathrm{PCl_5 \cdot BCl_3}$ produced by high-temperature chlorination was identical with the sample used here. Gal'chenko[7] reported his chlorinated product as a snow white solid, being nondeliquescent after prolonged exposure in air and analyzing as $\mathrm{BPCl_8}$. This description coincides with that for our sample. Gal'chenko also recorded an X-ray diffraction pattern, and these results, together with the powder pattern obtained for the sample used in this work, are compared with a corresponding pattern obtained by Petro and Shore for $\mathrm{PCl_5 \cdot BCl_3}$. The sample of these latter authors was prepared using a slightly modified technique of that used for our sample.[8] The X-ray data for the sample used in this work were obtained using CuKα radiation (λ 1.542 Å) with the intensities visually estimated. (See Table II.)

Our spacings include all those of Petro, *et al.*, and are in good agreement. Also, we record several addi-

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Table II

Spacings (d) and Intensities from X-Ray Diffraction Patterns for $BPCl_8$ Obtained by Different Workers[a]

Gal'chenko,[b] kX	Petro and Shore,[c] Å	This work,[d,e] Å
		6.73 vvw
6.24 m	6.28 vw	6.27 m
5.96 m	5.95 vw	5.91 w
5.21 vw	5.19 m	5.20 m
		4.93 vvw
4.716 m	4.75 s	4.72 s
4.595 m		
4.521 m	4.55 s	4.50 s
4.328 vw		4.32 w
3.750 m	3.77 m	3.74 ms
3.709 w		
3.585 mw		3.56 w
3.518 w	3.48 w	3.49 m
3.456 w		
		3.29 vw
3.207 mw	3.21 vw	3.18 mw
		3.06 vvw
2.951 mw	2.97 m	2.95 ms
2.882 w	2.89 w	2.875 mw
2.790 m	2.81 s	2.796 s[d]

[a] Cu Kα radiation in each case. [b] See ref 7; 1.00202 Å = 1 kX. [c] V. P. Petro and S. G. Shore, *J. Chem. Soc.*, 336 (1964). [d] Eight further weak reflections were also recorded. [e] Samples sealed in 0.3-mm capillaries under dry nitrogen.

tional weak reflections. The spacings are also coincident with those of Gal'chenko with the exception of his 4.595 (m), 3.709 (w), and 3.456 (w) kX, which neither our nor Petro's sample shows. Two of these are weak, and in view of the close correlation of the remaining 13 spacings, it is overwhelmingly probable that all three samples were identical.

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Raman Spectra of Solid Bismuth(III) Bromide and Chloride

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In the gas phase, $BiCl_3$ and $BiBr_3$ exist as discrete pyramidal molecules.[2] Largely owing to early photographic Raman evidence, a similar molecular structure has seemed likely for $BiCl_3$ in the solid state. The reported Raman frequencies are four in number, as expected of C_{3v} pyramidal symmetry, but the two sets of data are not in complete agreement: Bhagavantam[3] found Raman lines for solid $BiCl_3$ at 290, 240, 130, and 90 cm^{-1}, while Krishnamurti[4] found them at 288, 242, 169, and 153 cm^{-1}. In addition, the far-infrared spectrum of solid $BiBr_3$ dispersed in a polyethylene matrix exhibits four fundamentals at 196, 169, 104, and 89 cm^{-1} consistent with C_{3v} symmetry for this molecule as well (the hygroscopic nature of $BiBr_3$ prevented a Nujol mull from being used).[5]

A discrepancy arises, however, when the nuclear quadrupole resonance (nqr) spectra of $BiCl_3$ and $BiBr_3$ are examined. In the case of $BiCl_3$, the chlorine nqr spectrum reveals two nonequivalent positions for Cl in the unit cell, with approximately equal numbers of Cl atoms in each position.[6] For both $BiCl_3$ and $BiBr_3$, the large asymmetry parameter of ^{209}Bi ($\eta \sim 0.55$) indicates distortion from C_{3v} symmetry and has been interpreted in terms of cross bonding among the molecules in the solid.[6,7] The nqr studies rule out a formulation such as Bi_2Cl_6 and eliminate a structure similar to that of BiI_3, in which Bi(III) is octahedrally surrounded by iodine atoms. The deviation from C_{3v} symmetry reportedly is greater for $BiBr_3$ than for $BiCl_3$.

Available X-ray data for $BiCl_3$ and $BiBr_3$ are of uncertain value, as they consist only of powder patterns which indicate that the unit cells for both solids contain four molecules and are primitive cubic, the probable space group for both being P_{2_13}.[8]

To help clarify this structural question and determine accurate Raman frequencies for crystalline $BiCl_3$ and $BiBr_3$, photoelectrically recorded Raman spectra were obtained for these solids.

Experimental Section

Reagent grade anhydrous $BiCl_3$ (Baker) and $BiBr_3$ (Alfa) were dried *in vacuo* at *ca.* 55° for at least 2 days, while reagent grade $BiCl_3 \cdot H_2O$ (Mallinckrodt) was used without further treatment. In order to reduce hydrolysis in a methanolic solution of $BiCl_3$, anhydrous methanol (Fisher) was refluxed over CaH_2 and distilled. All solid samples were manipulated in a dry nitrogen-filled glove bag and the methanolic solution of $BiBr_3$ was prepared and filtered under a stream of dry N_2.

The Raman spectra reported herein were obtained at 46° using a Cary Model 81 spectrophotometer, with 4358-Å Hg excitation for white, crystalline $BiCl_3$ and $BiCl_3 \cdot H_2O$ and 5461-Å Hg excitation for yellow, crystalline $BiBr_3$ and the methanolic $BiBr_3$ solution. The 5461-Å mercury line could be isolated using the green filter solution described previously,[9] although in the case of solid $BiBr_3$ the spectrum was unchanged when this filter solution was not used. A sheet of Ozalid filter (General Aniline and Film), wrapped around the conical sample tube, served to remove the 4047-Å mercury line. The spectra of solid $BiCl_3$ and $BiCl_3 \cdot H_2O$ were examined up to 600 cm^{-1} and that of solid $BiBr_3$ to 330 cm^{-1}. For all three solids, the anti-Stokes Raman spectrum was also obtained (using 5461-Å excitation) to rule out possible "instrument lines." In addition, spectra of solid $BiBr_3$ and $BiCl_3$ were recorded using a Spex Industries helium–neon laser Raman spectrophotometer (6328-Å excitation) and, except for improved resolution, were identical with those from the Cary

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