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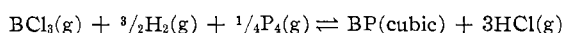
The Standard Heat of Formation of Boron Phosphide

By P. J. GARDNER

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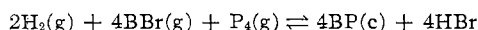
Although there is considerable current interest in boron phosphide because of its potential semiconductor properties (*cf.* other group III phosphides), literature values for ΔH_f° [BP(c)] vary between -20 and -115 kcal mol $^{-1}$. This note reports a new value for this datum, obtained indirectly. In 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



With an estimated heat capacity for BP, these workers derived for B(β rhom) + P(α white) = 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



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

Kischio⁴ has studied the following two reactions in a combustion calorimeter: BP(c) + 4Cl₂(g) = PCl₅·BCl₃(c) and B(am.) + 4Cl₂(g) + P(violet) = PCl₅·BCl₃(c). No experimental details were given and he derived for B(am.) + P(violet) = BP(c), $\Delta H^\circ_{295} = -29 \pm 2$ kcal mol $^{-1}$. Correcting to B(β rhom) and P(α white), ΔH_f° [BP(c)] = -28 ± 2 kcal mol $^{-1}$.

In the presence of benzoic acid as promoter, Thevenot⁵ found that the combustion of BP under 40 atm of oxygen was almost quantitative: for BP(c) + 2O₂(g) = BPO₄(c), $\Delta H^\circ_{298} = -224.9 \pm 4.7$ kcal mol $^{-1}$. Using Paule's figure,⁶ ΔH_f° [BPO₄(c)] = -339 ± 10 kcal mol $^{-1}$, Thevenot derived for B(c) + P(red) = BP(c), $\Delta H^\circ_{298} = -114.1 \pm 14.7$ kcal mol [-112.3 ± 14.7 kcal mol $^{-1}$ with reference to P(α white)].

Using an adapted bomb calorimeter, Gal'chenko⁷

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(2) Z. S. Medvedeva and Y. K. Grinberg, *Russ. J. Inorg. Chem.*, **9**, 270 (1964).

(3) "JANAF Thermochemical Tables," U. S. Department of Commerce, National Bureau of Standards, distributed by the Clearinghouse for Federal, Scientific, and Technical Information.

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(5) F. Thevenot, *Bull. Soc. Chim. France*, **98** (1968).

(6) R. C. Paule, "Studies at High Temperatures," University Microfilms, Ann Arbor, Mich., 1962, No. 62-2255.

combusted BP(c) in 7 atm of chlorine and obtained for BP(c) + 4Cl₂(g) = PCl₅·BCl₃(c), $\Delta H^\circ_{298} = -192.25 \pm 0.20$ kcal mol $^{-1}$. Using this datum and ΔH_f° [PCl₅·BCl₃(c)], reported below, we derive ΔH_f° [BP(c)].

Experimental Section

The complex PCl₅·BCl₃ was prepared according to Holmes.⁸ *Anal.* Calcd for BCl₃P: 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

PCl₅·BCl₃(c) hydrolyzed rapidly and quantitatively, but without undue violence, to phosphoric, boric, and hydrochloric acids: ΔH_f° [PCl₅·BCl₃(c)] = ΔH_f° [H₃PO₄, n H₂O] + $8\Delta H_f^\circ$ [HCl, ($n/8$)H₂O] + ΔH_f° [H₃BO₃, n H₂O] - $7\Delta H_f^\circ$ [H₂O(l)] - ΔH_{obsd} . See Table I for the parameters in this equation.

TABLE I

Temp, °C	n^a	$-\Delta H_{\text{obsd}}$, kcal mol $^{-1}$	$-\Delta H_f^\circ$, 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 ΔH_f° [PCl₅·BCl₃(c)] = -251.4 ± 0.8 kcal mol $^{-1}$; hence, ΔH_f° [BP(c)] = -59.15 ± 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 PCl₅·BCl₃ produced by high-temperature chlorination was identical with the sample used here. Gal'chenko⁷ reported his chlorinated product as a snow white solid, being nondeliquescent after prolonged exposure in air and analyzing as BPCl₃. 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 PCl₅·BCl₃. 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 CuK α 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 BiCl_3 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 $K\alpha$ 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: Bhagavantam³

found Raman lines for solid BiCl_3 at 290, 240, 130, and 90 cm^{-1} , while Krishnamurti⁴ 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 ²⁰⁹Bi ($\eta \sim 0.55$) 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_{213} .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 $\text{BiCl}_3 \cdot \text{H}_2\text{O}$ (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 $\text{BiCl}_3 \cdot \text{H}_2\text{O}$ 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 $\text{BiCl}_3 \cdot \text{H}_2\text{O}$ 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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(3) S. Bhagavantam, *Indian J. Phys.*, **5**, 35 (1930).