Table XXI, M(LL′)ABC—Process 4

R^4	AC	$\overline{BC}$	$\overline{AB}$	$\overline{CL}$	CL′	BL	$\overline{BL'}$	$\overline{AL}$	AL′
AC	E	2	2	1	1	2	2	1	1
$\overline{BC}$	2	E	2	1	1	1	1	2	2
$\overline{AB}$	2	2	E	2	2	1	1	1	1
$\overline{CL}$	1	1	2	E	1	1	2	1	2
CL′	1	1	2	1	E	2	1	2	1
BL	2	1	1	1	2	E	1	1	2
$\overline{BL'}$	2	1	1	2	1	1	E	2	1
$\overline{AL}$	1	2	1	1	2	1	2	E	1
AL′	1	2	1	2	1	2	1	1	E

context). The chain c_E is not an element of these groups; racemization cannot occur.

Stereochemical matrices are presented in Tables XVIII–XXII. In processes 4 and 6, only one of the isomorphic groups is tabulated. All classes are distinct,

Table XXII, M(LL′)ABC—Process 6

R^6	AC	$\overline{BC}$	$\overline{AB}$	$\overline{CL}$	CL′	BL	$\overline{BL'}$	$\overline{AL}$	AL′
AC	E	1	1	1	1	2	2	1	1
$\overline{BC}$	1	E	1	1	1	1	1	2	2
$\overline{AB}$	1	1	E	2	2	1	1	1	1
$\overline{CL}$	1	1	2	E	1	1	2	1	2
CL′	1	1	2	1	E	2	1	2	1
BL	2	1	1	1	2	E	1	1	2
$\overline{BL'}$	2	1	1	2	1	1	E	2	1
$\overline{AL}$	1	2	1	1	2	1	2	E	1
AL′	1	2	1	2	1	2	1	1	E

The Thermal Polymerization of Diphosphine-4

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Abstract: The pyrolysis of diphosphine-4 has been examined in static reactors over the temperature range 300–830°K and reactant pressure range 0.5–10 Torr. Both the loss of diphosphine-4 and the formation of phosphine were observed as a function of time. At the lower temperatures, the formation and subsequent decay of triphosphine-5 was measured, while at the higher temperatures tetraatomic phosphorus was a minor product. The overall reaction is controlled by the nature of the surface, but the role of the surface is not simply to provide catalytic sites. It has been shown by labeling studies that the solid formed on the surface during the reaction is a labile hydride and that this hydride reacts directly with diphosphine-4. In addition, there appears to be a dynamic equilibrium set up between the gas-phase hydrides and the polymeric surface hydride. The entire complex reaction may be explained in terms of two simple generalized reactions.

We have published recently a number of reports on the existence and nature of several hydrides of phosphorus.[3,4] The major part of this work was directed toward identifying and characterizing new hydrides. Pyrolysis of diphosphine-4 at low pressures yielded evidence for diphosphine-2,[3a] a species that was characterized mass spectrometrically.[4] Triphosphine-5 was observed[3b] and, as it was later isolated in the pure state, was characterized more thoroughly.[3d,e] Information on the energetics of these species, obtained mainly by the mass spectrometric method, strongly suggests that the characteristic instability of these hydrides is not due to very weak phosphorus–phosphorus bonds. Rather, the difficulty in isolating higher hydrides of phosphorus lies in the extremely facile condensation reaction which they undergo. This is a particularly rapid reaction in the liquid phase. Consequently, the most characteristic feature of the hydrides with phosphorus–phosphorus bonds is this facile reaction which produces solid hydrides of variable stoichiometry and phosphine.[5] An understanding of this reaction, then, is most pertinent to an understanding of the nature of the phosphorus hydrides.

There were several secondary objectives of this work also. First, we were interested in defining the role of triphosphine-5 as an intermediate in the production and growth of the solid polymeric hydride. Secondly, we wished to test, if possible, the usefulness of the low-pressure pyrolysis technique[3c,d] in making general mechanistic conclusions. Finally, we hoped a kinetic

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[1] Abstracted from the Ph.D. Thesis of R. B. Callen, University of Notre Dame, 1968.

[2] The Radiation Laboratory is operated by the University of Notre Dame under contract with the Atomic Energy Commission. This is AEC Document No. COO-38-657.

[3] (a) T. P. Fehlner, *J. Amer. Chem. Soc.*, **88**, 1819 (1966); (b) *ibid.*, **88**, 2613 (1966); (c) *ibid.*, **89**, 6477 (1967); (d) *ibid.*, **90**, 4817 (1968); (e) *ibid.*, **90**, 6062 (1968).

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

[5] A measurement of the molecular weight of this solid in molten red phosphorus yielded a formula of $P_{12}H_6$ as reported by R. Schenk and E. Buck, *Chem. Ber.*, 37, 915 (1904). They suggested that the solid was a low molecular weight polymer. A solid hydride with an empirical formula P_9H_2 formed by heating P_2H was reported by A. Stock, *et al.*, *ibid.*, **42**, 2839, 2847 (1909). It was later proposed that the solid, previously characterized as P_2H, was an adsorption complex of diphosphine-4 on a solid with the formula P_5H_2 (L. Hackspill, *Compt. Rend.*, **156**, 146 (1913)). Twenty years later, it was postulated that all solid hydrides were "adsorbates" of phosphine on a yellow modification of phosphorus (P. Royen and K. Hill, *Z. Anorg. Allg. Chem.*, **229**, 97, 112 (1936)). Support for this hypothesis resulted from the report by P. Royen, *ibid.*, **229**, 369 (1936), that the yellow solids were amorphous to X-rays. A reexamination of the thermal decomposition of diphosphine-4 has been reported by E. Evers and E. Street, *J. Amer. Chem. Soc.*, **78**, 5726 (1956). Their data indicate that a solid roughly of composition P_9H_4 is produced. They conclude that the yellow solids are not "adsorbates" of phosphine on phosphorus and that solids of practically any composition can be produced depending on the conditions.

approach would provide new insight into the nature of the solid, apparently polymeric, final product of the thermal decomposition of diphosphine-4.

Experimental Section

Reactors. To study the thermal decomposition of diphosphine-4 over the temperature range from 300 to 800°K, two experimental techniques were utilized. Below 400°K a 2-l. spherical Pyrex glass reactor was connected *via* a series of Teflon-on-glass vacuum stopcocks to a grease-free, mercury-free, vacuum manifold. All reactors and handling systems were covered with several heavy coats of black paint to reduce photodecomposition. The reactor was immersed in a constant-temperature (±0.1°) oil bath such that the reactor "dead space" was 1 cc. Since this "dead space" amounted to only 0.5% of the reactor volume, no dead space corrections were made on the data. A total of three reactors was used. The temperature of the bath was measured with two mercury-in-glass thermometers situated in the oil on either side of the reactor. To ensure that the temperature was homogeneous, temperature readings were taken at several points in the bath, and these readings agreed within 0.2°. Initial pressure in the reactor was measured using a Wallace-Tiernan Bourdon-type pressure gauge, and these measurements were accurate to within 0.50 Torr. The reaction time was monitored using an electric timer, and readings were accurate to within 15 sec. Errors in the measurement of time can result from mixing times and the sampling process. At temperatures below 400°K the mixing time was of the order of 1 sec, and errors in the zero time were considered negligible. The time between sampling and quenching was *ca.* 10 sec, and errors from this source were also neglected.

Low-temperature fractional codistillation chromatography[6] was used as an analytical method in this temperature range mainly because of its ability to quantitatively separate thermally unstable volatile species.[7] As the general features of the technique have been described previously,[6] only modifications in the procedure are described here. An unpacked Pyrex glass column (6 mm × 25 cm) was used for the separations to minimize decomposition on the column surface during the analysis. Even though this precaution was taken, some decomposition in the column occurred as evidenced by the gradual appearance of a yellow solid on the column walls after a number of kinetic experiments. This solid deposit is primarily due to decomposition of liquid triphosphine-5 and will tend to make the triphosphine-5 analysis low. In order to analyze for triphosphine-5 in the presence of relatively large amounts of diphosphine-4, it was necessary to remove the temperature gradient in the following manner. The liquid nitrogen dewar originally surrounding the column was replaced with a dewar containing an ethyl bromide slush raising the column temperature to 154°K. At this temperature, only phosphine was swept by the carrier gas out of the column to the detector (a Gowmac microcell, JDC 470, thermistor). After phosphine had emerged from the column, a chloroform slush was used to raise the column temperature to 210°K where diphosphine-4 was swept out of the column. Finally, the chloroform slush was replaced with an empty dewar at room temperature, the column temperature gradually rose from 210°K, and triphosphine-5 distilled away. The compounds were identified on the basis of their chromatographic retention times, and the assignments were confirmed by selective trapping and mass spectrometric analysis. The column is connected *via* a valve to a 10-cc sampling volume located directly above the reactor. At intervals, the gaseous contents of the reactor were expanded into the sampling volume, and the reaction was quenched by condensing the sample in the column at 77°K. For ten samples, the error resulting from the decrease in concentration in the reactor due to sampling was only 2.0%, and since the analytical precision was 5%, the error involved in the sampling process was considered negligible.

In the higher temperature interval, another experimental approach was used. A cylindrical quartz reactor with a volume of 840 cc was connected to the ion source of a Bendix Model 12-101 time-of-flight mass spectrometer *via* a glass leak with a pinhole approximately 0.013 mm in diameter. The leak rate was less than 10^{14} molecules/sec and, as this is a factor of 1000 less than the reaction rate, there was no significant "pumping out effect." The reactor was placed in the well of a heavy-duty electric furnace, and the temperature was controlled by means of a thermoregulator in series with the furnace. Two chromel-alumel thermocouples, placed in the well near the extreme ends of the reactor, were used to measure the temperature. The temperature gradient was less than 10°. The initial pressure was measured with the same Bourdon gauge described above. The leak sampled gas primarily from the 23-cc "dead space" which is 2.7% of the total reaction volume. Even though an average molecule diffuses from the center of the reactor to the leak in 9 sec, this reactor is not suitable for a rigorous kinetic study. However, the basically qualitative conclusions drawn from the data from the higher temperature interval are independent of these factors.

The PH_3^+ and $P_2H_4^+$ ion intensities were used to monitor PH_3 and P_2H_4, respectively, and this could be done simultaneously. The pressure in the ion source was always less than 10^{-6} Torr; however, as conventional sampling was being employed, it was necessary to determine how much decomposition occurred in the source.[4] With the reactor at room temperature, the PH_3^+ ion intensity was observed at various P_2H_4 pressures. It was concluded that source decomposition would yield errors of less than 5% in the determination of PH_3. Periodically the mass regions corresponding to triphosphines and tetraphosphines were scanned, and in the labeling experiments m/e 70 to 62 ($P_2D_4^+$ to P_2) and m/e 37 to 31 (PD_3^+ to P^+) were scanned.

Preparations. Phosphine and diphosphine-4 were prepared by the method of Evers and Street[5] in a grease-free, mercury-free vacuum system. Phosphine was separated from the crude diphosphine-4 by trap-to-trap distillation and was stored in a gas bulb at room temperature until further use. The crude diphosphine-4 was then purified by repeated fractional distillation through a Dry Ice-acetone trap and was stored in a "light tight" bulb at 77°K. The deuterated diphosphine-4 was prepared in an identical manner using D_2O (K and K Chemical Co.) for the hydrolysis. In order to prepare the compound with a high degree of isotopic purity, it was necessary to remove all traces of yellow solid from the walls of the vacuum system, and to condition the system for several hours with D_2O. The isotopic purity of the deuterated diphosphine-4 was 90% as determined from the mass spectrum. Triphosphine-5 was prepared by the pyrolysis of diphosphine-4 in a "hot-cold" reactor[3b,e] and was used to measure the retention time of this compound.

Calibration curves for both phosphine and diphosphine-4 were constructed by measuring the peak areas and the parent ion intensities at various pressures of the pure compounds. Peak areas were measured with a planimeter and were reproducible to within 5%. Butane and ethane were used as standards in the chromatographic experiments before, after, and sometimes during a run. A sensitivity for P_3H_5 was obtained by assuming the molar response of the detector to be a linear function of the molecular weight.[8] Argon was used as a standard for the mass spectrometric runs. No calibration was made for P_4.

Prior to each experiment, the diphosphine-4 reservoir was warmed to 154°K, and the bulb was pumped on for several minutes to remove small traces of phosphine. To introduce the diphosphine-4 into the reactor without decomposition, the reservoir was kept at a low temperature (between 210 and 238°K) and the vapor in equilibrium with the liquid was expanded into the reactor. The pressure on the Bourdon gauge was read and the reaction commenced. The phosphine peak area and the PH_3^+ (m/e 34) ion intensity were used as criteria of sample purity, and on this basis the diphosphine-4 in these experiments was always better than 95% pure.

Results

Products. Figures 1 and 2 show representative data for the low- and high-temperature regions. Phosphine was produced in both regions. Triphosphine-5 was observed as a product at the lower temperatures, but the maximum abundance decreased with increasing temperature becoming unobservable above *ca.* 380°K. Tetraatomic phosphorus is produced as a minor product in the high-temperature range. In both regions a solid product was produced and appeared as a uniform, tan-yellow, translucent film on the walls of the reactor. When backed by black paint, the film reflects light and

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

[7] T. P. Fehlner and W. S. Koski, *J. Amer. Chem. Soc.*, **86**, 1012 (1964).

[8] A. E. Messner, D. M. Rosie, and P. A. Argabright, *Anal. Chem.*, 31, 230 (1959).

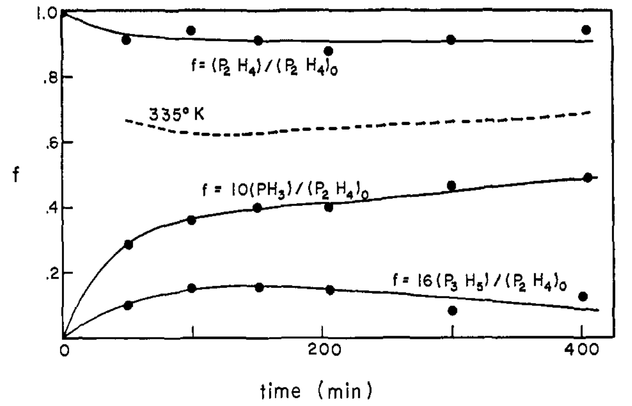

Figure 1. Fractional concentration–time profiles in the lower temperature region. The initial P_2H_4 pressure was 5.5 Torr. The dashed line is a plot of $1 - (P_f/P_L)$, where P_f is the phosphorus found as PH_3 and P_3H_5 and P_L is the phosphorus lost as P_2H_4.

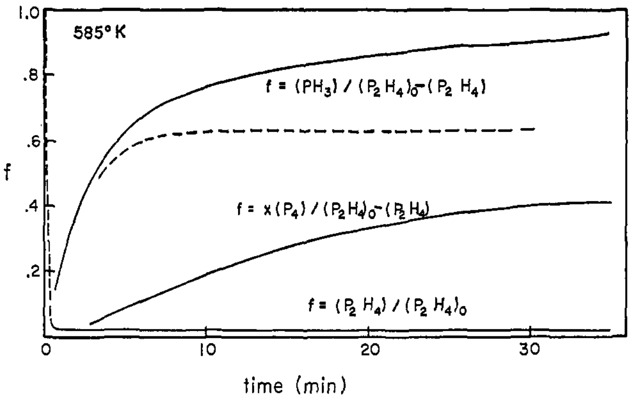

Figure 2. Fractional concentration–time profiles in the higher temperature region. The initial P_2H_4 pressure was 3.0 Torr. The dashed line corresponds to a PH_3 curve with a maximum correction for the PH_3 produced along with P_4.

no structure is observed under 43× magnification. The film is soft, being visibly (under magnification) scratched with cleaning tissues. Small amounts of PH_3 were evolved from the film on standing under vacuum, but the film did not visibly change on standing in the air for months. After roughly a millimole of P_2H_4 had been decomposed the solid coating became yellow and opaque. This surface did not reflect light and looked like velvet. Under magnification the velvety, porous nature was clearly observable. Unless otherwise specified, the results reported here refer to reaction on the film-like surface. As will be seen, the mechanism is the same with both surfaces, but the over-all rate is not. Diphosphine-2 was sought in the high-temperature region but was not observed. These products were observed over the range of initial diphosphine-4 pressures of 0.5–10 Torr.

The dashed line in Figure 1 corresponds to a phosphorus atom balance of the volatile reactants and products observed. As a value of zero corresponds to all volatile products, a considerable amount of the P_2H_4 lost ends up as nonvolatile material, presumably the solid appearing on the walls.[9] The formation of PH_3 qualitatively tracks the loss of P_2H_4 with *ca.* 0.6 mole of PH_3 produced per mole of P_2H_4 decomposed. The abundance of triphosphine exhibits the maximum typical of an intermediate formed in a consecutive process. The amount of P_3H_5 found was always well below the stoichiometric value predicted from the reaction $P_2H_4 = {}^1/_2PH_3 + {}^1/_2P_3H_5$. The phosphorus atom balance in the higher temperature range, illustrated in Figure 2, is complicated by the presence of P_4. However, this species is not very abundant, and it is clear that here too all the P_2H_4 lost is not accounted for by the volatile products. This figure also illustrates quite clearly that the formation of PH_3 does not track the loss of P_2H_4. The PH_3 curve plotted is the number of moles of PH_3 produced per mole of P_2H_4 lost. It varies from the unexpected value of 0.2–1—strikingly pointing to a gross difference between the process by which PH_3 is formed and that by which P_2H_4 is lost.

One of the dominant features of these data over the whole temperature range is the inhibition in both the rate of loss of P_2H_4 and formation of PH_3. After an initial rapid change, the abundance of these species changes only slightly with time.[10] As shown in Figures 1 and 2, the nearly constant concentrations of P_2H_4 and PH_3 measured with respect to the initial amount of P_2H_4 (defined by f and f', respectively) are temperature dependent.

Another characteristic common to both temperature ranges is the fact that as reactions are carried out the quantity of solid in the reactor increases. Essentially three regimes were established: fresh uncoated glass, translucent film, and opaque yellow solid. In a new reactor little inhibition was observed; f was poorly defined and certainly not constant. In addition no P_3H_5 was observed although it could easily be observed in a film-covered reactor under similar conditions. The characteristics of the film region are described in much more detail below as in this region the kinetics were reproducible. Consequently all results discussed in detail were taken under these conditions. In an opaque solid-coated reactor the value of f was depressed (f' enhanced) substantially over that for the film surface and with continued deposition of solid gradually approached a value of zero.[11]

The addition of 0.2 mole fraction of PH_3 at 304°K reduced the PH_3 produced in the decomposition by 20% (±20%). The amount of P_3H_5 produced is not grossly affected either. If there were a simple chemical equilibrium like $2P_2H_4 = PH_3 + P_3H_5$ being established, then this amount of PH_3 would have a much more drastic effect. For example, P_3H_5 should have been depressed below our detectablity level. The addition of 20 Torr of helium in the low-temperature range had no significant effect on the rates either.

Labeling Studies. As it was clear that the surface was intimately involved in the reaction, experiments involving labeled reactant were carried out in the higher temperature region. Pyrolysis of P_2H_4 in a protonated filmed reactor was followed by pyrolysis of P_2D_4. Illustrative results are shown in Figure 3. At the

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[9] As the P_3H_5 determination is probably low, the amount of P_2H_4 appearing as nonvolatile species is probably high.

[10] The dashed line in Figure 2 is the PH_3 curve that results from subtracting out a fraction of the P_4 curve. The fraction is chosen so that the PH_3 curve does not go through a maximum. Consequently, the fraction of PH_3 resulting from direct decomposition of P_2H_4 lies between the solid and dashed curves. We estimate that this fraction lies closer to the dashed than solid curve.

[11] An opaque and film-coated reactor were compared simultaneously with the same preparation of P_2H_4 to eliminate the possibility of impurities.

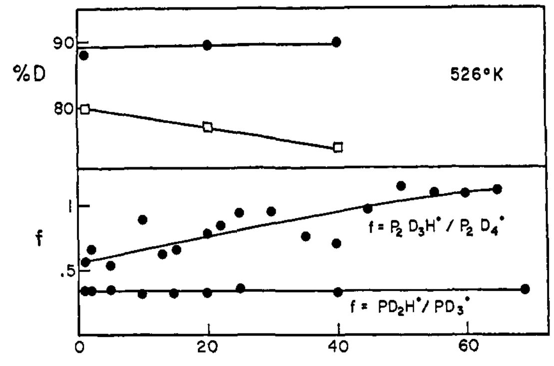


Figure 3. Data from the pyrolysis of P_2D_4 on a protonated surface. The initial P_2D_4 pressure was 3.5 Torr. The lower part of the figure shows two specific ion ratios as a function of time. The upper part of the figure shows the % D as calculated from the entire spectrum for phosphine (closed circles) and diphosphine-4 (open squares) as a function of time.

bottom of the figure the PD_2H^+/PD_3^+ ratio shows that the H content of phosphine does not change with time, while the $P_2D_3H^+/P_2D_4^+$ ratio shows that the H content of diphosphine-4 increases. From complete spectra the per cent D in phosphine and diphosphine-4 was calculated by assuming the fragmentation patterns were independent of isotopic substitution. The per cent D in phosphine remains constant at a value equal to that of the starting diphosphine-4. The per cent D in diphosphine-4 decreases immediately about 10% and then slowly decreases further. The relative amounts of phosphine and diphosphine-4 must be kept in mind (see Figure 2) as the phosphine could gain the same absolute amount of H from the polymer as diphosphine-4, and we would not be able to see it. The H in the product phosphine was statistically distributed as it was in the original diphosphine-4. However, the H-enriched diphosphine-4 did not have a statistical distribution of H, the abundance of $P_2H_2D_2$ being definitely enhanced at short times (see Table I). Finally P_2H_4 was again run and the phosphine observed. Only 3% of the phosphine produced contained a D label. These experiments show very clearly that the surface species are intimately involved in the reaction. In addition they show that there is a dynamic process taking place in the stationary-state region which results in the exchange of the H and D labels in diphosphine-4. These two observations are the most important ones, and the other details observed will be discussed in the mechanistic considerations presented later.

Table I. Isotopic Distribution in Residual Diphosphine-4 in a Typical Run[a]

Time, min	P_2D_4	P_2D_3H	$P_2D_2H_2$	P_2DH_3	P_2H_4
1	100	52	29	15	~0
20	100	75	39	20	~0
40	100	70	28	22	~0
Calcd 10% H	100	44	7.4	0.54	0.013
Calcd 20% H	100	100	37	6.1	0.39

[a] 526°K, $(P_2D_4)_0$ = 3.5 Torr.

Kinetics. The fraction of P_2H_4 remaining, $(P_2H_4)/(P_2H_4)_0$, and the fraction of PH_3 produced, $(PH_3)/(P_2H_4)_0$, were fitted to the equations

$$(P_2H_4)/(P_2H_4)_0 = f - at + [1 - (f - at)]e^{-bt}$$

$$(PH_3)/(P_2H_4)_0 = f' + a't - (f' + a't)e^{-b't}$$

where f, f', a, a', b, and b' are independent of time for a given initial diphosphine-4 pressure and temperature.

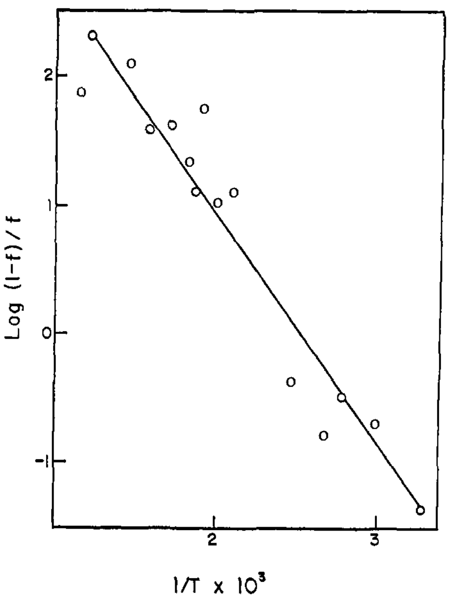


Figure 4. Plot of log $(1 - f)/f$ vs. $1/T$ where f is defined in the text.

Both equations may be simply viewed as a first-order (in time) approach to the nearly stationary state represented by f and f' and where b is the first-order constant. a represents the small zero-order change in f with time. Over a fourfold range of pressure f, f', a, a', b, and b' were constant at a given temperature in the low-temperature range. In the high-temperature range, only f, f', and b' could be examined as a function of pressure. Over a tenfold range of pressure these parameters were independent of pressure. The pressure order is not as well known (1 ± 0.5) as the time order because of the scatter in the data resulting from errors in the analysis of these somewhat unstable species and small fluctuations in the nature of the surface.

f and f' are related by a stoichiometric factor, namely $f = 1 - (f'/x)$, where x is the number of moles of phosphine produced per mole of diphosphine-4 lost. For the low-temperature runs $x = 0.63 \pm 0.24$ (average deviation), while for the high-temperature runs $x = 0.82 \pm 0.19$. After maximum correction of the latter data for the production of phosphine[10] with P_4, a value of $x = 0.63$ is obtained. As mentioned above, f is a function of temperature and empirically we find that a plot of log $(1 - f)/f$ vs. $1/T$ yields a fairly good straight line with a least-squares slope of −1770 (Figure 4).

Numerically the a's were much smaller than the b's. They had values of ca. 10^{-6} sec^{-1} and appeared independent of the temperature. a and a' are related by the equation $a = a'/x$. In the low-temperature range $x = 0.5 \pm 0.3$ (average deviation). One experiment at 313°K was allowed to proceed for 11,000 min at which point the diphosphine-4 was only 40% decomposed.

As shown quite vividly in Figures 1 and 2, b is not simply related to b' by a constant stoichiometric factor. b' is easily measurable over the whole tem-

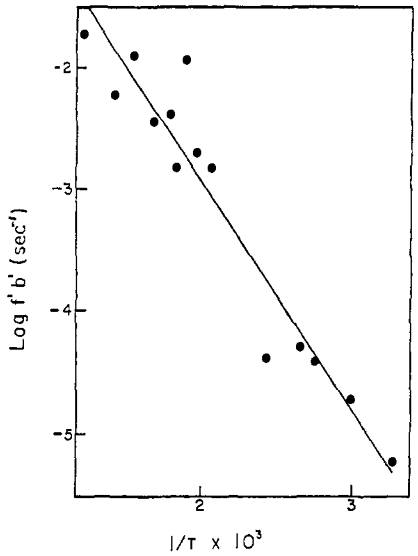


Figure 5. Plot of the log of the initial fractional rate of formation of PH_3 ($f'b'$) as a function of $1/T$.

perature range, and a plot of the log of the initial fractional rate ($f'b'$) *vs.* $1/T$ yields a fairly good straight line (Figure 5). The equation $\log (f'b') = 12.9 - 1870/T$ expresses the least-squares fit of the data and should be directly related to an over-all rate constant for the formation of PH_3. In the lower temperature range, $b \approx b'$ while at higher temperatures $b > b'$. This means that both the frequency factor and activation energy of b are larger than those of b'.

As the temperature range of this study overlaps that of the previous low-pressure pyrolytic study,[3c] it is worthwhile to compare the specific rates at 585°K. Here the initial rate for P_2H_4 loss is ≥ 1.4 Torr/sec which may be compared with a value of 13 Torr/sec observed in the low-pressure reactor. The factor of 10 difference in the rates may be attributed to the fact that the surface of the low-pressure reactor remained clean and/or to the 10^2–10^3 difference in reactant pressures.

The kinetics of triphosphine-5 were not examined in detail because of the uncertainties in the quantitativeness of the analytical procedure. Several qualitative features of the behavior of this species are significant, however. The maximum in the abundance of P_3H_5 observed at the lower temperatures (see Figure 1) moved toward zero time as the temperature was increased and was unobservable above 360°K because of our time resolution. Above 380° P_3H_5 itself was unobservable. At 335° the ratio $(P_3H_5)/(P_2H_4)$ at the time where (P_3H_5) is a maximum is a constant over a threefold change in initial diphosphine-4 pressure. As at the maximum the net change in (P_3H_5) is zero, the dependence of the rate of formation of P_3H_5 on P_2H_4 must be similar to the dependence of the rate of loss of P_3H_5 on P_3H_5. Consequently, as the rate of formation of P_3H_5 is directly related to the rate of loss of P_2H_4, the constancy of $(P_3H_5)/(P_2H_4)$ implies a similarity in the decomposition of P_2H_4 to produce P_3H_5 and the decomposition of P_3H_5 itself.

As noted in Figure 1, some of the diphosphine lost is not accounted for by the PH_3 and P_3H_5 formed. It is interesting to speculate on the nature of the products formed either concurrently or consecutively with PH_3 and P_3H_5. Using average values for the PH_3 and P_3H_5 stoichiometry somewhat past the maximum in the P_3H_5 abundance, one calculates the composition of the "lost hydride" as $PH_{1.48}$. Because of the scatter in the data the correspondence of this empirical formula to P_4H_6 must not be viewed as evidence that P_4H_6 is the exclusive product. However, it may be taken as evidence that higher hydrides are being produced in the polymerization process and P_4H_6 is undoubtedly one of them. This species has been tentatively identified previously.[3e]

The kinetics of formation of tetraatomic phosphorus were likewise not examined in detail. We assume that P_4 production is accompanied by PH_3 according to the stoichiometry, $P_2H_4 = {}^4/_3PH_3 + {}^1/_6P_4$. The data indicate quite clearly that the initial rate of formation of P_4 is zero and thus it is not a primary product (see Figure 2). The importance of P_4 as a product increases with increasing temperature.

Discussion

Mechanism. The kinetic behavior of this system as exhibited in Figures 1 and 2 is obviously complex and in many ways confusing. As usual there is not enough information to fully delineate a mechanism or elucidate the important activated complex. There are, however, a number of solid facts upon which to base a mechanism—the device used to summarize our knowledge on one aspect of the reactivity of this species. First the loss of P_2H_4 and the formation of PH_3 are uncoupled. Second, as shown by the isotope studies, the surface coating is a labile hydride and is involved in the loss of diphosphine-4. In addition there exists a dynamic process involving the surface hydride and diphosphine-4. Third, the reaction does not go to completion but reaches a nearly stationary state which is only slightly inhibited by PH_3. The extent of reaction at the stationary state is a function of temperature and the nature of the surface hydride. Finally, as P_3H_5 was not observed in a reactor in the absence of surface hydride, either it is not found in this system or decomposes much more rapidly. We rule out the latter as we have observed previously[3e] that less decomposition of P_3H_5 occurs in a clean apparatus.

We now postulate the following mechanism to explain our observations.

$$\begin{array}{llll}
P_2H_4 + S \underset{2}{\overset{1}{\rightleftarrows}} P_2H_4\cdot S & \underset{4}{\overset{3}{\rightleftarrows}} PH_3\cdot S' & \underset{6}{\overset{5}{\rightleftarrows}} PH_3 + S' \\
 & \underset{8}{\overset{7}{\rightleftarrows}} P_3H_5\cdot S'' & \underset{10}{\overset{9}{\rightleftarrows}} P_3H_5 + S'' \\
 & \underset{12}{\overset{11}{\rightleftarrows}} P_4H_6\cdot S''' & \\
 & \quad\vdots & \\
 & \rightleftarrows P_{n+1}H_{n+3}\cdot S^{n'} &
\end{array}$$

Here $P_mH_{m+2}\cdot S$ refers to an adsorption complex of the phosphorus hydride on the surface. S refers to the surface hydride and is presumably similar to P_mH_{m+2} with m very large. These reactions explain the basic features of this reaction system. First, the surface hydride is involved in the loss of P_2H_4, and there is a dynamic equilibrium between P_2H_4 and adsorbed P_2H_4 and adsorbed products. The production of P_3H_5

requires the surface hydride, and the loss of P_3H_5 is similar to the loss of P_2H_4. The loss of P_2H_4 and the formation of PH_3 need not be coupled as P_2H_4 is lost by paths which do not produce PH_3. The kinetics are consistent with this picture. The initial rate of formation of phosphine should be given by

$$R(\mathrm{PH_3}) = K_{1.2}k_3(\mathrm{P_2H_4})(\mathrm{S})$$

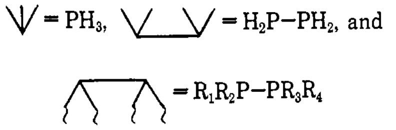
if reaction 5 is fast, the amount of P_2H_4 adsorbed is small compared to (S), and the adsorption equilibrium is rapidly established. If we also postulate that the number of reaction sites on the surface hydride is effectively constant during the reaction, then $f'b'$ is identified with $K_{1.2}k_3(\mathrm{S})$ and should be independent of the diphosphine-4 pressure. On the other hand, the rate of loss of P_2H_4 is given by

$$R(\mathrm{P_2H_4}) = K_{1.2}[k_3 + k_7 + k_{11} + \cdots](\mathrm{P_2H_4})(\mathrm{S})$$

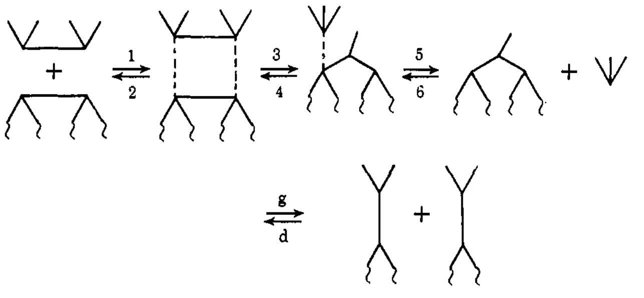
In the low-temperature range about 60% of the initial reaction is by (3), 15% by (7), and presumably a continually decreasing amount by the succeeding reactions. Therefore $R(\mathrm{P_2H_4}) \approx R(\mathrm{PH_3})$. $R(\mathrm{P_2H_4}) \approx 100R(\mathrm{PH_3})$ in the higher temperature range and this requires that $(k_7 + k_{11} + \cdots)$ exceed k_3. This in turn requires that $k_7, k_{11}, \cdots$ have higher frequency factors and activation energies than k_3 does. In other words, (3) is essentially different from (7), (11), $\cdots$. The change in the reaction rate and the net extent of reaction with the nature of the surface hydride may be explained on the basis of an increase in (S).

Note that in this mechanism the solid hydride does more than provide a site for reaction: it participates in the reaction. Justification for this statement comes from a consideration of the observed nearly stationary state. One explanation may be achievement of simple chemical equilibrium catalyzed by the wall. The studies with added phosphine definitely show that this is not correct. Another possible explanation of the stationary-state behavior that was considered is the possibility that the extent of reaction is limited by the number of reaction sites, this number increasing with increasing temperature. The small inhibition by PH_3 could then be explained by simple occupation of reactive sites by PH_3. However, we rule this out for two reasons, the latter of which is the stronger. First, we would expect some zero-order character in the rate law at the highest pressures, *i.e.*, saturation effects. Secondly, the extent of reaction in the stationary state would no longer be expected to be independent of the initial diphosphine-4 pressure. These are both at variance with the observations. Consequently, the explanation favored by us is one which requires participation of the surface hydride in the reaction. This provides an easy explanation of the labeling results (see below) and can account for the observed inhibition by PH_3 (*ca.* 20%) if it is assumed that n in the mechanism above is 12. The fact that a plot of log $[(1 - f)/f]$ *vs.* $1/T$ is a straight line (Figure 4) is also understandable on the basis of a mechanism which includes the surface hydride as a participant.

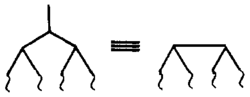
By accepting the participation of the solid hydride, the mechanism may be reduced to a very simple structural form. If we let



where R = P_nH_{n+1} (a more or less hydrogenated phosphine structure having P-P and P-H bonds), then we may write



First note that

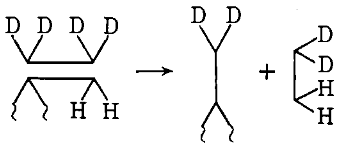


i.e., $n = 0$ for R_3. Therefore in the notation of the mechanism S = S′ = S′′, etc. Second, reactions g and d (growth and decay) represent reactions 7, 11, $\cdots$ and 8, 12 $\cdots$, respectively. This should be clear from an examination of Table II, where the products of g are given as a function of R_3 and R_4.

Table II. Products of Growth Step as a Function of Reaction Site

R_3	R_4	Product	
H	H	No reaction; exchange yielding $P_2H_2D_2$	
PH_2	H	P_3H_5	
H	PH_2	P_3H_5	
PH_2	PH_2	P_4H_6	"secondary"
P_2H_3	H	P_4H_6	"primary"
P_2H_3	PH_2	P_5H_7	
P_2H_3	P_2H_3	P_6H_8	
	etc.		

This mechanism also explains the labeling results. Considering the reaction of P_2D_4 with protonated surface hydride, this mechanism predicts that the vast majority of phosphine formed will have the isotopic composition of the starting material. This is what is found (Figure 4). The mechanism also predicts that in the rapid loss of diphosphine-4 (reaction g) some of the reaction will correspond to the first entry in Table II. The initial drop in % D in the residual diphosphine-4 is relatable to the fraction of reaction corresponding to



It also predicts that initially the isotopic distribution in diphosphine-4 will be nonstatistical, favoring $P_2H_2D_2$. This is exactly what is found. The continual decrease in % D with time corresponds to scrambling of the label by subsequent decomposition of the higher hydrides initially produced,

Conclusions

The essence of the mechanism with which we summarized our results on this complex system lies in the facility in which reaction g can take place in the condensed state. This conclusion is not necessarily restricted to this hydride system as it appears that diarsine is also very unstable in the condensed state.[12] This reaction may be easily visualized as proceeding *via* a four-center activated complex or intermediate. Such a four-center complex may well be stabilized by interactions similar to the $p\pi$–$d\pi$ bonding suggested for cyclopolyphosphines on the basis of their uv spectra.[13,14] This facile reaction must be considered a property of species containing phosphorus–phosphorus bonds.[15] However, in a recent study of inversion in quadruply substituted diphosphine,[16] a very similar reaction is ruled out. In addition, substituted diphosphines are much less subject to polymerization.[15] We suggest, then, that a minimum requirement for this reaction is the possession of a PH_2 group by at least one of the reactants.

Triphosphine-5 does not appear to be an exclusive intermediate in the over-all polymerization. It is, however, the first molecule of the homologous series that can act as its own reaction site. Consequently it is much more unstable toward polymerization than P_2H_4. Triphosphine-5 can be isolated simply because its vapor pressure is high enough at temperatures where the polymerization reaction is slow. For this reason, the prospects of isolating quantities of the less volatile higher hydrides appear slim. However, some evidence for the existence of a series of higher hydrides has been presented previously by others.[17]

The study also shows quite clearly that the results of the low-pressure pyrolytic studies[3c,d] with hydride free walls apply to an essentially different system. Although many helpful insights in interpreting the over-all pyrolysis resulted from the low-pressure work, it is clear that the low-pressure, high-temperature results cannot be simply extrapolated to the system examined here.

It appears quite clear that the surface hydride is polymeric in nature and contains $-PH_2$ terminal units, $>PH$ middle units, and, as suggested by Table II, $\geqslant P$ branching units. The mechanism we propose provides a path for the previously suggested redistribution equilibrium between these units and the gaseous hydrides.[18] Consequently, the concept[18] of these solid hydrides being networks of triply bonded phosphorus atoms with interstices containing chain-like hydrides may well be a good one. Our evidence on the film, however, does not require a continuously bonded network of phosphorus but suggests the presence of many hydrides of varying sizes. Finally, as diphosphine-4 can be adsorbed on the polymeric hydride and as phosphine is slowly evolved from the solid hydride, it is not surprising that the earlier investigations[5] resulted in apparently conflicting conclusions,

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