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A Mass Spectrometric Study of Phosphorus Oxide

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Phosphorus pentoxide has been investigated with a mass spectrometer over the temperature range from 60°C to 650°C. A Knudsen cell has been installed in the source of the mass spectrometer. Two samples were used in the experiment. One was commercially-available phosphorus pentoxide, while the other had been purified from the commercial phosphorus pentoxide by Finch's method. The ionization efficiency curves near the appearance potential of $P_4O_9^+$ and $P_4O_{10}^+$, and the fractional yield of each ion versus the ionizing voltage have been investigated and interpreted as evidence for the presence of the P_4O_9 molecule. Three curves representing the intensity of the mass 284 ($P_4O_{10}^+$) peak as a function of the temperature have been obtained. Two of them, which set on at about 250°C and 450°C respectively, are related to the known vapor pressure curves of phosphorus pentoxide. The curve with the lowest onset temperature, about 100°C, may be interpreted as a vapor pressure of a new low temperature phase of phosphorus pentoxide.

The nature of phosphorus oxides has been investigated by various authors,[1-3] since the oxides have a great significance in the chemistry of fertilizer manufacture, and an accurate knowledge of their behavior in the pure state is a prequisite to a complete understanding of complex systems of a more practical importance. Especially, phosphorus pentoxide is known to be a component of several phase systems. This has not, however, been determined unequivocally, because the oxides cannot be handled conveniently, as they absorb moisture from air immediately and attack glass at elevated temperatures.

Some people believe that "phosphorus pentoxide" is not as a very favorable drying agent for a vacuum system, as lower oxides of phosphorus sublime.

Several works have been published studying the sublimation products from solid state compounds by mass spectrometry.[4,5] Manometric investigations based upon various principles have been reported and used; these studies have measured a quantity which is proportional, in some sense, to the total pressure of the gas under investigation, whereas mass spectrometry gives information about the partial pressure of each species of molecules contained in the gas phase. Such being the case, the present study was undertaken in order to investigate the properties of phosphorus oxides with a mass spectrometer.

Experimental

The phosphorus oxides used in this investigation were obtained from two sources. One was an extra pure phosphorus pentoxide available commercially (hereafter referred to as commercial phosphorus pentoxide) and obtained from Miyazaki Shōten, while the other was prepared from the commercial product by sublimation in a current of oxygen in an iron tube at about 800°C, according to the method of Finch and Frazer.[6] The iron tube was heated electrically instead of by gas. In this process the lower oxides of the phosphorus are reported to be oxidized completely. After sublimation, the oxidized product (hereafter referred to as purified phosphorus pentoxide) was handled carefully so as to prevent it from absorbing moisture.

Most of the work was carried out with a 60° Nier-type mass spectrometer of our own construction.[7] The median radius of the stainless-steel analyzer of this instrument was 20 cm., and the resolving power was about 150. The ion current was amplified by an Applied Physics Corporation, model 36, vibrating reed amplifier. The other electronic circuits and the construction of the ion source were much the same as those reported by Nier.[8] Figure 1 shows the mass spectrometer mounting, containing a Knudsen effusion cell similar to that of Porter, Schissel and Inghram.[4] The cell consisted of two crucibles, an outer stainless-steel crucible and an inner crucible made of aluminum oxide; the latter contained the phosphorus oxide to be

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[1] J. R. van Wazer, "Phosphorus and its Compounds," Vol. I, Interscience Publishers, New York (1958).

[2] J. C. Southard and R. A. Nelson, *J. Am. Chem. Soc.*, **59**, 911 (1937).

[3] W. L. Hill, G. T. Faust and S. B. Hendricks, ibid., **65**, 794 (1943).

[4] R. F. Porter, P. Schissel and M. G. Inghram, *J. Chem. Phys.*, **23**, 339 (1955).

[5] J. D. Louw and J. W. L. DeVilliers, *Rev. Sci. Instr.*, **25**, 1226 (1954); M. G. Inghham, W. A. Chupka and J. Berkowitz, *J. Chem. Phys.*, **27**, 569 (1957); M. G. Inghram, W. A. Chupka and J. Berkowitz, *Mem. soc. roy. sci. Liege*, **18**, 513 (1957); T. A. Milne, H. M. Klein and D. Cubicciotti, *J. Chem. Phys.*, **28**, 718 (1958); R. E. Powell, *J. Sci. Instr.*, **37**, 252 (1950); R. P. Burns, G. Demaria, J. Droward and M. G. Inghram, *J. Chem. Phys.*, **38**, 1035 (1963).

[6] G. I. Finch and R. P. Fraser, *J. Chem. Soc.*, **129**, 117 (1926).

[7] To be reported elsewhere.

[8] A. O. Nier, *Rev. Sci. Instr.*, **18**, 398 (1947).

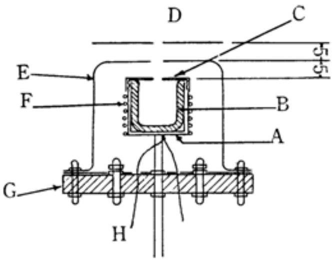

Fig. 1. Crucible for mass spectrometer.
(A) Stainless-steel crucible, (B) Alumina crucible, (C) Cap, (D) Position of ionization chamber, (E) Radiation shield (F) Filament (G) Steatite base, (H) Thermocouple

investigated. The stainless-steel cover of the outer crucible had an effusion hole (0.15 mm. in diameter). As the ratio of the total vaporizing area of the phosphorus oxide to the effusion area was approximately 1000, a true equilibrium partial pressure of each gaseous species with the charged oxide can exist inside the Knudsen cell. The stainless-steel crucible was heated directly by means of a surrounding tungsten filament coated with aluminum oxide or by electron bombardment from the filament. The Knudsen cell and the heating filament were enclosed by a stainless-steel radiation shielding, which had an effusion hole 2 mm. in diameter. The distance between the holes of the outer crucible and the radiation shielding was about 5 mm. The temperature was measured with a platinum-platinum-rhodium thermocouple attached to the bottom of the stainless-steel crucible. Gases effusing out of the Knudsen cell pass through the hole in the top of the radiation shielding and enter the ionization chamber of the ion source, where they are ionized.

As soon as the compound to be investigated was loaded in the inner crucible, the stainless-steel cover was placed on; then, in about 5 min., the ion source system, including the crucible, was mounted on the analyzer of the mass spectrometer and evacuated.

Since thr resolving power of the mass spectrometer described above was insufficient, a CEC 21-103C mass spectrometer was used to determine the mass numbers of those ions which have mass numbers higher than 150. In this case the material to be investigated was charged in an ampoule. The ampoule was then positioned at the necessary depth in a flask of liquid nitrogen just prior to the evacuation and during the sealing. The ampoule was attached directly to the sample manifold of the mass spectrometer, as is shown in Fig. 2. Such ampoules were fabricated from pyrex and in the approximate dimensions shown.

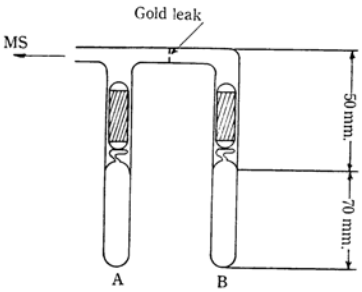

Fig. 2. Mounting of ampoules containing sample.
(A) Phosphorus pentoxide, (B) *n*-eicosane

In order to determine the mass numbers of the ion peaks, *n*-eicosane was introduced simultaneously with phosphorus oxide as a reference. The location of the ampoule containing *n*-eicosane is shown in Fig. 2. The vapor of the sample was extracted from the ampoule by breaking the breakable seal and by then heating the ampoule to an appropriate temperature with an electric furnace. The vapor was introduced into the ion source of the mass spectrometer directly or through the gold leak. The mass numbers of the spectral peaks of phosphorus oxides were determined by comparing them with those of *n*-eicosane. In some cases, the intensity of the isotope peak contributed by ^{18}O was calculated[9] and used to indentify the mass number.

A Pirani-type manometer was constructed, and the vapor pressure of phosphorus pentoxide was checked through the temperature range from 90°C to 260°C. The manometer, which had a platinum filament 30 μ in diameter, was of an ordinary type and was calibrated with reference to a thermocouple gauge obtained from the Showa Rikagakukikai Co. At a constant wall temperature of the manometer, the calibration curve was a straight line, the tangent of which was a function of the temperature. A glass tube containing the phosphorus pentoxide was connected directly with the manometer. After the interior was pumped down to 10^{-4} mm Hg or lower, the glass tube with the manometer was closed off, with the vacuum still applied. Then it was immersed in a thermostat and the pressure was measured.

Results

Pattern Coefficient.—Table I shows the pattern coefficients of the mass spectra of the phosphorus oxides corresponding to *m/e* values greater than 47. No peak of an *m/e* value greater than

TABLE I. PATTERN COEFFICIENTS OF PHOSPHORUS PENTOXIDES

m/e	Purified phosphorus pentoxide*	Commercially available phosphorus pentoxide**	Constitution
286	2.1	2.1	$P_4O_9{}^{18}O$
284	100	100	P_4O_{10}
268	1.1	30.1	P_4O_9
205	26.0	34.0	P_3O_7
142	2.9	4.1	P_2O_5
63	22.3	54.8	PO_2
47	70.4	224.8	PO

Mass spectrometer: CEC 21-103C
Electron accelerating voltages: 70 V.
* Oxidized according to Finch and Frazer from the guaranteed reagent phosphorus pentoxide at Kanto Kagaku Co.
** Extra pure phosphorus pentoxide obtained from Miyazaki Shōten.

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[9] J. H. Beynon, "Mass Spectrometry and its Applications to Organic Chemistry," Elsevier Publ. Co., Amsterdam (1960), pp. 294—298.

that at 288, which is due to an isotope peak of $P_4O_{10}^+$, was observed. Under the present experimental conditions, the pattern coefficients corresponding to $P_4O_6^+$ or $P_2O_3^+$ were smaller than 1. The pattern coefficients of the commercial phosphorus pentoxide varied with the time. The variation in the pattern coefficients of the $P_4O_9^+$ is shown in Table II. The pattern coefficient of the *m/e* 47 ion was found to have a poor reproducibility, the reason for this was not studied.

TABLE II. VARIATION OF THE PATTERN COEFFICIENTS OF P_4O_9 WITH TIME

m/e	1	2	3	4
284	100	100	100	100
268	153.5	78.0	51.2	40.4

Measurement was made at about every 10 min.
Temperature of the crucible was at 100°C during the measurements.
Phosphorus pentoxide used in this measurement was extra pure.

The Intensity of the Peaks as a Function of the Electron Accelerating Voltage.—Figures 3 and 4 show the fractional yields (the percentage ratio of a peak height to the sum of all peaks in a mass spectrum of a substance) of several main peaks in the spectra of the commercial phosphorus pentoxide and in the purified phosphorus pentoxide respectively; the yields are shown as a function of the electron-accelerating voltage above the appearance potential. The voltage scale is not corrected for contact potentials or any other conditions.

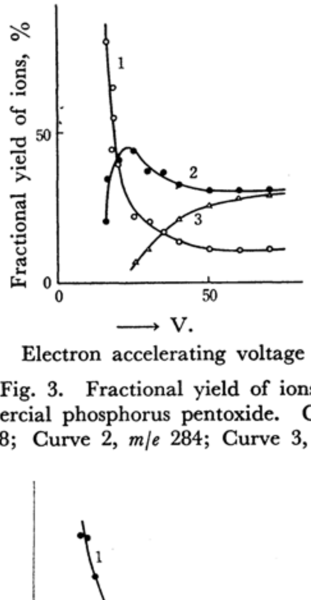

Fig. 3. Fractional yield of ions. Commercial phosphorus pentoxide. Curve 1, *m/e* 268; Curve 2, *m/e* 284; Curve 3, *m/e* 47

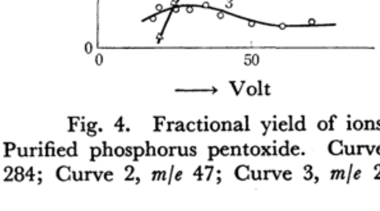

Fig. 4. Fractional yield of ions. Purified phosphorus pentoxide. Curve 1, *m/e* 284; Curve 2, *m/e* 47; Curve 3, *m/e* 268

The ionization efficiency curves near the appearance potentials of the *m/e* 268 and *m/e* 284 ions from the commercial phosphorus pentoxide are shown in Fig. 5. Though the energy scale was not corrected and though the absolute values of the appearance potentials of the ions were not estimated, it is clear that the *m/e* 268 ion, $P_4O_9^+$, appears at an ionizing voltage about 0.5 eV. lower than that of the *m/e* 284 ion, $P_4O_{10}^+$.

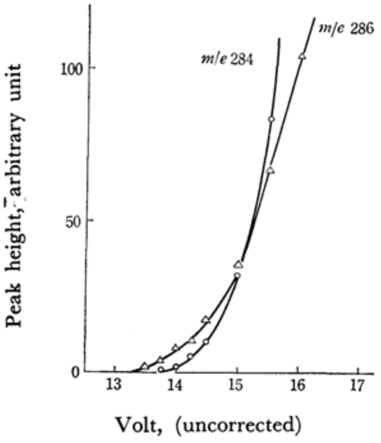

Fig. 5. Ionization efficiency curves. Commercial phosphorus pentoxide.

The Variation in *m/e* 284 Ion Intensity with the Temperature.—Figure 6 shows the relation between the *m/e* 284, $P_4O_{10}^+$, ion intensity and the temperature of phosphorus pentoxide. In the intermediate temperature ranges between curves 1, 2 and 3 of Figure 6, which had onset points at about 100°C, 250°C and 500°C respectively, the ion intensity was found to be zero. After the sample had been heated at about 200°C for a while, the intensity of the ion corresponding to curve 1 gradually dropped; after the temperature had been maintained for a few hours, the ion disappeared completely. Then when the temperature was raised, the ion began to appear again at about 250°C and curve 2 could be traced. A phosphorus pentoxide sample, previously heated to a temperature higher than 250°C in the crucible, gave almost no *m/e* 284 ions at about 200°C.

While vapor pressure curves which are very similar in shape and onset point to curves 2 and 3 have been reported by other authors[1,2,10,11] (curves

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[10] A. Smits, *Z. phys. Chem.*, **B46**, 43 (1940).
[11] A. Smits and A. J. Rutgers, *J. Chem. Soc.*, **125**, 2573 (1924).

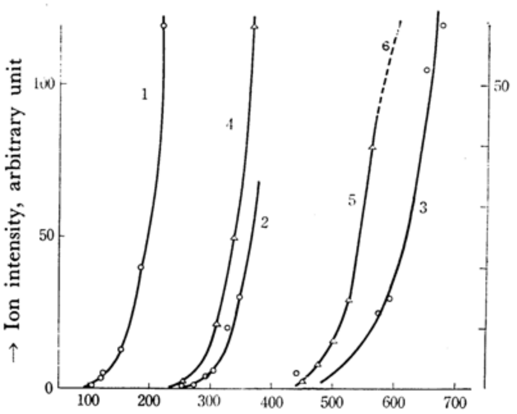

Fig. 6. Intensity of m/e 284 ion versus temperature of purified phosphorus pentoxide.
Curves 1, 2 and 3, ion intensity of m/e 284 ion; Curves 4, 5 and 6, vapor pressure obtained by A. Smits and A. J. Rutgers.[11]

4 and 5 in Fig. 6[2]), the one which sets on at about 100°C has not yet been reported. A Pirani gauge was used in order to check the vapor pressure in this temperature range by a means other than mass spectrometry. The determination of the absolute value of the pressure was not carried out, however, as the sample material may corrode the filament of the gauge during the measurement. However, as in the case of determination with the mass spectrometer, the pressure rise was observed to begin at about 100°C. The pressure was roughly estimated to be at least of an order of magnitude higher than the value estimated by the extrapolation of curve 4 in Fig. 6, which was obtained by Southard and Nelson.[2]

Discussion

Previous Works on Phosphorus Pentoxide.—The vapor pressures of phosphorus pentoxide have been investigated, either with a Jackson-type manometer or with a platinum bulb gauge, by many authors.[1-3,10,11] From these vapor pressure data, together with their microscopic observation of the crystalline form of the compound, Hill, Faust and Hendricks[3] have concluded that phosphorus pentoxide exists in three crystalline modifications. The low-temperaurte polymorph belongs to the rhombohedral division of the hexagonal system (referred to as the H-form). A high-temperature form obtained by heating the hexagonal crystals below 420°C for an appropriate period belongs to the orthorhombic system (referred to as the O-form). When the aggregate of the O-form is heated at 450°C for twenty-four hours, it is converted into a stable crystalline modifications, which is thought to be tetragonal (designated as the T-form). The H-form is metastable with respect to the O-form. This change takes place very slowly at 70°C, but it is completed in one hour at 378°C. Alternatively, the O-form is metastable with respect to the T-form. The H-, the O- and the T-forms exist, respectively, in the three temperature ranges bounded by curve 4 and curve 5 in Fig. 5. While various papers have since been published discussing the higher temperature forms, the H- and the O-forms have been considered to be corroborated. Curve 6 has been reported by Southard and Nelson to be a vapor pressure curve on a liquid phase.

According to Southard and Nelson, the vapor pressure curves, 4, 5, and 6, are represented by the following equations respectively:

Low temperature form:

$$\log p = -(50000/T) + 9.792 \quad (1)$$

High temperature form:

$$\log p = -(7930/T) + 11.113 \quad (2)$$

Liquid:

$$\log p = -(4320/T) + 6.809 \quad (3)$$

They determined the heats of vaporization per gram of the molecule from Eqs. 1, 2 and 3 for the low-temperature form (the H-form according to Hill et al.), the high-temperature form (the O-form) and the liquid respectively. The data are listed in the last column of Table III.

TABLE III. HEATS OF VAPORIZATION L (kcal./mol.) OF P_4O_{10}

Curve	L	Crystalline form	L*
1	19.2		
2	23.8	H	22.8
		O	36.3
3	20.6	liq.	19.7

* J. C. Southard and R. A. Nelson, *J. Am. Chem. Soc.*, **59**, 911 (1937).

The only available calorimetric work on the heat of vaporization is that of Frandsen[12] on the low-temperature form. He obtained the value of 8800+1300 cal. per gram formula weight of phosphorus pentoxide. On the basis of the assumption that the molecular formula P_4O_{10} is nearly correct, the heat of vaporization was calculated to be 17600 +2600 cal. par gram mole, which deviates considerably from the value of 22800 obtained by Southard and Nelson and from the 22600 calculated from the data of Hoeflake and Scheffer.[13]

Heats of Vaporization.—The curves 1, 2 and 3 obtained in the present experiment are represented by Eqs. 4, 5 and 6 respectively:

$$\log p = -(42 \times 10^2/T) + 13.06 \quad (4)$$

$$\log p = -(52 \times 10^2/T) + 11.06 \quad (5)$$

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[12] M. Frandsen, *Bur. Standards J. Res.*, **10**, 54 (1933).

[13] J. M. A. Hoeflake and F. E. C. Scheffer, *Rec. trav. chim.*, **45**, 191 (1926).

$$\log p = -(45\times10^2/T)+7.55 \qquad (6)$$

The constants in Eqs. 1—6 are functions of the sensitivity of the manometer used and of the unit of pressure. The heats of vaporization calculated from Eqs. 4—6 are listed in column two, Table III. When we compare these values with those of Southard and Nelson given in column four, and when we take the temperautre range of each curve into account, we see that curve 2 and curve 3 of the intensity correspond to curve 4 and curve 6 of the vapor pressure respectively.

As has been shown in the present study, no polymer of P_4O_{10} was observed in the gas phase. This shows that Frandsen's assumption is correct. As may be seen in Table III, Frandsen's value, 17600±2600 cal. per gram mole, is in agreement with the one calculated from curve 1 within the tolerance of experimental error.

A New Modification of Phosphorus Pentoxide.—In mass spectrometry, a measured ion-peak height is proportional to the pressure, in the ionization chamber, of the parent compound of the ion, as long as an ion peak of a certain mass number is concerned. In the present instance, although the pressure coefficient of the peak height may be a function of the temperature of the parent molecules, the peak height was assumed to be approximately proportional to the pressure, since the temperature range was not very wide. From the arrangements of the Knudsen cell and the ionization chamber, the pressure in the chamber was properly assumed to be proportional to the P_4O_{10} vapor pressure, which is in equilibrium, at that temperature, with the charged phosphorus pentoxide in the cell.

While curves 2 and 3 of the intensity obtained in the present study are considered to correspond to curves 4 and 6 of the vapor pressure respectively, given by Southard and Nelson, no vapor pressure curve which corresponds to the curve 1 of the intensity obtained in the present study is yet known. One of the significant differences in the experimental conditions between those of Southard and Nelson and ours is the treatment of the sample materials. Whereas they distilled the sample directly into a measuring manifold, we exposed the sample to air for a short time in a room kept at a low humidity. This procedure has been mentioned previoulsy. Under these circumstances, the possible amount of water absorbed by the sample is estimated to be of the order of a 10^{-2} weight percentage of the sample.¹⁾ Nothing is known about the pressure of P_4O_{10} vapor on a phosphorus pentoxide containing a minute quantity of water. The pressure of P_4O_{10} vapor on a phosphorus pentoxide containing a minute quantity of water cannot be considered to exceed that on a pure phosphorus pentoxide by an order of magnitude. As has been mentioned already, the evaporation of P_4O_{10} vapor near 200°C lasts for a few hours and the heat of evaporation coincides with the calorimetric value. Taking these circumstances into consideration, we infer that curve 1 in Fig. 6 is a vapor pressure curve attributable to a phase of pure phosphorus pentoxide, and that there exists a new phase (which we shall refer to as the α-form phosphorus pentoxide), which has not yet been reported on, corresponding to the curve. The behavior of the *m/e* 284 ion in the temperature range between 100°C and 250°C may be understood if we assume that the α-form substance changes readily into a higher temperature form, presumably into the H-form. One possible explanation of the fact that the α-form or curve 1 has not been reported by previous investigators may be that from the outset they investigated phosphorus pentoxide in a form other than the α-form. If the distilled phosphorus pentoxide condenses on a wall at a temperature higher than about 250°C, the prepared substance may be in a form other than the α-form.

P_4O_9—King and Long¹⁴⁾, in a study of the mass spectrum of some simple esters, showed that the curves representing the fractional yield of each ion versus the ionizing voltage fall into three distinct types. According to these authors, the first group of curves, designated by them as Type I, is for those ions whose fractional yields vary inversely with the electron energy. Type I curves are observed only for parent ions and for primary ions with a low activation energy. Type II curves are for those ions whose relative yields rise rapidly to a maximum at about 10 V. above the ionization potential, and then drop off slightly at higher voltages. This type of curve arises from primary products with a slightly higher energy; the slight drop in yield observed at the higher electron voltages probably arises from competition with primary processes with still higher activation energies or from a slight secondary decomposition. Type III curves are for those ions whose relative yields rise slowly and do not level off until at much higher voltages. Type III ions result from high energy processes; they are either primary ions with a high activation energy, or secondary or further fragmentation products which require a high energy for their formation.

Their conclusion is for a pure substance, but according to circumstances it may furnish useful information on a composite system. Curve 1 in Fig. 3 and curve 1 in Fig. 4; curve 2 in Fig. 3 and curve 3 in Fig. 4; and curve 3 in Fig. 3 and curve 2 in Fig. 4 of the present investigation assume forms typical of curves of types I, II and III respectively.

In the spectrum of commercial phosphorus pentoxide, the appearance potential of the $P_4O_9{}^+$ ion is lower than that of the $P_4O_{10}{}^+$ ion, as may be

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14) A. B. King and F. A. Long, *J. Chem. Phys.*, **29**, 374 (1958).

seen in Fig. 5, and no ion peak of a mass greater than the *m/e* 284 ion, $P_4O_{10}^+$, is observed, as has been mentioned previously. Table II shows that the peak height of the $P_4O_9^+$ ion, at a constant temperature, decreased with time. These results suggest that some part of the $P_4O_9^+$ may not be produced by electron bombardment from the P_4O_{10} molecule by the loss of an oxygen atom and an electron, but that the P_4O_9 itself is a parent molecule. Curve 1 in Fig. 3, indeed, assumes a typical parent ion type, i. e., type I. In the oxidation process of commercial phosphorus pentoxide, lower oxides of phosphorus are reported to be oxidized completely. Curve 3 in Fig. 4, which represents the behavior of the *m/e* 268 ion, $P_4O_9^+$, of purified phosphorus pentoxide, shows that the ion current is far less intense at lower electron energies, where further fragmentations of the P_4O_9 are of minor importance, than that of commercial phosphorus pentoxide. The finding that curve 2 in Fig. 3, the $P_4O_{10}^+$ ion curve from commercial phosphorus pentoxide, is not of the parent ion type, i. e., type I of King and Long, can be accepted if we consider that the oxide contanis a P_4O_9 molecule, the appearance potential of its parent ion, $P_4O_9^+$, being lower than that of $P_4O_{10}^+$ from the P_4O_{10} molecule. In fact, curve 1 in Fig. 4, for $P_4O_{10}^+$ from purified phosphorus pentoxide which contains no P_4O_9 molecule at all, is of the typical parent ion type. A graph similar to Fig. 3 was also obtained from a commercial phosphorus pentoxide at 295°C.

From the standpoint of mass spectrometry, we may conclude that a vapor equilibrium with a commercial phosphorus pentoxide, which is oxidized incompletely, contains the P_4O_9 molecule as well as the P_4O_{10} molecule, and no stable polymers heavier than P_4O_{10}. The molecular structrues of P_4O_{10} and P_4O_6 have been well established by electron diffraction studies.(15) In P_4O_6 the four phosphorus atoms are at the corners of a tetrahedron, each bonded to three oxygen atoms along the tetrahedron edges. The P_4O_{10} molecule is very similar to the P_4O_6 molecule in structure, with the addition of an oxygen atom to each phosphorus atom completing the PO_4 tetrahedra. The structure of P_4O_9 might be much the same as the P_4O_{10} molecule, with the exception of the loss of an unshared oxygen atom from a phosphorus atom. This phosphorus will be trivalent, while the other three atoms are pentavalent. Recently, Thilo, Heinz and Host(16) and Heinz(17) have reported on a mixed crystal consisting of P_4O_9 and P_4O_8 molecules.

From the difference in pattern coefficients between purified phosphorus pentoxide and the commercially-available guaranteed reagent phosphorus pentoxide, the amount of P_4O_9 contained in the latter is estimated to be of an order of a percentage points.

Summary

Phosphorus oxides have been investigated by means of mass spectrometers. The mass spectrometers used were a Nier-type spectrometer equipped with a Knudsen cell and a CEC 21-103C type. From the ionization efficiency curves, P_4O_9 molecules have been found to be contained in vapor equilibrium with a commercially available phosphorus pentoxide. From the relation between the vapor pressure and the temperature of phosphorus pentoxide, the existence of a new low-temperature phase of the oxide has been inferred.

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15) G. C. Hampson and A. J. Stosick, *J. Am. Chem. Soc.*, **60** 1814 (1938); L. R. Maxwell, S. B. Hendricks and L. S. Deming, *J. Chem. Phys.*, **5**, 626 (1937).

16) E. Thilo, D. Heinz and K.-H. Host, *Angew. Chem.* **76**, 229 (1964).

17) D. Heinz, *Z. anorg. u. allgem. Chem.*, **336**, 137 (1965).