chemical behavior in monoglyme[4a,b] and acetonitrile suggest that solvent effects may play a significant rôle in determining the mechanistic pathways of boron hydride oxidation and reduction processes.

Acknowledgment. William O'Deen built the potentiostat described in the Experimental Section. Helpful discussions of this work with D. E. Smith and S. W. Feldberg are also acknowledged.

The Preparation and Mass Spectrometry of Triphosphine-5

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Abstract: A convenient photochemical method for the preparation of triphosphine-5, P_3H_5, is described. The purification and the determination of some of the physical properties of this unstable compound are reported. The fragmentation pattern and appearance potentials of selected ions have been determined using a mass spectrometer with molecular beam sampling. The latter results allow the phosphorus–hydrogen and phosphorus–phosphorus bond energies and the proton affinity of phosphine to be estimated. This compound, which is an intermediate in the thermal decomposition of diphosphine-4, thermally decomposes at 300°K to yield diphosphine-4 and tetraphosphine-6. This reaction is the prototype for a generalized chain growth step in the net polymerization of diphosphine-4.

The formation of triphosphine-5, P_3H_5, as an intermediate in the thermal decomposition of diphosphine-4 has been reported previously.[2] This unstable compound is of considerable interest as it contains two phosphorus–phosphorus bonds. Evidence suggesting its existence has appeared several times in the past. The unidentified white solid melting at $-34°$ observed by Evers and Street in liquid diphosphine-4 was no doubt P_3H_5.[3] In a series of reports Baudler and coworkers have presented a substantial amount of evidence for the existence of triphosphine and higher hydrides of phosphorus.[4] Some mass spectrometric evidence has also been presented by others.[5] However, none of these workers has isolated and studied triphosphine-5, and we now wish to report on the preparation, isolation, and characterization of this compound.

Results and Discussion

Preparation. Triphosphine-5 was originally prepared by the pyrolysis of diphosphine-4 in a special reactor (see below). Although the yields were fair, the method proved unsatisfactory as a preparative method as the removal of the unreacted diphosphine-4 could not be accomplished without destroying a majority of the triphosphine-5 product. This simply reflects the instability of this compound, especially in the liquid phase. With this method we were never able to obtain triphosphine-5 with less than 40% diphosphine-4. Consequently we sought a preparation procedure that would minimize the contamination of the crude product with P_2H_4. Along with other workers, we had noted that diphosphine-4 decomposition was enhanced by ordinary daylight.[4,6,7] By photolyzing diphosphine-4 in a bulb and analyzing the products, it was easily shown that triphosphine-5 was a product of the photodecomposition. A circulating flow reactor described in the Experimental Section was then developed to prepare larger quantities of this compound. The trick in the preparation is that by the proper choice of cold baths, nearly pure (95%) triphosphine-5 can be obtained.[8]

Phosphine is also produced in the photolytic reaction, and after a period of time the reactor line became contaminated with solid material. The yield of phosphine and triphosphine-5 as a function of irradiation time is shown in Figure 1. Both compounds were measured utilizing a modified codistillation–fractionation apparatus.[9] Calibration relating peak area to moles was carried out for phosphine, but the yields for triphosphine-5 are estimates based on peak areas. Unexpectedly, this apparatus was not useful for the purification of triphosphine-5 due to problems of decomposition.

There are a few enlightening clues as to the nature of the photolysis reaction. First, in some earlier studies on diphosphine-4,[10] the action of light on diphosphine-4

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[1] The Radiation Laboratory is operated by the University of Notre Dame under contract with the Atomic Energy Commission. This is AEC Document No. COO-38-599.

[2] T. P. Fehlner, *J. Amer. Chem. Soc.*, **88**, 2613 (1966).

[3] E. C. Evers and E. H. Street, Jr., *ibid.*, **78**, 5726 (1956).

[4] M. Baudler and L. Schmidt, *Naturwissenschaften*, **46**, 577 (1959); M. Baudler, H. Ständeke, M. Borgardt, and H. Strabel, *ibid.*, **52**, 345 (1965); M. Baudler, H. Ständeke, M. Borgardt, H. Strabel, and J. Dobbers, *ibid.*, **53**, 106 (1966).

[5] P. Royen, C. Rocktäschel, and W. Mosch, *Angew. Chem.*, **76**, 860 (1964).

[6] E. R. Nixon, *J. Phys. Chem.*, **60**, 1054 (1956).

[7] S. R. Gunn and L. G. Green, *ibid.*, **65**, 779 (1961).

[8] It should be emphasized that experiments in dark reactors showed that triphosphine-5 is also produced by pyrolytic decomposition.

[9] G. H. Cady and D. P. Seigwarth, *Anal. Chem.*, **31**, 618 (1959).

[10] T. P. Fehlner, *J. Amer. Chem. Soc.*, **89**, 6477 (1967).

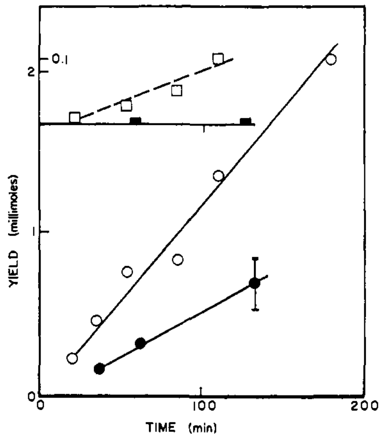

Figure 1. Yield as a function of irradiation time at 25°. The open circles and squares refer to phosphine and triphosphine-5, respectively. The solid points refer to dark runs.

in a clear glass inlet line of a mass spectrometer resulted in an observable stationary-state concentration of diphosphine-2. Secondly, using the rated intensity of the photolytic reactor (*ca.* 3 × 10^{16} photons sec^{-1} cm^{-3}) and assuming all the radiation is absorbed, a minimum over-all quantum yield for the production of phosphine can be calculated from the data contained in Figure 1.[11] The value obtained is greater than 1, and thus some chain process must certainly be involved in the formation of phosphine and probably triphosphine-5. With these two pieces of information a tentative mechanism can be written as

$$P_2H_4 \xrightarrow{h\nu} PH_3 + {}^1/_2P_2H_2$$

$$^1/_2P_2H_2 + P_2H_4 \longrightarrow {}^1/_2P_3H_5 + {}^1/_2PH_3 + {}^1/_2P_2H_2 \text{ chain}$$

$$nP_2H_2 \xrightarrow{\text{wall}} \text{polymer}$$

where more than one step could be involved in each of the reactions. The second reaction can take place throughout the circulation system if the destruction of P_2H_2 is not too rapid.

Characterization. Several of the physical properties of this molecule have been measured. The vapor pressure of triphosphine-5 is given in Figure 2 as a function of temperature. As this compound is known to be in the solid phase below −40°, a melting point of −34° is estimated from the intersection of the sublimation and vaporization curves. Assuming a Trouton's constant of 20, the boiling point is estimated at 96°.[12] The molecular weight of this compound was measured by measuring the average velocity of gaseous molecules in a collimated molecular beam.[13-15] A value of 95 ± 10 was obtained.[16] We were not successful in obtaining an infrared spectrum of this molecule.

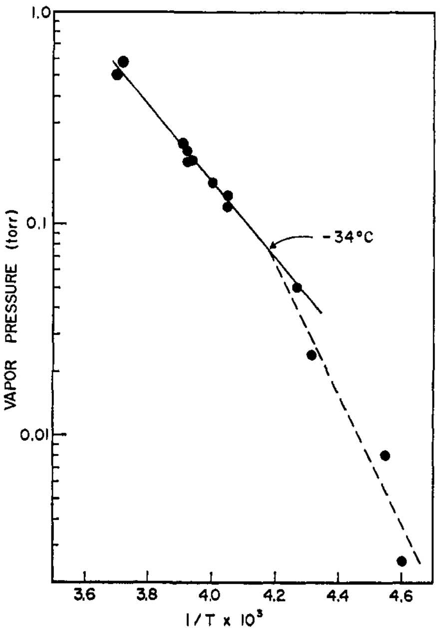

Figure 2. The vapor pressure of triphosphine as a function of temperature. The solid line is the vapor pressure curve, while the dashed line is the approximate sublimation curve.

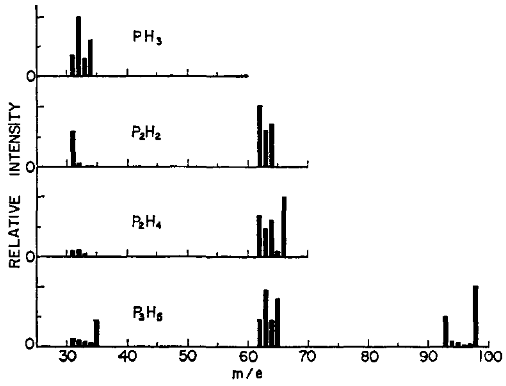

Figure 3. The fragmentation patterns for the hydrides of phosphorus at 70 eV.

To avoid the very real problem of thermal decomposition in the ion source, the mass spectrometry of this molecule was examined by utilizing a spectrometer with molecular beam sampling.[10] The relative ionic abundances of the fragments produced by electron bombardment of this molecule are compared with those produced from the other hydrides in Figure 3.[17] In the comparison of these spectra, one notes that with the exception of the parent ion, the hydrogen-containing P_3 ions have very low relative intensities. As originally there was the real possibility that this compound could be $P_2H_4O_2$, the completely deuterated compound was also prepared. The resulting spectrum clearly showed

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[11] It will be noted that there is a large dark reaction yielding phosphine but not triphosphine-5. This is probably decomposition on the solid polymer in the circulation system resulting in the production of phosphine and net polymer growth.

[12] This is a reasonable assumption as both phosphine and diphosphine-4 have Trouton's constants of nearly this value. In addition, using this method to estimate the boiling point is more accurate than extrapolation of the measured curve.

[13] R. M. Yealland, R. L. LeRoy, and J. M. Deckers, *Can. J. Chem.*, **45**, 2651 (1967).

[14] M. H. Boyer, E. Murad, H. Inami, and D. L. Hildenbrand, *Rev. Sci. Instrum.*, **39**, 26 (1968).

[15] T. P. Fehlner, *J. Amer. Chem. Soc.*, **90**, 4817 (1968).

[16] The use of a gas-density balance failed to give a good value for the molecular weight because of decomposition.

[17] T. P. Fehlner and R. B. Callen, Advances in Chemistry Series, No. 72, American Chemical Society, Washington, D. C., 1968, pp 181–190.

that the compound being examined contained five hydrogen atoms. One also notes the rather prominent $P_2H_3^+$ ion peak and also the presence of an intense PH_4^+ ion peak. The identity of the latter was likewise proved by deuterium substitution. The latter ion peak has previously been observed at low relative intensities in the mass spectra of the alkyl phosphines. Although these features are interesting, it is not presently known how to relate them to the structure of triphosphine-5.

The appearance potentials of selected ions from triphosphine-5 have been measured. The appearance potential of the $P_3H_5^+$ ion is found to be 8.7 ± 0.1 eV and is identified with the ionization potential of triphosphine-5.[18] With the ionization potentials of phosphine and diphosphine-4 as parameters,[17] the ionization potential of triphosphine-5 can be calculated using the semiempirical treatment of Franklin. If one assumes a "propane-like" structure ($H_2P-PH-PH_2$) with no interaction between terminal groups, a value of 8.81 ± 0.11 eV is calculated. The agreement between the empirical and theoretical values suggests that one can view this molecule as a simple chain phosphorus hydride and the third member in the homologous series P_nH_{n+2}.

The appearance potential of $P_2H_3^+$ from triphosphine-5 is of interest as it allows an estimation of the phosphorus–hydrogen and phosphorus–phosphorus bond energies. Utilizing the appearance potential of this ion from diphosphine-4 and assuming the processes

$$e + P_2H_4 = P_2H_3^+ + H + 2e$$
$$A(P_2H_3^+/P_2H_4) = 12.2 \pm 0.2 \text{ eV}$$

$$e + P_3H_5 = P_2H_3^+ + PH_2 + 2e$$
$$A(P_2H_3^+/P_3H_5) = 10.6 \pm 0.1 \text{ eV}$$

occurring with negligible excess energy, the difference between the average phosphorus–hydrogen, *E*(P–H), and phosphorus–phosphorus, *E*(P–P), bond energies is 1.6 eV. Using a value of 77 kcal/mole for *E*(P–H),[7] one obtains a value of 40 kcal/mole for *E*(P–P). Alternatively, by utilizing the heats of formation of phosphine and diphosphine-4, the heat of formation of the PH_2 radical can be calculated in terms of the heat of formation of triphosphine-5. The latter has been estimated previously to be 14–18 kcal/mole[15] which yields a heat of formation for the PH_2 radical of 24–28 kcal/mole. This in turn implies a $D(PH_2-H)$ = 75–79 kcal/mole and a $D(H_2P-PH_2)$ = 43–51 kcal/mole. One must of course use these values with caution for reasons which have been discussed many times previously.[19] An interesting comparison of bond energies for the phosphorus compounds with their nitrogen analogs is made in Table I. The relative weakness of $P_\pi-P_\pi$ bonding in phosphorus compounds is obvious.

Table I. Bond Energies (kcal/mole)

	X = N	X = P
$D(H_2X-H)$	104[d]	77[a]
$D(H_2X-XH_2)$	58[d]	47[a]
$D(HX-XH)$	104[e]	80[b]
$D(X-X)$	225[e]	117[c]

[a] This work. [b] This work and ref 17. [c] T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworth and Co., Ltd., London, 1958. [d] S. N. Foner and R. L. Hudson, *J. Chem. Phys.*, **29**, 442 (1958). [e] S. N. Foner and R. L. Hudson, *ibid.*, **28**, 719 (1958).

The appearance potential of the PH_4^+ ion is useful also. Assuming the process

$$e + P_3H_5 = PH_4^+ + P_2H + 2e$$
$$A(PH_4^-/P_3H_5) = 10.0 \pm 0.2 \text{ eV}$$

occurs with negligible excess energy, the proton affinity of phosphine can be calculated. A value of 172 kcal/mole is calculated, and it is noted that this is a minimum value both by virtue of the process chosen and the assumption of no excess energy.[20] This value may be compared with one previous calculation of 207 kcal/mole[21] and another indirectly measured value of 153 kcal/mole.[22] The latter value suffers somewhat from the fact that it is derived from two appearance potential measurements on very weak ion peaks (relative intensities of *ca.* 1% of the base peak). Our value suffers from the fact that it appears incompatible with solution chemistry and the reported value for the proton affinity for water.[21,22] On the other hand, the ion–molecule reaction

$$PH_3^+ + PH_3 \longrightarrow PH_4^+ + PH_2$$

has been studied recently[23] and the rate for this reaction has been found to be 10^{-9} cm^3 molecule^{-1} sec^{-1}. This may be compared to a rate of 0.5×10^{-9} cm^3 molecule^{-1} sec^{-1} of the analogous nitrogen reaction[24] which is exothermic by 30 kcal/mole. Using the heat of formation of the PH_2 radical given above and our proton affinity for phosphine, an exothermicity of 11 kcal/mole is calculated for this reaction. Using the low value for the proton affinity, the reaction is endothermic by 8 kcal/mole. This suggests that our value may be closer to the true one. Unfortunately these results are not conclusive.

Reactions. As triphosphine-5 is an intermediate in the net thermal decomposition of diphosphine-4, the thermal decomposition of this compound is of great interest also. A detailed study of the low-pressure pyrolysis of this species has been reported elsewhere.[15] Over the pressure range 0.2–10 mtorr and the temperature range 450–660°K, triphosphine-5 decomposes *via* two parallel paths. Diphosphine-4 and diphosphine-2 are the products of one path, while phosphine and diphosphine-2 are the products of the other.

Triphosphine-5 also reacts rapidly in the liquid phase. This compound melts into a clear liquid which, in about a minute at room temperature, turns yellow with an accompanying release of diphosphine-4. The liquid becomes increasingly viscous and finally solidifies into a yellow apparently polymeric material.

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(18) In the original communication the ionization potential of P_3H_5 was reported to be 0.3 ± 0.2 eV less than that of diphosphine-4. The value of the ionization potential of P_2H_4 contained in the original communication is incorrect. The correct value is 9.17 ± 0.05 eV as given in ref 17.

(19) C. A. McDowell, Ed., "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1963.

(20) The process that produces P_2 and H rather than P_2H requires about 40 kcal more energy.

(21) W. Wendlandt, *Science*, **122**, 831 (1955).

(22) Y. Wada and R. W. Kiser, *J. Phys. Chem.*, **68**, 2290 (1964).

(23) M. Halmann and I. Platzner, *ibid.*, **71**, 4522 (1967).

(24) F. W. McLafferty, Ed., "Mass Spectrometry of Organic Ions," Academic Press, New York, N. Y., 1963, p 93.

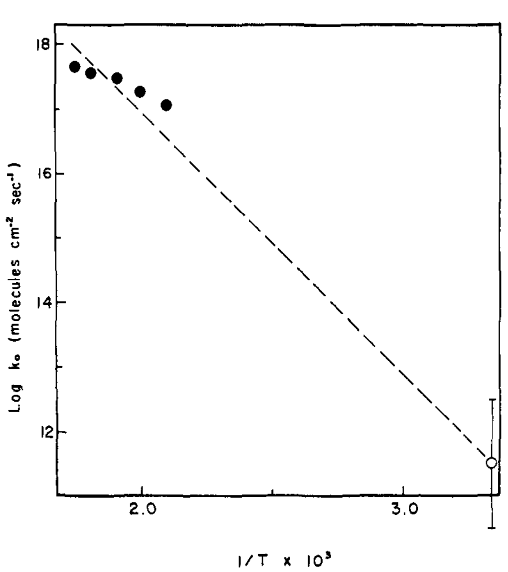
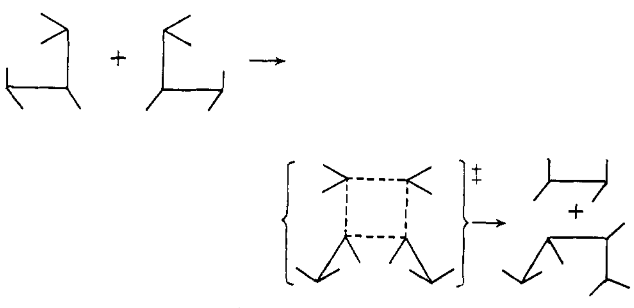


Figure 4. Zero-order rate constant for the decomposition of triphosphine-5 as a function of temperature. The closed circles are data from ref 15, and the open circle is the rate constant for the inlet reaction.

Decomposition was also observed in the inlet line during the mass spectrometric measurements. Diphosphine-4 is a product of this reaction, and the observation of a small ion intensity at *m/e* 130 indicates the presence of tetraphosphine-6, P_4H_6. The inlet line can be considered as a small flow reactor, and as under the conditions of pressure employed the diffusional mixing time is much smaller than the average time a molecule spends in the reactor, the reactor behavior may be approximated by the equations of LeGoff discussed in an earlier paper.[10] The reaction appears to be zero order in triphosphine-5 pressure and a zero-order rate constant can be calculated. Now it has already been shown that triphosphine-5 decomposes *via* a zero-order path to yield diphosphine-4 and diphosphine-2 at temperatures above 450°K and smaller average reaction times. Consequently, as tetraphosphine-6 might well be unstable at these temperatures, these two reactions may be identical. Indeed, if one plots the zero-order rate constants for both studies in an Arrhenius-type plot, there is a fair correlation (Figure 4). It appears then that the reaction path

$$2P_3H_5 \longrightarrow P_2H_4 + P_4H_6$$
$$\qquad\qquad\qquad\qquad \llcorner\!\!\longrightarrow P_2H_4 + P_2H_2$$

is being observed where the second reaction is fast above 450°K. One might picture the first reaction path as



$$2P_3H_5 \longrightarrow \left\{P_6H_{10}\right\}^{\ddagger} \longrightarrow P_4H_6 + P_2H_4$$

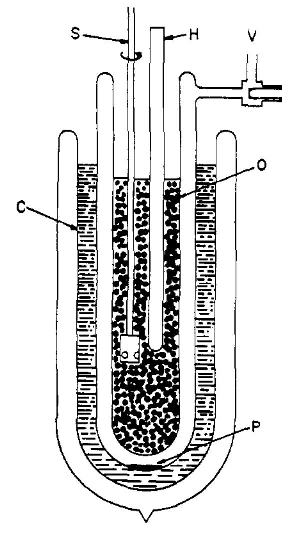


Figure 5. Pyrolytic reactor for the preparation of triphosphine-5. C is the cold bath and O is the hot bath. S and H are the mechanical stirrer and immersion heater, respectively. V is the valved connection to the vacuum system and P represents liquid diphosphine-4. The reactor dimensions were 8 cm i.d. × 30 long and it was constructed out of Pyrex glass.

The four-center cyclic transition state envisioned is quite feasible here as there are a number of four-membered cyclic phosphorus compounds known. It should be particularly noted that this reaction path is a prototype reaction for a generalized chain growth step in the net polymerization of diphosphine-4. This reaction may be written[25] $P_nH_{n+2} + P_mH_{m+2} \rightarrow P_{m+n-2}H_{m+n} + P_2H_4$. Consequently this reaction is one of the keys to the understanding of the nature of the net polymerization process.

Experimental Section

Preparation of Diphosphine-4. Diphosphine-4 was prepared by the addition of water to calcium phosphide in a grease-free and mercury-free vacuum system. The crude product was purified by trap-to-trap distillation and stored at 77°K in the dark. The details of the preparation have been given elsewhere.[3]

Preparation of Triphosphine-5 by Pyrolysis. Triphosphine-5 was originally prepared in the apparatus pictured in Figure 5. The operation of this reactor, which is known as a hot-cold reactor, has been described elsewhere.[26] In these experiments the inner tube was maintained at a temperature of 65–70° while the outside tube was immersed in a slush bath at −63° at a temperature at which diphosphine-4 has a vapor pressure of 2 torr.[3] Diphosphine-4 was held in the annular space between the two tubes (*i.e.*, pyrolyzed) for 1 hr under the above conditions. The resulting phosphine was then distilled away with the unreacted diphosphine-4. The hot bath was removed and the remaining white solid triphosphine-5 was distilled out at −23°. The triphosphine-5 prepared in this method was always contaminated with diphosphine-4 (*ca.* 40%) and attempts to purify the product further by redistillation resulted in large losses of product by decomposition. Although this reaction is not useful from a preparative viewpoint, it is important from a mechanistic viewpoint for the following reason. This reactor has the important feature that any products less volatile than diphosphine-4 will be rapidly removed from the reaction by condensation on the cold surface. This method of production is then

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(25) This reaction can take place between two diphosphine-4 molecules or diphosphine-4 and triphosphine-5 but would yield no net reaction.

(26) M. J. Klein, B. C. Harrison, and I. J. Solomen, *J. Amer. Chem. Soc.*, 80, 4149 (1958).

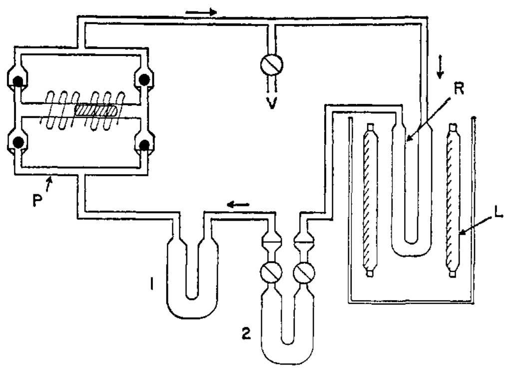

Figure 6. Photolytic reactor for the preparation of triphosphine-5. P is the circulating pump with a circulation rate 1.3 l./min (H. Melville and B. G. Gowenlock, "Experimental Methods in Gas Reactions," Macmillan & Co., Ltd., London, 1964, p 49). R is the reaction volume of clear Pyrex glass with a volume of 325 cc. 1 and 2 are traps and 2 is removable. V is the vacuum line connection. L is one of the 16 lamps (3500 Å) of a Srinivasan–Griffin Rayonet photochemical reactor. The arrows show the direction of circulation. With the exception of the reaction zone, the entire system was painted with several layers of black paint. The system volume was 1.3 l.

good evidence for the role of triphosphine-5 as an intermediate in the pyrolysis of diphosphine-4.

Preparation of Triphosphine-5 by Photolysis. Triphosphine-5 was prepared in the apparatus shown in Figure 6 and described in the accompanying caption. A typical preparation was carried out as follows. About 2 cc of liquid diphosphine-4 was distilled into trap 1 and the circulation system was charged with about 160 torr of helium for efficient pumping. Chlorobenzene slushes (−45°) were then placed around both traps 1 and 2 and the circulation pump was started. The lamps were turned on initiating the reaction, and circulation was continued for about 3 hr. Yields as a function of irradiation time are given in Figure 1. In contrast to the pyrolytic preparation where the slush bath had to be continually renewed, this preparation requires no attention during the reaction. After the reaction is complete, trap 1 is immersed in liquid nitrogen and circulation is continued for about 20 min to remove the phosphine and diphosphine-4 from the system. The helium is then pumped away and trap 2 is pumped on until the pressure falls below 50 mtorr (*ca.* 1 min). The product remaining in trap 2 is about 95% triphosphine-5 and 5% phosphine-4 as judged mass spectrometrically.

Vapor Pressure Measurements. Trap 2 was attached to the inlet system of a mass spectrometer,[10] and the vapor over the solid or liquid triphosphine-5 was monitored as a function of the slush bath temperature around the trap. Temperatures were measured using a pentane thermometer, and pressures were measured using a thermocouple gauge calibrated against a Bourdon tube gauge for diphosphine-4. The intensity of the *m/e* 98 ion peak was also used as a relative measure of the vapor pressure. The method is somewhat crude but has the advantage of continuous monitoring of the sample purity. The values obtained appeared to be independent of sample size. At the high-pressure end of the curve, decomposition in the liquid was a problem and the values recorded may be low. This is shown by the fact that the extrapolated boiling point is much higher than that calculated using Trouton's rule.

Mass Spectrometric Measurements. The mass spectrometer used in these studies has been described previously.[10,15] A molecular beam sampling technique is used to eliminate complications due to source reactions. Decomposition in the inlet line of the mass spectrometer was kept to a minimum by evaporating triphosphine-5 from a reservoir kept at a constant low temperature. Transfer to the spectrometer was through a light-tight, mercury-free vacuum line. The appearance potentials were measured using the log matching method.[27] The ionization potential of diphosphine-4 was used to calibrate the energy scale.

Acknowledgments. This work was supported in major part by the Radiation Laboratory of the University of Notre Dame which is operated under contract with the Atomic Energy Commission. The mass spectrometer with the molecular beam sampling system was constructed with support from the National Science Foundation (NSF-GP-6820). The author wishes to thank Robert B. Callen for his aid in some of the intial mass spectrometric experiments and Richard P. Terrell for his efforts on the gas density balance.

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(27) S. N. Foner and R. L. Hudson, *J. Chem. Phys.*, **25**, 602 (1956).