MASS SPECTROMETRIC STUDIES OF THE VAPORIZATION OF PHOSPHORUS OXIDES

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Abstract — Mass spectrometric investigations of the evaporation of commercially available "phosphorus pentoxide" have shown that at temperatures below 150°C, the equilibrium vapor consists primarily of $P_4O_{10}(g)$ with small amounts of $P_4O_9(g)$. At temperatures between 175°C and approximately 350°C, the vapor contains $P_4O_{10}(g)$, $P_4O_9(g)$ and $P_4O_8(g)$, while at temperatures greater than 400°C, the molecular species $P_4O_7(g)$ is observed as well. Second-law heats of reaction for equilibria among the gaseous molecular species have been obtained. Also, free evaporation studies of both solid and liquid P_4O_6 indicate that the vapor consists primarily of $P_4O_6(g)$. Average values for the (P—O) and (P=O) bond energy have been calculated.

INTRODUCTION

THE POLYMORPHIC nature of "phosphorus pentoxide" has been the subject of several previous investigations[1–3]. Based upon vapor pressure measurements, optical properties and crystal structure studies, the existence of three crystalline modifications of the solid seems to be well established. The low-temperature polymorph, volatile at temperatures up to approximately 200°C, belongs to the rhombohedral division of the hexagonal system; an intermediate-temperature form, obtained by heating the hexagonal crystals between 300°C and 400°C for an appropriate period, belongs to the orthorhombic system, and, at temperatures in excess of 450°C, there exists still another stable crystalline modification, thought to be tetragonal.

In an early electron diffraction study[4] of the vapor above the solid, the existence of the P_4O_{10} molecule was confirmed and the molecular configuration established. With the symmetry of the point group T_d, the phosphorus atoms occupy the corners of a regular tetrahedron with each bound to three bridge oxygen atoms (in planes of symmetry passing through the trigonal axes) and one apical oxygen atom to give a tetrahedral configuration of oxygen atoms about each phosphorus atom. Molecules of P_4O_{10} having the same structure as in the vapor have also been shown to be present in the two lower-temperature polymorphic forms of the solid[5]. More recently, crystallographic studies[6–8] on monoclinic crystals of the phosphorus(III), (V) oxides have shown the existence of mixed crystals con-

1. J. C. Southard and R. A. Nelson, J. Am. chem. Soc. **59**, 911 (1937).
2. H. C. J. de Decker and C. H. MacGillavry, Recl. Trav. Chim. **60**, 153 (1941).
3. W. L. Hill, G. T. Faust and S. B. Hendricks, J. Am. chem. Soc. **65**, 794 (1943).
4. G. C. Hampson and A. J. Stosick, J. Am. chem. Soc. **60**, 1814 (1938).
5. H. C. J. de Decker, Recl. Trav. Chim. **60**, 413 (1941).
6. K. H. Jost, Acta crystallogr. **17**, 1593 (1964).
7. D. Heinz, Z. anorg. allg. Chem. **336**, 137 (1965).
8. K. H. Jost, Acta crystallogr. **21**, 34 (1966).

taining the molecules, P_4O_8 and P_4O_7 as well as those containing P_4O_9 and P_4O_8. These molecules differ from the P_4O_{10} molecule by one, two and three missing terminal oxygen atoms. A recent electron diffraction study[9] of gaseous "phosphorus pentoxide" also revealed the presence of the gaseous molecule, P_4O_9. The molecular dimensions and stereochemistry of these oxides therefore seems to be well characterized.

Although a recent mass spectrometric investigation[10] of vaporizing "phosphorus pentoxide" confirmed the presence of gaseous P_4O_{10} and P_4O_9 molecules, little information exists on the characterization of the vapor over the entire temperature range for which polymorphic behavior of the solid has been reported. Also, there have been no quantitative studies of the vaporization of P_4O_6. The complete characterization of the vaporization processes for both P_4O_{10} and P_4O_6 was therefore the objective of the present study.

EXPERIMENTAL PROCEDURES AND RESULTS

1. The vaporization of "phosphorus pentoxide"

Samples of commercially available reagent grade anhydrous "phosphorus pentoxide" were loaded into an alumina-lined tantalum Knudsen cell and vaporized within a high temperature cell assembly[11] of a Bendix, model 14-206A, time-of-flight mass spectrometer[12]. A movable shutter, separating the Knudsen cell region from the ion-source region, permitted one to distinguish between molecules originating from the cell and those present as background gases. The orifice of the alumina cell-lid was knife-edged and had a dia. of 0·5 mm. Temperatures were measured with a chromel–alumel thermocouple positioned into a small hole located in the bottom of the cell.

After the system had been outgassed, the temperature of the Knudsen cell was slowly raised, over a 12-hr period, to approximately 150°C and the mass spectrum recorded. Ions originating from molecules within the Knudsen cell were identified by their shutterability. The intensities of the ionic species resulting from bombardment with 40-V electrons were measured relative to the intensity of $P_4O_{10}^+$, arbitrarily set at 100, and are recorded in column 2 of Table 1. Appearance potentials of all ionic species were then measured by the vanishing-current method using water and mercury as calibrants. By comparison with the known ionization potentials for atomic and molecular phosphorus[13], the relatively low appearance potentials of $P_4O_{10}^+$ and $P_4O_9^+$, the very small intensities of peaks corresponding to the masses of the ions $P_4O_8^+$, $P_4O_7^+$ and $P_4O_6^+$, and, from the high appearance potentials of all other remaining oxygen-containing species (including that for $P_4O_6^+$), it can be concluded that the gaseous molecular species present over commercial "phosphorus pentoxide" at 150°C are $P_4O_{10}(g)$ and $P_4O_9(g)$, with trace amounts of $P_4(g)$ arising from a phosphorus impurity in the solid. Although the observed non-shutterability of the O_2^+-ion prevents one from distinguishing background $O_2(g)$ from that possibly originating from within the Knudsen cell, the small but measurable temperature-dependence of the O_2^+-ion intensity suggests that a small concentration of $O_2(g)$ is most likely present as a product of vaporization as well. All remaining ionic species result therefore, from the dissociative ionization of $P_4O_{10}(g)$, $P_4O_9(g)$ and $P_4(g)$. The values of the appearance potentials for all ionic species are collected in column 2 of Table 2. Also, the concentration of $P_4O_{10}(g)$ relative to that of $P_4O_9(g)$ was approximated by measuring the intensities of the corresponding ions using 15-V ionizing electrons, thereby minimizing the amount of fragmentation. The ratio of $P_4O_{10}^+$ to $P_4O_9^+$ at 150°C was approximately 10:1.

9. B. Beagley, D. W. J. Cruickshank and T. G. Hewitt, *Trans. Faraday Soc.* **63**, 836 (1967).
10. A. Hashizume, N. Wasada and T. Tsuchiya, *Bull. chem. Soc. Japan.* **39**, 150 (1966).
11. A. Kant, *J. chem. Phys.* **41**, 1872 (1964).
12. D. B. Harrington, *Time of Flight Mass Spectrometry*, in *Encyclopedia of Spectroscopy* (Edited by C. F. Clark), p. 628. Reinhold New York (1960).
13. R. W. Kiser, *Introduction to Mass Spectrometry and Its Applications* pp. 305, 316. Prentice-Hall (1965).

Table 1. Mass spectra of vapors over P_4O_{10}

| Ion | Relative intensities (40-V electrons) at temperature T | | |
	($T = 150°C$)	($T = 315°C$)	($T = 400°C$)
P^+	50	65	70
PO^+	50	80	80
PO_2^+	50	70	70
PO_3^+	10	40	50
P_2^+	5	10	50
$P_2O_2^+$	10	20	40
$P_2O_3^+$	20	20	45
$P_2O_4^+$	30	25	50
$P_2O_5^+$	40	40	70
P_3^+	10	20	30
$P_3O_4^+$	2	5	35
$P_3O_5^+$	30	40	40
$P_3O_6^+$	60	70	70
$P_3O_7^+$	80	80	80
P_4^+	10	15	20
$P_4O_6^+$	0·5	0·6	1·5
$P_4O_7^+$	<0·1	0·4	25
$P_4O_8^+$	0·3	25	50
$P_4O_9^+$	10	60	75
$P_4O_{10}^+$	100	100	100
O_2^{+*}	2	10	14

*Intensity above background at 100°C.

The temperature dependence of the intensity of the $P_4O_{10}^+$ ion (at 15 eV) was then measured over a temperature range from 40°C to approximately 150°C, and used to calculate the heat of the reaction:

$$P_4O_{10}(s) = P_4O_{10}(g). \qquad (1)$$

Using second-law procedures and the relation:

$$P_i = k_i I_i^+ T \qquad (2)$$

where P_i is the partial pressure of the indicated species, I_i^+ the measured intensity, and k_i a proportionality constant, one can plot the ion current analog of the equilibrium constant for Reaction (1) vs. reciprocal temperature. The slope of this plot yielded $\Delta H_{356}° = 24·1 \pm 0·6$ kcal. mole^{-1}. This value is in good agreement with the values of 23·8 kcal. mole^{-1} and 22·8 kcal. mole^{-1} reported earlier[1, 10] for the heat of sublimation of the low temperature crystalline modification of P_4O_{10}. A similar plot using the measured intensities of $P_4O_9^+$ gives a value of $19·0 \pm 2·0$ kcal. mole^{-1} at a mean temperature of 385°K. The significance of the latter value, however, is not certain since the equilibria between $P_4O_9(g)$, $O_2(g)$ and the vaporizing solid has not been unequivocally established. Furthermore, attempts to study the gas phase dissociation reaction:

$$P_4O_9(g) + \tfrac{1}{2}O_2(g) = P_4O_{10}(g) \qquad (3)$$

by "leaking" $O_2(g)$ over vaporizing $P_4O_{10}(s)$ were unsuccessful due to the difficulty in obtaining reliable and shutterable O_2^+ intensities.

After the sample had been heated at 150°C, for about a 6 hr period, it was observed that the ion intensity of the $P_4O_{10}^+$ peak slowly began to decrease relative to that of the $P_4O_9^+$ mass peak. Con-

Table 2. Appearance potential data for the P_4O_{10} system

Ion	Appearance potential (eV) at cell temperature T		
	($T = 150°C$)	($T = 315°C$)	($T = 400°C$)
P^+	$12·4 \pm 0·5$	$12·6 \pm 0·5$	$12·8 \pm 0·5$
PO^+	$23·6 \pm 0·5$	$24·1 \pm 0·5$	$24·0 \pm 0·5$
PO_2^+	$22·5 \pm 0·5$	$22·9 \pm 0·5$	$22·9 \pm 0·5$
PO_3^+	$33·0 \pm 0·5$	$33·8 \pm 0·5$	$33·2 \pm 0·5$
P_2^+	$11·7 \pm 0·5$	$11·5 \pm 0·5$	$11·7 \pm 0·5$
$P_2O_2^+$	$29·5 \pm 0·5$	$29·4 \pm 0·5$	$29·0 \pm 0·5$
$P_2O_3^+$	$28·0 \pm 0·5$	$28·0 \pm 0·5$	$28·3 \pm 0·5$
$P_2O_4^+$	$24·3 \pm 0·5$	$23·8 \pm 0·5$	$24·0 \pm 0·5$
$P_2O_5^+$	$22·9 \pm 0·5$	$22·8 \pm 0·5$	$23·0 \pm 0·5$
P_3^+	$11·8 \pm 0·5$	$11·9 \pm 0·5$	$11·9 \pm 0·5$
$P_3O_4^+$	$34·0 \pm 0·5$	$33·5 \pm 0·5$	$33·5 \pm 0·5$
$P_3O_5^+$	$32·9 \pm 0·5$	$32·9 \pm 0·5$	$32·8 \pm 0·5$
$P_3O_6^+$	$22·3 \pm 0·5$	$21·9 \pm 0·5$	$22·0 \pm 0·5$
$P_3O_7^+$	$17·8 \pm 0·5$	$17·5 \pm 0·5$	$18·1 \pm 0·5$
P_4^+	$9·5 \pm 0·5$	$10·2 \pm 0·5$	$9·9 \pm 0·5$
$P_4O_6^+$	$32·8 \pm 0·5$	$32·6 \pm 0·5$	$32·5 \pm 0·5$
$P_4O_7^+$			$12·1 \pm 0·5$
$P_4O_8^+$		$12·4 \pm 0·5$	$12·6 \pm 0·5$
$P_4O_9^+$	$13·1 \pm 0·5$	$13·0 \pm 0·5$	$13·0 \pm 0·5$
$P_4O_{10}^+$	$13·6 \pm 0·5$	$13·5 \pm 0·5$	$13·6 \pm 0·5$

tinued heating at this temperature for an additional two hours caused the $P_4O_{10}^+$ peak to disappear completely and the $P_4O_9^+$ peak to become vanishingly small. Then, as the temperature of the cell was slowly raised to approximately 175°C, the $P_4O_9^+$ ion increased in intensity and the $P_4O_{10}^+$ mass peak began to appear again, as well as a new peak at a mass corresponding to the $P_4O_8^+$ ion. The cell temperature was then slowly increased, over an additional 3 hr period, to approximately 300°C and held at this temperature until the measured $P_4O_{10}^+$ ion-current reached the value as obtained previously with the cell at 150°C. The relative intensities of all ionic species (using 40-V electrons) and appearance potentials were then measured and are recorded in column 3 of Table 1 and 2, respectively. Since the appearance potential for the $P_4O_8^+$ ion is lower than that for either the $P_4O_{10}^+$ or $P_4O_9^+$ ions, one concludes that the $P_4O_8^+$ ion is a "parent" as well. Furthermore, from the vapor pressure measurements of Southard and Nelson[1], together with the heat treatment used by Hill et al.[3] for the preparation of the various crystalline modifications of P_4O_{10}, and, an ion-intensity decrease over the phase transition as reported in the mass spectrometric study of Hashizume et al.[10], it seems fairly certain that the solid has undergone the expected phase transformation and that equilibria among the gaseous molecular species has been obtained. From the intensities of the three ions, $P_4O_{10}^+$, $P_4O_9^+$ and $P_4O_8^+$, taken with 15-V ionizing electrons, the relative concentrations of the corresponding neutral molecules, above the solid at 300°C, were estimated to be in the approximate ratio, $10:3:1$.

The intensities of each of these three ionic species were then followed as a function of temperature. The measurements were made at a constant cell temperature, sequentially decreased to approximately 175°C and then increased to 350°C. As before, using relation (2) and the integrated form of the Clausius-Clapeyron equation one can determine a value for the heat of sublimation. A least-squares treatment of the log (IT) vs. $1/T$ data (Fig. 1) yields a heat of sublimation of $\Delta H_{533}^\circ = 26·4 \pm 1·1$ kcal. $mole^{-1}$. Unlike for the low-temperature form of the solid, a comparison of this heat with those obtained from several previous vapor pressure and calorimetric measurements[14] was found to be of somewhat
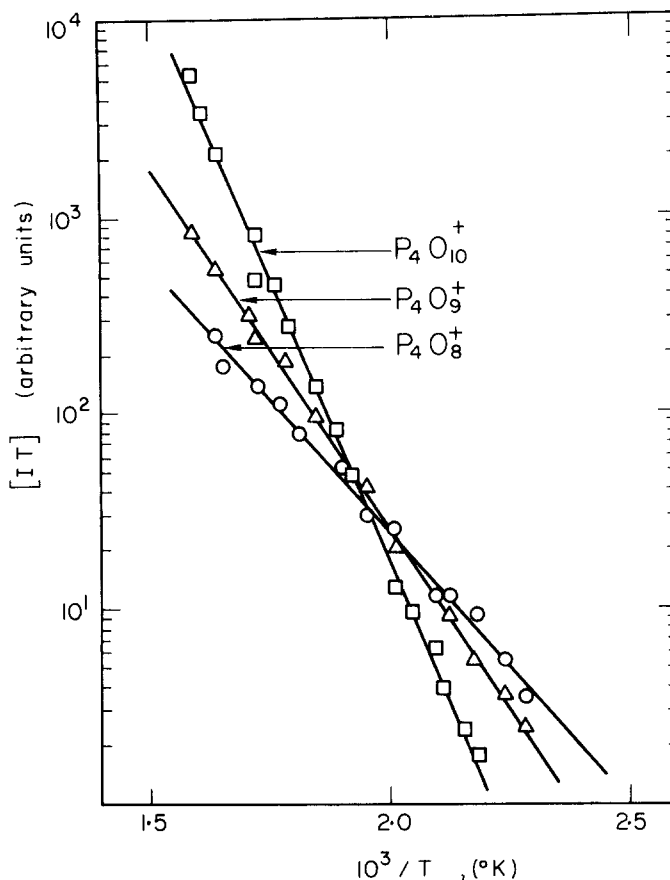
14. *Phosphorus, Properties of the Element and Some of Its Compounds*. Chemical Engineering Report No. 8, p. 25. U.S. Government Printing Office, (1950).

Fig. 1. Log (IT) vs. $1/T$ plots for vapor species over solid P_4O_{10} in the temperature range 175°C–350°C.

questionable value since the complete thermal history of the crystals studied was either not mentioned or is difficult to determine from the experimental procedures employed. However, using the measured slopes corresponding to $18·4 \pm 0·6$ kcal. mole^{-1} at a mean temperature of 527°K for $P_4O_9{}^+$, and $11·8 \pm 0·6$ kcal. mole^{-1} at a mean temperature of 522°K for $P_4O_8{}^+$, as well as that for $P_4O_{10}^+$, one may calculate the heat of the gas phase reaction:

$$P_4O_8(g) + P_4O_{10}(g) = 2P_4O_9(g). \tag{4}$$
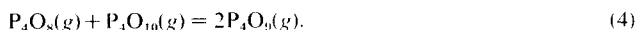
The ion-current analog of the equilibrium constant of Reaction (4) was plotted vs. reciprocal temperature and the slope of this plot yielded $\Delta H^\circ_{529} = -1·2 \pm 1·8$ kcal. mole^{-1}.

In an attempt to produce the high-temperature polymorphic modification of the solid, the cell temperature was then slowly increased to about 400°C and the intensities of the three molecular ions, $P_4O_{10}^+$, $P_4O_9{}^+$ and $P_4O_8{}^+$, monitored as a function of time. Continued heating at these temperatures, however, increased the cell pressure to values which exceed those usually considered necessary for maintaining a condition of molecular-flow within a Knudsen cell. Consequently, the temperature was reduced to 375°C and maintained there until some noticeable reduction in the recorded ion-currents were observed. At the end of approximately 6 additional hr at 375°C the ion-currents corresponding to the $P_4O_{10}^+$ and $P_4O_9{}^+$ ions showed the expected decrease, while the $P_4O_8{}^+$ ion-current intensity remained fairly constant. Continued heating at this temperature for another 4 hr caused both the $P_4O_{10}^+$ and $P_4O_9{}^+$ ion-currents to decrease to approximately one-tenth the intensity of the $P_4O_8{}^+$ ion. The cell

temperature was then raised while the intensity of the $P_4O_{10}^+$ ion was allowed to increase to its former value. At 400°C a scan of the mass spectrum was made and the appearance potentials of all observed ionic species measured. These data appear in column 4 of Tables 1 and 2, respectively. The ionization-efficiency curves for this system are also given in Fig. 2; the break in the curve for the $P_4O_9^+$ ion at 20-V electrons indicates the on-set for the formation of this ion from the dissociative ionization of P_4O_{10}.

Of most significance is the appearance of a mass peak corresponding to the $P_4O_7^+$ ion. Since its appearance potential of $12 \cdot 1 \pm 0 \cdot 5$ eV is lower than any of the other previously observed "parent" ions, it too may be considered a "parent". A complete shutter-effect also indicated that its neutral molecular precursor originated from within the Knudsen cell. Consequently, at these temperatures the gas phase above the solid must contain P_4O_7 molecules as well as the species P_4O_8, P_4O_9 and P_4O_{10}.

The temperature dependence of the ion intensities for each of these four species was then measured over a temperature range extending from 375°C to 500°C. A least-squares treatment of the log (IT) vs. $1/T$ data yields a heat of sublimation of $\Delta H_{663}^\circ = 28 \cdot 0 \pm 1 \cdot 3$ kcal. mole^{-1}. Slopes for the ions $P_4O_9^+$, $P_4O_8^+$ and $P_4O_7^+$ at a mean temperature of 688°K yielded values of $20 \cdot 8 \pm 1 \cdot 5$ kcal. mole^{-1}, $19 \cdot 1 \pm 2 \cdot 0$ kcal. mole^{-1} and $18 \cdot 2 \pm 0 \cdot 7$ kcal. mole^{-1}, respectively.

From a second-law treatment of the ion-current analogue of the equilibrium constant for Reaction (4) and the two additional gas phase reactions:
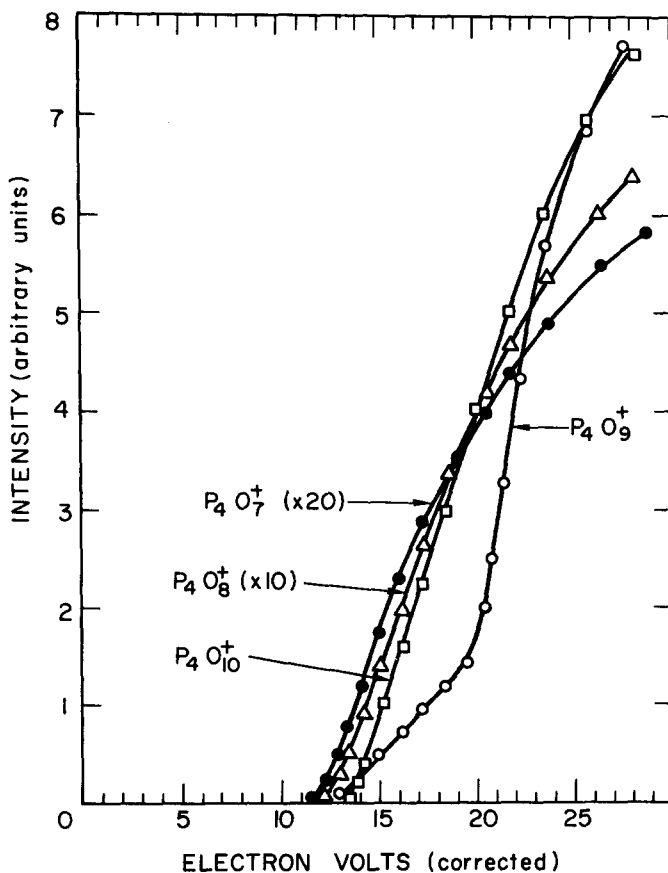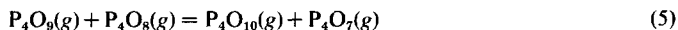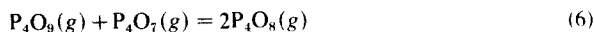
$$P_4O_9(g) + P_4O_8(g) = P_4O_{10}(g) + P_4O_7(g) \tag{5}$$

Fig. 2. Ionization-efficiency curves for vapor species over $P_4O_{10}(s)$ at 400°C.

and

$$P_4O_9(g) + P_4O_7(g) = 2P_4O_8(g) \qquad (6)$$

one finds the heats of reaction for these equilibria to be $\Delta H^{\circ}_{878} = -5 \cdot 5 \pm 3 \cdot 0$ kcal. mole^{-1}, $\Delta H^{\circ}_{679} = 5 \cdot 2 \pm 3 \cdot 4$ kcal. mole^{-1} and $\Delta H^{\circ}_{688} = -1 \cdot 3 \pm 2 \cdot 3$ kcal. mole^{-1}, respectively.

After the cell temperature was slowly cooled from 500°C it was also observed that the $P_4O_8{}^+$ and $P_4O_7{}^+$ ion-currents were still measurable at a temperature as low as 200°C. Apparently once the crystalline solid has changed into the stable high-temperature modification, the conversion back to a low-temperature form takes place very slowly.

To determine the qualitative effects moisture might have upon the vaporization of the solid, a fresh sample of the crystals was exposed to moist air (approximately 10 min) before loading in the high-temperature source of the mass spectrometer. After slowly heating the sample to 400°C over a 36-hr period, a mass spectrum at 40 eV revealed the additional ionic species: HPO^+, $HPO_2{}^+$, $HPO_3{}^+$, $H_2PO_3{}^+$, $H_3PO_4{}^+$, $H_2P_2O_5{}^+$, $H_2P_3O_7{}^+$, $H_2P_4O_6{}^+$, $HP_4O_7{}^+$, $H_2P_4O_7{}^+$, $HP_4O_8{}^+$, $H_2P_4O_9{}^+$, $H_2P_4O_{10}^+$, $H_3P_4O_{10}^+$ and $H_2P_4O_{11}^+$. Significant, were the low appearance potentials of $11 \cdot 9 \pm 0 \cdot 5$ eV, $13 \cdot 5 \pm 0 \cdot 5$ eV and $14 \cdot 0 \pm 0 \cdot 5$ eV for the $H_2P_4O_7{}^+$, $H_2P_4O_9{}^+$ and $H_2P_4O_{10}^+$ ions, respectively. Appearance potentials for all remaining ionic species could not be obtained because the intensities of the corresponding ions were either too small for quantitative measurement, or were not stable. The existence of species such as $H_2P_4O_{10}^+$ is not too surprising, at least from a structural point of view, if one associates these "extra" hydrogen atoms with the apical oxygen atoms on the tetrahedral cage of P_4O_{10}. The appearance of the $H_2P_4O^+$ ion, is easily explained but one must postulate a structure differing considerably from that of P_4O_{10} for this "hydrate".

11. *The vaporization of* P_4O_6

A sample of P_4O_6, manufactured by Albright and Wilson Ltd., was examined by mass spectrometric identification of the vapors over the liquid at 25°C and the solid at 0°C. To study the solid, a gas-inlet system was used with a Bendix model 14-107 time-of-flight mass spectrometer, and for the liquid, measurements were made with a 60° sector-field 12 in. radius, first-order direction-focussing mass spectrometer[15]. For both systems, the vapors were "bled" into the ion-source region with the aid of a variable-leak valve. The only difference between the two experimental methods employed was that for studies in the magnetic mass spectrometer the vapors above the liquid were first introduced into a platinum-lined Knudsen cell before being allowed to enter the ion-source region, thereby establishing a pseudo-equilibrium in the gas phase prior to mass analysis.

For both systems, the mass spectra and relative intensities at 50-V electrons were identical within experimental uncertainty. These data as well as the appearance potentials for all recorded ions are given in Table 3. The low appearance potential of the parent $P_4O_6{}^+$ ion is also consistent with the observed trend of decreasing appearance potentials for the sequence of ions, $P_4O_{10}^+$, $P_4O_9{}^+$, $P_4O_8{}^+$ and $P_4O_7{}^+$, previously measured for the P_4O_{10} system. On the basis of complete shutter-effects and appearance potentials it appears that over the temperature range studied, the vapor species present above solid and liquid P_4O_6 are the same and consist of P_4O_6 molecules with trace amounts of $P_4(g)$ (the latter most likely arising from a phosphorus impurity). In an attempt to produce higher phosphorus oxides from P_4O_6, both $O_2(g)$ and $P_4O_6(g)$ were simultaneously introduced into an alumina-lined Knudsen cell and the mass spectrum examined for mass peaks corresponding to the ions $P_4O_7{}^+$, $P_4O_8{}^+$, $P_4O_9{}^+$ and $P_4O_{10}^+$. At cell temperatures ranging from 25°C to 150°C and variable flow rates for the two gases, the highest mass peak observed was that corresponding to the $P_4O_6{}^+$-ion.

DISCUSSION

On the basis of the results of the present vaporization studies and those of previously cited investigations, the existence of three polymorphic modifications of "phosphorus pentoxide" appears to be well established. In addition, the presence of P_4O_7 and P_4O_8 molecules in the gas phase, as well as the previously characterized P_4O_9 and P_4O_{10} species, is further evidence for the complex behavior of phosphorus–oxygen compounds.

15. G. D. Blue, J. W. Green, R. Bautista and J. L. Margrave, *J. phys. Chem.* **67**, 877 (1965).

Table 3. Relative intensities and appearance
potentials for vapors over P_4O_6

Ion	Relative intensity at 50 eV	Appearance potential (eV)
P^+	55	$18 \cdot 2 \pm 0 \cdot 5$
PO^+	80	$18 \cdot 0 \pm 0 \cdot 5$
PO_2^+	35	$23 \cdot 0 \pm 0 \cdot 5$
P_2^+	15	$14 \cdot 2 \pm 0 \cdot 5$
P_2O^+	20	$23 \cdot 6 \pm 0 \cdot 5$
$P_2O_2^+$	50	$18 \cdot 8 \pm 0 \cdot 5$
$P_2O_3^+$	30	$17 \cdot 5 \pm 0 \cdot 5$
P_3^+	2	$11 \cdot 9 \pm 0 \cdot 5$
$P_3O_3^+$	4	$18 \cdot 8 \pm 0 \cdot 5$
$P_3O_4^+$	70	$16 \cdot 1 \pm 0 \cdot 5$
$P_3O_5^+$	65	$15 \cdot 0 \pm 0 \cdot 5$
P_4^+	15	$10 \cdot 3 \pm 0 \cdot 5$
$P_4O_6^+$	100	$10 \cdot 6 \pm 0 \cdot 5$

Finally, from the appearance potential measurements and the calculated heats of reaction for Equations (1), (4), (5) and (6) one may estimate the heats of formation for P_4O_{10}, P_4O_9, P_4O_8, P_4O_7 and P_4O_6, as well as deduce the mean bond energies $\bar{E}$ (P—O) and $\bar{E}$ (P=O). Using the heat of Reaction (1), the heat of formation of crystalline P_4O_{10}[16, 17], and enthalpy functions from the *JANAF Tables* [17], one calculates the heat of formation of $P_4O_{10}(g)$ to be -672 ± 2 kcal. mole^{-1}, which is in excellent agreement with the value of -675 ± 2 kcal. mole^{-1} adopted by the *JANAF Tables*. From the appearance potential of $20 \cdot 0 \pm 0 \cdot 5$ eV (Fig. 2) for the process:

$$e^- + P_4O_{10}(g) = P_4O_9^+(g) + O(g) + 2e^- \tag{6}$$

the appearance potential of $P_4O_9^+$ from $P_4O_9(13 \cdot 0 \pm 0 \cdot 5$ eV), and the heats of formation of $P_4O_{10}(g)$ and $O(g)$[18], one estimates the heat of formation of $P_4O_9(g)$ to be -590 ± 17 kcal. mole^{-1}. From the heat of reaction (4) and the ΔH_f values of $P_4O_{10}(g)$ and $P_4O_9(g)$, one also finds the heat of formation of $P_4O_8(g)$ to be -502 ± 29 kcal. mole^{-1}. A similar calculation using either Reaction (5) or (6) yields an estimated value for the heat of formation for $P_4O_7(g)$ of -412 ± 35 kcal. mole^{-1}. The uncertainties were estimated by the propagation-of-errors.

The literature also contains two widely divergent values for the heat of formation of $P_4O_6(g)$. Koerner and Daniels[19] report a value of -512 ± 8 kcal. mole^{-1}, and, in a later study, Hartley and McCoubrey[20] report a value of -378 ± 6 kcal. mole^{-1}. The former is the value adopted for use in the *JANAF Tables*. By using

16. W. S. Holmes, *Trans. Faraday Soc.* **58**, 1916 (1953).
17. *JANAF Thermochemical Tables* (Edited by D. R. Stull), Clearinghouse for Federal Sci. and Tech. Information, Springfield, Va., Doc. No. PB-168-370 (August, 1965).
18. D. R. Stull and G. C. Sinke, *Advances in Chemistry Series No. 18*. American Chemical Society, Washington, D.C.
19. W. E. Koerner and F. Daniels, *J. chem. Phys.* **20**, 113 (1952).
20. S. B. Hartley and J. C. McCoubrey, *Nature, Lond.* **198**, 476 (1963).

the appearance potential of $P_4O_6^+$ from P_4O_{10} ($32 \cdot 6 \pm 0 \cdot 5$ eV) and that from P_4O_6 ($10 \cdot 6 \pm 0 \cdot 5$ eV), one estimates the heat of formation of $P_4O_6(g)$ to be -405 ± 17 kcal. mole^{-1}. Thus, the measurement of Hartley and McCoubrey for the heat of formation of $P_4O_6(g)$ appears to be the more reliable and should therefore be preferred over the earlier value.

By using -405 kcal. mole^{-1} for $\Delta H_f^\circ(P_4O_6)$ and the heats of formation of $P(g)$ and $O(g)$ [18], one calculates the average (P—O) bond energy to be 88 ± 3 kcal. mole^{-1}. From the difference in the appearance potentials of $P_4O_6^+$ from P_4O_{10} and P_4O_6, one finds the mean (P=O) bond energy in P_4O_{10} to be 127 ± 12 kcal. mole^{-1}. These values are in good agreement with the values of 86 and 138 kcal. mole^{-1} derived by Hartley and McCoubrey[20].