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THERMODYNAMIC STABILITY OF ORTHORHOMBIC BLACK PHOSPHORUS *

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ABSTRACT

The energy of combustion in fluorine of orthorhombic black phosphorus has been measured. On the basis of this result and a similar earlier measurement on α-white phosphorus, the enthalpy of the P(α, white) = P(orthorhombic, black) transition was found to be $-(21.2 \pm 2.1)$ kJ mol^{-1}. Our earlier reported value for $\Delta_f H_m^\ominus(PF_5, g, 298.15\ K)$ [Trans. Faraday Soc., 62 (1966) 2709] is revised slightly to $-(1593.6 \pm 1.2)$ kJ mol^{-1}.

INTRODUCTION

Phosphorus obtained by condensation of P_4(g) is a white, waxy solid given the designation α. When heated in a sealed container to temperatures in excess of approximately 700 K, α-white phosphorus is converted to red phosphorus, the most common form of which is amorphous. At somewhat higher temperatures, several crystalline modifications of red phosphorus are formed. Application of very high pressures transforms white or red phosphorus to the black allotrope—a soft, graphite-like solid discovered by Bridgman [1].

Some time ago, as part of an investigation [2] whose main objective was the establishment of a precise value for the standard molar enthalpy of

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Dedicated to Professor Oswald Kubaschewski in honour of his contribution to thermochemistry.

formation $\Delta_f H_m^\ominus$ of PF_5 at 298.15 K, we reported the standard energies of combustion in fluorine and, by derivation, the relative thermodynamic stabilities and enthalpies of transition of several allotropes of phosphorus. Unsuccessful efforts were made at that time to procure some black phosphorus. However, such a specimen has recently been made available for our studies, and the present investigation reports a calorimetric determination of the energy of combustion of this material in fluorine. On the basis of this work, it is shown that black phosphorus is the most stable phosphorus allotrope at 298.15 K.

EXPERIMENTAL PROCEDURE AND OBSERVATIONS

Black orthorhombic phosphorus was prepared [3] from red phosphorus at the Muroran Institute of Technology. A wedge-type, cubic-anvil, high-pressure apparatus was used. The phosphorus was melted in a carbon furnace at 1273 K under a pressure of 1 GPa and then cooled. The black phosphorus sample thus obtained was nearly of single-crystal quality; it was sealed under vacuum in a glass tube and sent to Argonne National Laboratory, where it was opened and stored in a helium-atmosphere glovebox. There was only one thermodynamically significant impurity: (0.79 ± 0.08) mass per cent of oxygen, measured by means of a Leco oxygen determinator.

We used essentially the same combustion–calorimetric procedure and apparatus as in our earlier work [2]. High-purity (> 99.99 mol%) fluorine was compressed into the storage tank of the reaction vessel to a pressure of approximately 1.825 MPa. Upon expansion the (combustion) pressure was approximately 0.81 MPa. Black phosphorus, supported on a prefluorinated nickel dish, ignited spontaneously in the expanded fluorine. After the first combustion experiment, in which a 10.6-g dish underwent significant additional fluorination, we subsequently used a 48-g dish, which did not. The results of a series of blank experiments [4] were reproducible with the exception of the first one, and it was applied only to the first combustion experiment, which it immediately followed.

We have previously shown [2] that phosphorus combines quantitatively with high-pressure fluorine according to the reaction

$$P(s) + 2\tfrac{1}{2}F_2(g) = PF_5(g) \qquad (1)$$

It was also shown that the oxygen impurity, assumed to have been combined as P_4O_{10}, reacted to form mostly PF_5 and O_2 along with amounts of POF_3 equivalent to about 10% of the oxygen. We have evidence from IR spectroscopic measurements [5] of the presence of comparable quantities of POF_3 in the present combustion gases.

RESULTS

Detailed results of the energy-of-combustion measurements are given in Table 1. The symbols in the table are explained as follows: m is the mass of black phosphorus reacted; ε(calor), the energy equivalent of the calorimetric system inclusive of the empty combustion bomb and tank, (13908.1 ± 0.7) J K^{-1} for experiment no. 1, and (13905.8 ± 0.7) J K^{-1} for the other experiments, was determined by combustion in oxygen of National Bureau of Standards sample 39i of benzoic acid; $\Delta\theta_c$ is the corrected temperature rise of the calorimeter; ΔU(contents) is a correction for the contents of the bomb, and is based on literature values for the heat capacities of Ni, P(black), F_2, and PF_5; ΔU(gas), calculated as described by Hubbard [6], incorporates the intermolecular-force constants for F_2 [7] and PF_5 [8]; the origins of ΔU(blank) and its determination have been detailed in reference 4; $\Delta U(NiF_2)$ is a correction for the fluorination of the Ni crucible (in just one experiment) and is derived from $\Delta_f H_m^{\ominus}(NiF_2)$ [9]; and $\Delta_c U_m^{\ominus}/M$(sample) is the specific energy of combustion of the sample, obtained by combining the energy quantities and dividing by m for a given experiment. The impurity correction assumes, as in our previous study [2], that the oxygen was present as P_4O_{10} which reacted with fluorine

$$P_4O_{10}(cr) + 10F_2(g) = 4PF_5(g) + 5O_2(g) \qquad (2)$$

We mentioned earlier that IR scans of the combustion products indicated the presence of small ($\leqslant$ 10 mol%) quantities of POF_3. Had we allowed for such quantities of POF_3, the impurity correction would not have been changed significantly from the value given in Table 1.

TABLE 1

Detailed calorimetric results for the combustion of black phosphorus in fluorine ($T = 298.15$ K; $p^{\ominus} = 101.325$ kPa)

	Expt. no.				
	1	3	4	6	7
m (g)	0.25112	0.24120	0.23898	0.25612	0.23702
ε(calor)($-\Delta\theta_c$) (J)	−12620.3	−12088.0	−11944.2	−12790.3	−11839.0
ΔU(contents) (J)	−6.5	−22.1	−21.8	−23.4	−21.6
ΔU(gas) (J)	0.2	0.5	0.5	0.5	0.5
ΔU(blank) (J)	8.9	−4.0	−4.0	−4.0	−4.0
ΔU(impurities) (J)	−134.9	−129.5	−128.3	−137.5	−127.3
$\Delta U(NiF_2)$ (J)	26.3	0.0	0.0	0.0	0.0
$\Delta_c U_m^{\ominus}/M$(P,black) (kJ g^{-1})	−50.678	−50.759	−50.623	−50.581	−50.592
$\langle \Delta_c U_m^{\ominus}/M(\text{P,black}) \rangle = -(50.647 \pm 0.033)$ kJ g^{-1} [a]					

[a] Mean specific energy of combustion of P(black); the uncertainty is the standard deviation of the mean.

STANDARD MOLAR ENTHALPY OF FORMATION OF PF_5

The correction ΔU(blank) has been discussed at length in a previous paper [4]. Briefly, this quantity, determined in separate experiments, combines the endothermic effect of the expansion of fluorine from the storage tank into the empty bomb and the subsequent exothermic reaction of the expanded fluorine with traces of moisture still present in the bomb despite careful preconditioning. In the same paper, we outlined a new method for calculating the corrected temperature rise in such experiments. As a result, the ΔU(blank) values published as part of our previous study [2] of α-white phosphorus have to be changed.

The consequent change in $\Delta_f H_m^\ominus(PF_5, g)$ is minor, from $-(1593.3 \pm 1.3)$ kJ mol^{-1} [2] to $-(1593.6 \pm 1.2)$ kJ mol^{-1}. In the recalculation, we have also used the most recent value for the relative atomic mass of phosphorus, 30.973762 g mol^{-1}.

The specific energy of combustion of black phosphorus given in Table 1 is $-(50.647 \pm 0.033)$ kJ g^{-1} and the recalculated specific energy of combustion of α-white phosphorus (on which $\Delta_f H_m^\ominus$ given above is based) is $-(51.331 \pm 0.018)$ kJ g^{-1}. Thus, the specific energy (and enthalpy) of transition is $-(684 \pm 38)$ J g^{-1}, and the molar enthalpy of transition at 298.15 K and a pressure of 101.325 kPa $\Delta_{trs} H_m^\ominus = -(21.2 \pm 2.1)$ kJ mol^{-1} for the reaction

$$P(cr, \alpha, white) = P(cr, orthorhombic, black) \qquad (3)$$

The uncertainty in $\Delta_{trs} H_m^\ominus$ has been estimated, due allowance being made for common uncertainties in the calorimetry, ΔU(blank) and, in part, the impurity correction.

DISCUSSION

Our value for the energy of combustion of P(black) is more positive than for any of the other allotropes; therefore it is the most stable form at 298.15 K. The next most stable allotrope, P(V), has a specific energy of combustion of $-(50.75 \pm 0.02)$ kJ g^{-1}.

Enthalpies of transition of the phosphorus allotropes have been discussed in the literature most notably by Rodewald [10], Stephenson et al. [11], and Jacobs [12]. Measurements of the enthalpies of reaction of several phosphorus samples with (carbon disulfide + bromine) in a twin-calorimetric system have been reported by Jacobs; it is clear from that study that black phosphorus is the most stable allotrope (measurements were made on two samples, one prepared by Bridgman and the other by Jacobs).

The vapor pressures of various forms of phosphorus have been critically reviewed by Rodewald [10]. He used the measurements of Smits and

Bokhorst [13] to recalculate the enthalpy of vaporization

$$4\mathrm{P(cr, black)} = \mathrm{P_4(g)} \qquad (4)$$

From the enthalpy of vaporization relation given by Rodewald, and with the most recent enthalpy increments [14] for P(black) and P_4(g), we derive $\Delta_r H_m^\ominus = (160.8 \pm 8.0)$ kJ mol^{-1} for reaction (4). Combination of this result with $\Delta_f H_m^\ominus(\mathrm{P_4, g}) = (58.9 \pm 0.3)$ kJ mol^{-1} [15] gives $\Delta_{trs} H_m^\ominus = -(25.5 \pm 2.1)$ kJ mol^{-1} for the transition depicted in eqn. (3). This value does not quite overlap our value of $-(21.2 \pm 2.1)$ kJ mol^{-1}. Part of the disagreement can certainly be attributed to the low reliability of the measurements of Smits and Bokhorst; it is well known, and discussed by Stephenson et al. [11], that the P_4 vapor over black phosphorus is not in equilibrium with the solid.

As Rodewald has pointed out, previously reported values for $\Delta_{trs} H_m^\ominus$ on the basis of energy of combustion measurements in oxygen are not reliable and differ widely from each other.

Clearly, the enthalpy of transition reported in the present paper leads to the conclusion that black phosphorus is, at $T = 298.15$ K and a pressure of 101.325 kPa, the most stable allotrope of phosphorus. Whether this relative stability persists at higher temperatures must await the provision of high-temperature thermodynamic quantities for the black and other forms of phosphorus.

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