complexes with identical ligands, whose contact shifts are primarily the result of direct contact interactions produced by unpaired π-electron density, reveals that the d orbitals of the lighter metal interact preferentially with the ligand antibonding orbitals. This observation is in full agreement with Eaton's argument, based on the contact shifts for metal acetylacetonates,[5] that with increasing nuclear charge the d orbitals contract and become relatively more stable.

Although the foregoing interpretation of the contact shifts of **1** and **2** is necessarily qualitative, it is believed to be essentially correct. By way of supporting evidence, it is noted that delocalization *via* path iii has also been concluded to be primarily responsible for the contact shifts of β-diketone[4,5] and β-ketoamine[1] V(III) complexes, which are structurally and electronically similar to **1** and **2**, respectively, and for which the neglect of pseudo-contact interactions, particularly in the *cis* isomers, is on firmer ground. Further analysis of the contact shifts of any of these complexes is not feasible until or unless the magnitude and directions of g tensors are determined and the effects of σ-spin delocalization[25,26] can be semiquantitatively assessed.

Acknowledgment. This research was supported by the U. S. Public Health Service under National Institutes of Health Grant GM-12920. We thank Dr. M. J. O'Connor for communication of certain of the results in ref 10 prior to publication.

(26) Z. Luz, B. L. Silver, and D. Fiat, *J. Chem. Phys.*, **46**, 469 (1967).

A Mass Spectrometric Investigation of the Low-Pressure Pyrolysis of Diphosphine-4

T. P. Fehlner

Contribution from the Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556. *Received June 9, 1967*

Abstract: Diphosphine-4, P_2H_4, thermally decomposes in a Pyrex reactor over the pressure range of 0.5–50 mtorr into phosphine and diphosphine-2 by a reaction which is zero order in diphosphine-4. Over the temperature range 570–650°K, the rate of the reaction is expressed by $\log h(T) = 20.8 - 4800/T$ molecules cm^{-2} sec^{-1}. In addition, the intermediate product diphosphine-2 decomposes to give tetraatomic phosphorus as one product in a reaction which is inhibited by phosphorus hydrides. The relevance of these results to the thermal stability of diphosphine-4 is discussed.

The nature of the reactions of diphosphine-4, P_2H_4, is of considerable interest and importance as this is one of the simplest molecules containing a phosphorus–phosphorus bond. Pyrolysis is perhaps the simplest reaction that this compound can undergo, at least from the point of view of number of reactants. In possibly the most complete study to date, Evers and Street have examined the final products of the thermal decomposition of diphosphine-4 in the liquid and/or gaseous phases under anhydrous conditions.[1] They found phosphine and a hydride having a composition P_9H_4 as final products. However, it has been noted in several instances that the decomposition of diphosphine-4 is also sensitized by light and various impurities[1-3] and, as yet, no study of the gas-phase pyrolysis in the absence of light and other impurities has been published.

Some preliminary results of this study in which intermediate products of the pyrolysis were identified have been reported.[4,5] Diphosphine-2 was definitely identified in the low-pressure pyrolysis of diphosphine-4 in a quartz tubular flow reactor. Later, this molecule was found to be produced in the ion source of a mass spectrometer probably by pyrolysis on the filament or source walls.[6] Triphosphine-5 was tentatively identified in these studies and was also prepared in substantial quantities outside of the mass spectrometer.[5] Evidence for the existence of this compound has been presented by others also.[7-9] Here we present a more comprehensive report of the low-pressure pyrolysis of diphosphine-4 which includes a detailed study of the products, reaction order, stoichiometry, and reaction rate.

Experimental Section

The pyrolytic reactor for these studies was patterned after a reactor pictured and theoretically described by LeGoff in a series of papers.[10-12] This short, cylindrical reactor, which is illustrated on the left side of Figure 1, was fabricated completely out of Pyrex glass (80% SiO_2, 14% B_2O_3, 4% Na_2O, 2% Al_2O_3) and had a volume of 3.2 cc. The reactant gas entered through a 0.35-mm diameter capillary leak and exited through a 0.40-mm diameter thin-walled orifice. The capillary leak was cooled with water both to prevent a change in conductance and to prevent decomposition in the capillary. The cylindrical sides of the furnace were heated with noninductively wound nichrome wire imbedded in Sauereisen

---

(1) E. C. Evers and E. H. Street, Jr., *J. Am. Chem. Soc.*, 78, 5726 (1956).

(2) S. R. Gunn and L. G. Green, *J. Phys. Chem.*, **65**, 779 (1961).

(3) E. R. Nixon, *ibid.*, 60, 1054 (1956).

(4) T. P. Fehlner, *J. Am. Chem. Soc.*, **88**, 1819 (1966).

(5) T. P. Fehlner, *ibid.*, **88**, 2613 (1966).

(6) T. P. Fehlner and R. B. Callen, Advances in Chemistry Series, No. 68, American Chemical Society, Washington, D. C., in press.

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

(8) M. Baudler and L. Schmidt, *Naturwissenschaften*, **46**, 577 (1959).

(9) M. Baudler, H. Ständeke, M. Borgardt, H. Strabel, and J. Dobbers, *ibid.*, **53**, 106 (1966).

(10) P. LeGoff, *J. Chim. Phys.*, **53**, 359 (1956).

(11) P. LeGoff, *ibid.*, **53**, 369 (1956).

(12) P. LeGoff, *ibid.*, **53**, 380 (1956).

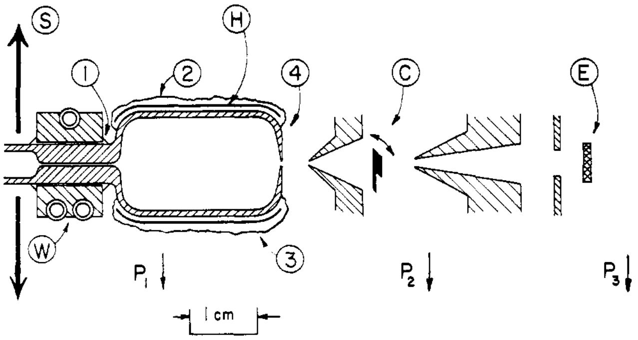


Figure 1. Schematic drawing of the reactor and beam-forming system. 1, 2, 3, and 4 refer to the thermocouple positions. C is the mechanical chopper. E is the electron beam cross section. H is the heating element. S refers to the direction in which the reactor may be scanned. W is the water cooling, and P_1, P_2, and P_3 refer to the three separate pumping systems.

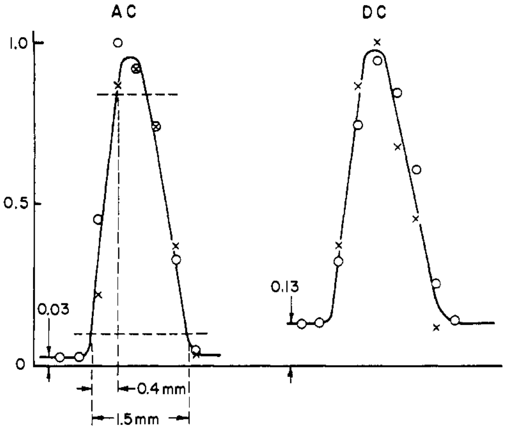


Figure 2. Profiles of the molecular beam for modulated (AC) and unmodulated (DC) operation.

cement. The temperature of the reactor was measured with three 0.005-in. diameter platinum—platinum-rhodium (90:10) thermocouples imbedded in the cement. The temperature difference between a point midway between two coils and a point adjacent to a coil was 15° at a reactor temperature of 650°K. The midpoint temperature was used in the following when a temperature is specified. The capillary temperature was also measured and was 350°K at a reactor temperature of 650°K. Both ends of the reactor were cooler than the sides (thermocouple 4 read a temperature of 600°K at a reactor temperature of 650°K), and thus this reactor must be treated as one in which only part of the reactor surface is active in the decomposition.[10] The conductance of the capillary leak and exit orifice in series was empirically measured, and from the pressure upstream of the leak and a calculated orifice conductance the actual reactor pressure was calculated. The pressure drop across the capillary leak was about 20 while that across the orifice was about 500.

Mass spectrometry was chosen as an analytical method because of its high intrinsic sensitivity, its inherently quantitative nature, and the possibility of rapid qualitative identification of both products and unstable intermediates. However, in this type of an experiment, where one is interested expressly in the reactions taking place in the reactor, one must have confidence that the analyzed composition corresponds to the actual reactor composition. There are a number of possible ways the composition can be distorted, and these were anticipated in the following manner.

If the reactor pressure exceeds the value for pure molecular flow through the exit orifice, then the analyzed beam composition need not correspond to the reactor composition.[13] At the highest reactor pressures used in these studies the mean free path was about twice the orifice diameter. If the molecules analyzed do not yield an appreciable parent ion intensity, an error can be made in the assignment of the neutral species. All of the phosphorus hydrides known thus far have substantial parent ions. As the temperature of the molecules is raised, it is quite possible that the rate of parent ion decomposition will be enhanced, and an apparent decrease in the parent ion intensity and a corresponding increase in the fragment ion intensities which is not due to molecular decomposition will be observed. This is discussed in detail below and is shown to be relatively unimportant in this case.

Finally, large background ion peaks may obscure small ion signals of interest, and if a thermally unstable molecule is being analyzed, it will more than likely decompose in the hot ion source to yield interfering products. These two complicating effects were eliminated by using modulated molecular beam sampling, a technique which has been described recently in some detail by Foner.[14] The beam system used in these studies is shown schematically in Figure 1. The molecules effusing from the reactor are collimated into a molecular beam with an individually pumped three-stage system, and the beam is ionized with an electron beam at right angles to the molecular beam axis. The ions are extracted in the direction of the molecular beam, mass analyzed, and detected in a normal circle, 90°, 8.75-cm radius of curvature, magnetic sector machine using electron multiplier detection. The neutral beam is modulated at 590 Hz, and the total output of the mass spectrometer is fed into a narrow-band amplifier locked-in to the frequency and phase of the chopper. The use of a modulated beam system eliminates unmodulated signals arising from background gas, residual gas (gas which enters the source as beam but is ionized after being scattered), and pyrolysis products although they still compete with the modulated signal as noise. In addition, the entire reactor can be scanned across the beam-forming system giving beam profiles such as those shown in Figure 2. By taking a profile with modulation (AC) and without modulation (DC), it is evident that, for nitrogen as a beam gas, 3% of the total unmodulated signal is due to scattered gas from chamber 1 and 10% is due to scattered gas in the source, chamber 3.[15] Even in the modulated mode, scanning the reactor is necessary to show that low abundance products are due to reaction in the reactor and not to the 3% of scattered gas from chamber 1. The ion signals observed then are due to gas introduced into the source in an essentially collision-free manner.

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 diphosphine-4 was evaporated from a liquid reservoir which was kept at a constant low temperature and transferred to the reactor through a light-tight, mercury-free vacuum line.[16] The *m/e* 34 ion peak intensity was used as a criterion of purity as the relative intensity of this ion from diphosphine-4 is very small.[6] Phosphine was obtained as a by-product of the preparation of the diphosphine. Sensitivity calibration for pure phosphine and pure diphosphine-4 was accomplished by simply measuring the pertinent ion intensities for various pressures of the compounds. In addition, known mixtures were used for calibration and were obtained by adding phosphine to streams of diphosphine-4 of known pressure and measuring the total pressure. Pressures were measured using a thermocouple gauge calibrated against a Bourdon tube gauge for each of the gases. The accuracy of the pressure measurement is not better than 10%. The vapor pressures observed for pure diphosphine-4 were considerably lower than those reported previously.[1]

Results

Identification of Products. The products of the decomposition of diphosphine-4 were identified by their characteristic fragmentation patterns,[6] the appearance potentials of selected ions,[6] their dependence on the diphosphine-4 supply, and the intensity dependence of the pertinent ions on the alignment of the reactor exit orifice with respect to the line of the beam system. Diphosphine-4 was introduced into the reactor through the

---

[13] T. A. Milne and F. T. Greene, *J. Chem. Phys.*, **44**, 2444 (1966).

[14] S. N. Foner, "Advances in Atomic and Molecular Physics," D. R. Bates, Ed., Academic Press Inc., New York, N. Y., 1966, p 385.

[15] Use of a mechanical shutter in chamber 2 made it possible to show that less than 0.3% of the total signal is from gas scattered in this chamber.

[16] In spite of these necessary precautions it usually took about 10 min at the start of each day to obtain pure diphosphine-4 at the reactor.

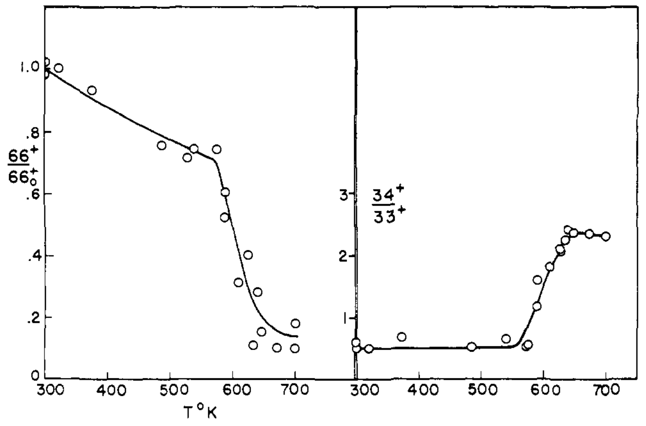


Figure 3. Variation in the *m/e* 66 ion intensity and the *m/e* 34 to 33 ion intensity ratio with reactor temperature.

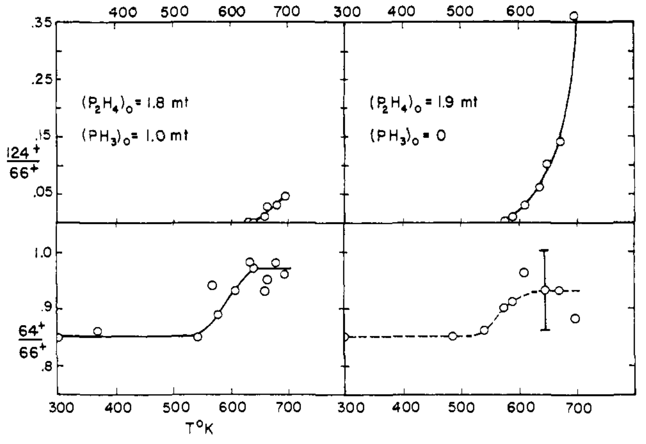


Figure 4. Variation in the *m/e* 124 to 66 ion intensity ratio and the *m/e* 64 to 66 ion intensity ratio with reactor temperature and initial phosphine pressure in millitorr.

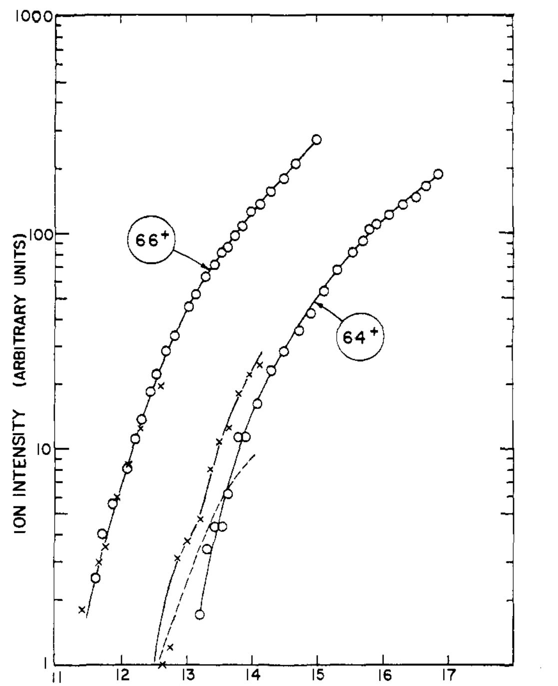


Figure 5. Variation in the ion efficiency curves for *m/e* 66 and 64 as a function of reactor temperature. The open circles refer to a reactor temperature of 300°K while the crosses refer to a reactor temperature of 650°K. The dashed curve is the difference of the *m/e* 64 curves.

capillary leak at a given pressure, and the mass spectrum was obtained.[17] The temperature of the reactor was then increased in a stepwise fashion, and the mass spectrum was obtained at each temperature after allowing time for temperature equilibration. Changes in the following ion intensities were observed: P_4^+, P_3^+, $P_2H_x^+$ (x = 0–4), PH_x^+ (x = 0–3). No ions containing hydrogen and three phosphorus atoms or hydrogen and four phosphorus atoms were observed in these experiments. Unfortunately, as the spectrometer magnetic field was produced by a permanent magnet, H_2^+ could not be monitored with the present instrument.

Selected ion intensity ratios which were observed are shown in Figures 3 and 4 as a function of temperature. In Figure 3 the ratio of the intensity of *m/e* 66 to the intensity of *m/e* 66 at 300°K (denoted as $66^+/66_0^+$) shows that decomposition sets in at about 570°K (the gradual decrease in the *m/e* 66 intensity is explained below and is not due to decomposition). The formation of phosphine beginning at a reactor temperature of about 560°K was immediately evident from the appearance of the characteristic fragmentation pattern of phosphine. The ratio $34^+/33^+$ in Figure 3 illustrates the production of this molecule. The increase in the P_4^+ ion intensity with increasing temperature along with a corresponding small increase in the P_3^+ intensity is attributed to the formation of the P_4 molecule as a product of the decomposition. This is illustrated in Figure 4 where the change in the ratio $124^+/66^+$ is shown. Finally, the increase in $64^+/66^+$ (shown in Figure 4), at the decomposition temperature of diphosphine-4, suggests that diphosphine-2 is formed in this reactor also. However, it was necessary to confirm its presence by measuring the appearance potential of the $P_2H_2^+$ ion as a function of the reactor temperature. The results are presented in Figure 5 where it is seen that there is a definite shift in the appearance potential of this ion to lower energy at a reactor temperature of 650°K. Similar shifts were observed in the P_2H^+ and P_2^+ ion appearance potentials, and, by reasoning identical with that presented previously,[4] it is concluded that diphosphine-2 is a product. In short, tetraatomic phosphorus, diphosphine-2, and phosphine were observed as products. No tetraphosphine, triphosphine, or free radicals were observed in these experiments.

At this point, it is useful to indicate several other observations. First, the decomposition was inhibited for a short period of time in the run immediately after pumpdown. Second, the addition of nitrogen gas appeared to inhibit the reaction slightly. Third, phosphine itself did not decompose at the temperatures used in this study. Finally, the addition of phosphine to the reactant diphosphine-4 did not significantly (10%) inhibit the loss of diphosphine-4 or the formation of phosphine. However, as is illustrated in Figure 4, it did inhibit the formation of P_4 and apparently enhanced the net amount of P_2H_2 formed. These observations are very suggestive of a surface reaction and furthermore

---

(17) It should be pointed out in passing that unless one takes the precautions noted in the Experimental Section, a mixture of hydrides will be introduced into the reactor instead of pure diphosphine-4; see also ref 6.

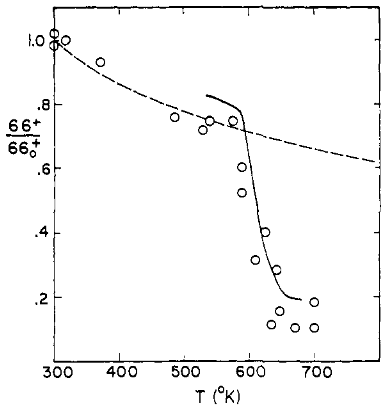


Figure 6. Variation in the m/e 66 ion intensity with reactor temperature. The open circles are experimental points, the dashed line is a plot of $(T_0/T)^{1/2}$, while the solid line refers to a calculated $66^+/66_0^+$ ratio.

point to the formation of P_4 by a reaction essentially different from that by which P_2H_2 is formed.

Treatment of Rate Data. Diphosphine-4 and phosphine are available in a pure state, and thus, in principle, it is possible to calibrate the mass spectrometer and measure the loss of diphosphine-4 and the formation of phosphine quantitatively. However, it is here that the effect of temperature on the rate of parent ion decomposition enters because, although the phosphine calibration can be carried out over the whole temperature range, the diphosphine-4 calibration cannot be carried out above the decomposition temperature. The question that arises is whether the total decrease in parent ion intensity with increasing reactor temperature is due only to molecular decomposition or is substantially due to enhanced parent ion fragmentation. Likewise, is the increase in the fragment ion intensities due to the formation of lighter molecular products or is part of it due to enhanced parent ion fragmentation? Fortunately in this system one can test the magnitude of this source of error as m/e 34 and 33 result only from diphosphine-4 and phosphine (the contribution of diphosphine-2 to m/e 33 is small[4]), and the ratio $34^+/33^+$ is a very sensitive function of the relative amounts of phosphine and diphosphine-4 present (see Figure 3). Thus from the ratios, $33^+/33_0^+$ and $34^+/33^+$, one can calculate in a simple manner a value of $66^+/66_0^+$ If the temperature effect is of significant magnitude then it would be expected that the ratio of $66^+/66_0^+$ calculated from the fragment ion peaks would be considerably larger than the observed $66^+/66_0^+$. In Figure 6 the observed $66^+/66_0^+$ ratio is compared with the calculated value, and, although the temperature effect is certainly not zero, it is not much larger than the scatter in the experimental points. Consequently, we feel justified in neglecting it.

The ion intensity of an ion produced by a single neutral species, I^+, is directly proportional to the molecular beam intensity, Q, and inversely proportional to the molecular velocity.[18] Thus one can write

$$I^+ = cQ/(T/M)^{1/2}$$

where T is the absolute temperature, M the molecular weight, and c a constant which depends on the cross section for the formation of the ion, the electron-beam density, and the area of intersection of the neutral and electron beams. Therefore, as in principle c is independent of the reactor temperature, one could evaluate the constant c at a temperature T_0 below the decomposition temperature and calculate the molecular-beam intensity at any temperature (assuming no decomposition) from the equation

$$Q/Q_0 = I^+/I_0^+(T/T_0)^{1/2}$$

There are several factors, however, which may cause c to be a function of the reactor temperature. The actual temperature of the gas may be different from that measured and used in the expression above. A significant amount of the gas may pass directly through the reactor with no collisions (see below also). The collection efficiency of the spectrometer may be a function of the molecular velocity. The rate of parent ion fragmentation may be enhanced with increasing temperature (see above). Finally, the mass flow through the capillary leak may change significantly with the reactor temperature. It is difficult to assess the individual contribution of all of these factors, and fortunately it is not necessary to do so. $c(T)$ can be determined empirically below the decomposition temperature and an extrapolation made over the relatively short decomposition temperature range. As may be seen in Figure 6, for diphosphine-4 the ratio $66^+/66_0^+$ lies close to a curve of $(T/T_0)^{1/2}$ below the decomposition temperature, and thus it would appear that $c(T)$ is independent of the temperature. However, this may merely indicate that there was a fortuitous cancellation of errors.

As a surface-type reaction was indicated by the qualitative observations noted above, it is convenient to present the data by using the terminology of LeGoff.[10] If the rate of the reaction, R, is given by

$$R = S(P_2H_4)^n k(T)$$

where S is the effective surface area, (P_2H_4), the concentration of diphosphine-4, n the order of the reaction, and $k(T)$ the rate constant, then the rate may also be written as

$$R = Sgb$$

where g is the density of collisions on the surface and b is the probability of reaction per collision (the collisional efficiency). It follows that b is a function of both g and the temperature and is given by

$$b = g^{n-1}h(T)$$

where $h(T)$ is a function of the temperature only and generally has the form $\exp(-E/RT)$, where E is an activation energy and R is the gas constant. If b is the probability of reaction per collision, the net yield of the reactor, B, is given by

$$B = v_m b/(1 + v_m b)$$

where v_m is the average number of collisions of a molecule with the reactive surface. If A is the area of the reactor exit orifice, then v_m is equal to S/A, which for this reactor equals 1.7×10^4.[19] It may be simply shown that

$$B/(1 - B)^n = v_m(g_0)^{n-1}h(T)$$

---

[18] W. L. Fite and R. T. Brackmann, *Phys. Rev.*, 112, 1141 (1958).

[19] It will be noted that when $b = 1$ at high temperatures, $1 - B$ gives the fraction of molecules that do not collide with the reactive

where g_0 is the initial density of collisions and thus by examining $B/(1 - B)^n$ as a function of g_0 at constant temperature and $B/(1 - B)^n$ as a function of temperature at constant g_0, one can determine the order, n, and $h(T)$, respectively.

Loss of Diphosphine-4. The reactor yield, B, is simply $(1 - g/g_0)$ and as g is related to Q, the beam intensity, by a geometrical factor; then

$$B = (1 - Q/Q_0) = 1 - (T/T_0)^{1/2}(66^+/66_0^+)$$

for the loss of diphosphine-4. At a constant temperature, a plot of log BQ_0 *vs.* log $(1 - B)Q_0$ or, as Q_0 is directly proportional to the initial diphosphine-4 pressure, a plot of log BP_0 *vs.* log $(1 - B)P_0$ should yield a straight line of slope n. The results are shown at the bottom half of Figure 7, and it may be seen that the reaction is zero order. As similar plots at other temperatures yield the same result, $h(T)$ is given by

$$h(T) = g_0B/v_m$$

By examining $h(T)$ as a function of temperature at constant g_0, it was found that $h(T)$ could be expressed by the following equation.

$$\log h(T) = 20.8 - 4800/T \text{ molecules cm}^{-2}\text{ sec}^{-1}$$

The apparent activation energy, 22 kcal/mole, had a precision of ±5 kcal/mole.

Formation of Phosphine. The formation of phosphine was followed by observing the $34^+/33^+$ ratio which was particularly sensitive to the phosphine/diphosphine-4 ratio at low extents of reaction. Calibrations with known mixtures of phosphine and diphosphine-4 were carried out and a calibration curve was constructed such that for any value of $34^+/33^+$ a corresponding phosphine to diphosphine-4 pressure ratio, $P(PH_3)/P(P_2H_4)$, could beread off. If the reaction to produce phosphine is

$$P_2H_4 \longrightarrow xPH_3$$

then B is given by

$$B = Q(PH_3)/xQ(P_2H_4)_0 = Q(PH_3)Q(P_2H_4)/xQ(P_2H_4)Q(P_2H_4)_0$$

or

$$xB = (M_2/M_1)^{1/2}[P(PH_3)/P(P_2H_4)](T/T_0)^{1/2}(66^+/66_0^+)$$

As before, a plot of log xBP_0 *vs.* log $(1 - B)P_0$ should yield a straight line of slope n, and this plot is presented in the upper half of Figure 7. Once again the slope is zero within experimental error. A comparison of curves similar to those in Figure 7 at various temperatures yields values of $x = 0.99$ at 650°, $x = 0.95$ at 630°, and $x = 1.02$ at 615°K with an average uncertainty of ±0.3 in each value. Therefore $h(T)$ for the formation of phosphine is given by the same equation as that for the loss of diphosphine-4.

Formation of Diphosphine-2 and Phosphorus. It was not possible to calibrate for diphosphine-2 and P_4, but an approximation of the stoichiometry for the formation of these species could be made. By assuming that the cross section for the ionization of diphosphine-2 is the same as that for diphosphine-4, the ratio of diphosphine-2 to diphosphine-4 could be estimated from the appearance potential curves near the threshold. As the ratio of phosphine to diphosphine-4 is already known, the ratio of phosphine to diphosphine-2 could be obtained. This comparison is made in Figure 8, and it may be seen that at high diphosphine-4 concentration the last ratio is close to 2 while at low diphosphine-4 concentration the ratio is much higher. A clue to this complex behavior was given in Figure 4 where the enhancing effect of added phosphine on the formation of diphosphine-2 and the concurrent inhibition of P_4 is illustrated. A possible explanation then, is that the diphosphine-2 produced undergoes a decomposition reaction to produce phosphorus, and this decomposition reaction is inhibited by both phosphine and diphosphine-4.

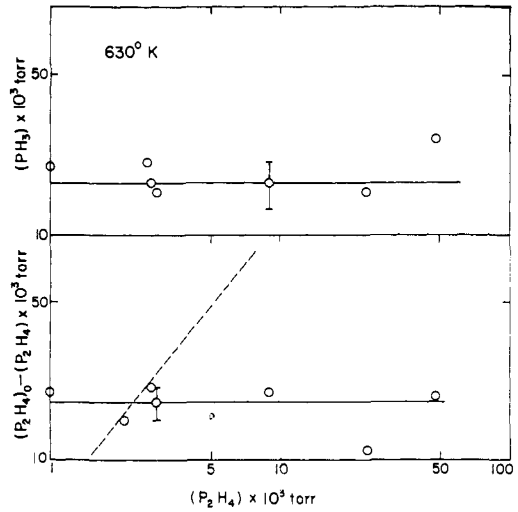


Figure 7. A plot of log BP_0 *vs.* log $(1 - B)P_0$ (lower curve) and a plot of log xBP_0 *vs.* log $(1 - B)P_0$ (upper curve) at a temperature of 630°K. The dashed line has a slope of 1.

If so, the logical question is what the hydrogen-containing product of this secondary reaction is. The most likely reactions are

$$P_2H_2 \longrightarrow {}^1/_3P_4 + {}^2/_3PH_3$$

$$P_2H_2 \longrightarrow {}^1/_2P_4 + H_2$$

The evidence for the most probable reaction is only indirect in nature. If the former reaction takes place, in the region where diphosphine-2 is extensively decomposed, the ratio of phosphine produced to diphosphine-4 lost should be greater than 1 and should approach a value of 1.3. However, the experimental error is of the same order of magnitude and no conclusions can be reached. Another approach would be to estimate the ratio of phosphorus produced to diphosphine-2 lost. Unfortunately only crude sensitivities could be obtained for P_4, and, even though the ratio obtained was closer to 1/3 than 1/2, not too much confidence can be placed in it. Although the decomposition reaction cannot be definitely established, it should be noted that the pyrolysis of a large quantity of diphosphine-4 at room temperature produced no noncondensables at 77°K. Consequently the first reaction is the favored reaction.

---

surface. From Figure 6 it may be seen that this fraction is about 0.2. This can be attributed to the fact that the ends of the reactor are cooler than the walls, that a fraction of the molecules proceed directly through the reactor with no collisions, or that a combination of the two occurs. In any case the observed B can be corrected accordingly.

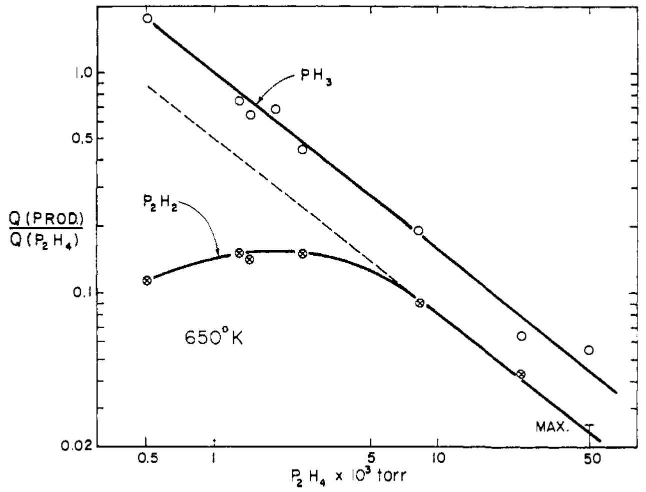


Figure 8. A plot of $Q(PH_3)/Q(P_2H_4)$ *vs.* $(1 - B)P_0$ (upper curve) and a plot of $Q(P_2H_2)/Q(P_2H_4)$ *vs.* $(1 - B)P_0$ (lower curve) at a temperature of 650°. The dashed line is a plot of $Q(PH_3)/2Q(P_2H_4)$.

Discussion

The results may be summarized as follows. Diphosphine-4 is thermally decomposed in a Pyrex vessel over the pressure range of 0.5 to 50 mtorr into phosphine and diphosphine-2 by a reaction which is zero order in diphosphine-4. The stoichiometry indicates 1 mole of phosphine and 0.5 mole of diphosphine-2 are produced per mole of diphosphine-4 decomposed. There was no evidence for the loss of diphosphine-4 by a first-order path or a parallel zero-order path. In addition diphosphine-2 decomposes to give tetraatomic phosphorus as one product under these conditions in a reaction which is inhibited by phosphorus hydrides. The reaction path may be written as

$$P_2H_4 \xrightarrow{1} PH_3 + {}^1/_2P_2H_2$$
$$\xrightarrow{2} [{}^1/_6]P_4 + [{}^2/_6PH_3]$$

where the brackets indicate uncertain results.

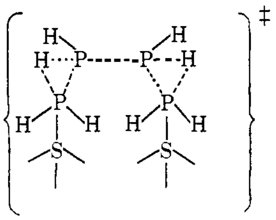
There are some aspects of these results which initially strike one as being somewhat surprising. First, if anywhere near the number of sites available were participating in the reaction, one would not expect the surface to be saturated and thus would expect first-order kinetics at these pressures. To explain the observed zero-order kinetics, one must postulate that there are a very limited number of active sites available and that the surface is saturated with respect to them. Some confirmation of this hypothesis is obtained if one calculates an absolute rate for the reaction assuming an average number of sites (*ca.* 10^{15}) and using the experimental activation energy.[20] The calculated rate is some seven powers of ten larger than the experimental value. In a previous instance of such disagreement, it was suggested that the reaction involved took place only on a limited number of special sites.[20]

The second point is that the activation energy is rather low compared to the bond energies involved. As pointed out by LeGoff,[12] however, the magnitude of the activation energy measured is not necessarily simply related to the actual activation energy of the process, and the apparent activation energy can be considerably different from the real activation energy. Consequently no significance is placed on the value of the apparent activation energy except as a means of expressing the results.

Perhaps the simplest mechanism which can account for the observations on reaction 1 is the direct reaction of two molecules of diphosphine-4 on the surface.

$$2P_2H_4 + 2S \longrightarrow 2P_2H_4\cdot S$$
$$2P_2H_4\cdot S \longrightarrow \{P_4H_8S_2\}^{\ddagger} \longrightarrow 2PH_3\cdot S + P_2H_2$$
$$2PH_3\cdot S \longrightarrow 2PH_3 + 2S$$

The activated complex for the reaction is visualized as having a cyclic structure involving the simultaneous shift of two protons, the breaking of two P–P bonds, and the formation of a "double" bond.



There are several factors which favor this mechanism. First, NH_3 is both physically adsorbed and chemisorbed on glass, and similar behavior might be expected for phosphorus hydrides.[21,22] Second, this mechanism requires adjacent sites of similar bonding characteristics, and the number of such pairs might well be a small fraction of the total number of sites. Third, this is the simplest reaction, not involving the direct rupture of a P–P or P–H bond, that accounts for the products. Finally, diphosphine-2 is formed essentially in the gas phase and thus, if its decomposition reaction (reaction 2) is also a surface reaction, adsorption on the surface would be required and inhibition by phosphorus hydrides becomes understandable.

These results agree quite well with previous observations and add to our understanding of the nature of the instability of this compound. It was observed earlier that large surface areas enhance the net decomposition at room temperature.[1] Also, it was noted that phosphine seemed to inhibit the net reaction.[1] As there is no apparent reason for postulating a different mechanism in the two temperature ranges, we postulate that diphosphine-2 is one of the active species involved in the thermal decomposition of diphosphine-4 in the room-temperature range. In addition we feel that this is the reactive intermediate involved in the surface-catalyzed reaction path. It may be concluded then that the thermal instability of diphosphine-4 is not due to a weak P–P bond[23] but to the availability of this surface-catalyzed path involving the formation of diphosphine-2. It is interesting to note in this regard that some organo-substituted diphosphines are considerably more stable than diphosphine-4.[24] The former cannot form a substituted diphosphine-2 by the mechanism postulated here.[25]

Acknowledgments. This work was supported by a National Science Foundation grant, NSF-GP-4186.

---

[20] K. J. Laidler, "Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1965.

[21] M. Folman, *Trans. Faraday Soc.*, 57, 2000 (1961).

[22] N. W. Cant and L. H. Little, *Can. J. Chem.*, 42, 802 (1964).

[23] From the fact that no first-order path for the loss of diphosphine-4 was observed in this temperature range, one may estimate that the bond energy of the weakest bond in diphosphine-4 must be greater than 40 kcal/mole.

[24] A. H. Cowley, *Chem. Rev.*, 65, 617 (1965).

[25] NOTE ADDED IN PROOF. Examination of the H_2^+ ion intensity with the recently modified spectrometer did not reveal any production of H_2 during pyrolysis.