sense, the tetratomic molecules might be considered to have six single bonds with heteronuclear bond energies equal to the average of homonuclear single-bond energies. Thus, three-fourths the atomization energy of Sb_4 plus one-fourth the atomization energy of Bi_4 give 8.29 eV, in excellent agreement with the experimental value, 8.27 eV, for $BiSb_3$.

Although these comparisons must be viewed entirely as empirical correlations rather than fundamental relationships, as we shall point out, they tend to confirm the assumption of structural similarities for the group of Bi–Sb molecules. Together with the trends in binding energies for all other known molecules of this family,[2b] they tend also to confirm that this group is only one part of a complete class of related molecules composed of all combinations of the group Va atoms. Only a few of these possible combinations have been observed to date,[2a] but their dissociation energies should be predictable on the basis of empirical bond energies. Conspicuously absent among the known tetratomic molecules is N_4, but its dissociation energy cannot be predicted directly from available bond energies.

The usual tabulation of single-bond energies for the nitrogen family molecules shows an anomalously low value of 1.67 eV for the N–N single bond based on data for hydrazine and similar molecules.[13] A P–P bond energy of 2.07 eV taken as one-sixth of the atomization energy of P_4 is considerably larger, and others down the family systematically decrease. Recent theoretical calculations[14] on the electronic structure of P_4, however, have shown that the bonding in this molecule and presumably others in the same family does not involve localized two-centered bonds but instead involves delocalized electrons in an unsaturated structure. The so-called anomaly is, therefore, a result of an irrelevant comparison between localized N–N bonding in hydrazine and delocalized bonding in the tetrahedral molecules. It is not unreasonable to presume that a stable tetrahedral N_4 molecule does exist as a member of the same class of group Va molecules with a dissociation energy considerably larger than that of P_4.

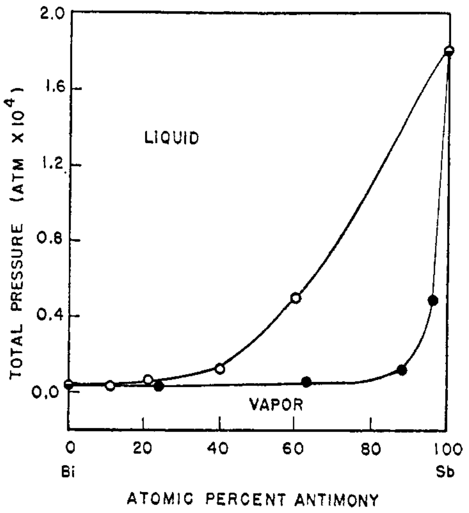

Figure 1. Pressure–composition phase diagram for the Bi–Sb system at 625°.

Acknowledgments. The authors thank Mr. Kenneth R. Thompson for helpful discussions concerning the estimation of the molecular parameters and Mr. C. Larry Sullivan for assistance in carrying out the experiments.

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(13) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 85.

(14) R. R. Hart, M. B. Robin, and N. A. Kuebler, *J. Chem. Phys.*, **42**, 3631 (1965).

A Mass Spectrometric Investigation of the Low-Pressure Pyrolysis of Triphosphine-5

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Contribution from the Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556. *Received March 1, 1968*

Abstract: Triphosphine-5, an intermediate in the pyrolysis of diphosphine-4, thermally decomposes in a Pyrex reactor over the pressure range 0.2–10 mtorr into phosphine and diphosphine-2 by a reaction which is first order in triphosphine-5, and into diphosphine-4 and diphosphine-2 by a reaction which is zero order in triphosphine-5. The first-order reaction is autocatalytic in diphosphine-2, and the zero-order reaction is similar to the thermal decomposition of diphosphine-4. Both reactions appear to be heterogeneous. The products diphosphine-4 and diphosphine-2 decompose further to yield phosphine and tetraatomic phosphorus. These results are discussed from the viewpoint of the stability of higher phosphorus hydrides.

The apparent instability of the phosphorus hydrides poses the intriguing question of whether these compounds contain inherently weak bonds or whether they possess some type of excessive reactivity under ordinary conditions. To explore this problem, we are carrying out a number of studies which entail the intimate examination of reacting systems containing phosphorus hydrides. In a preceding paper[1] we reported that the low-pressure pyrolysis of diphosphine-4 in a Pyrex vessel proceeds *via* a surface reaction and results in the formation of diphosphine-2 and phosphine. The unstable intermediate, diphosphine-2, de-

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(1) T. P. Fehlner, *J. Amer. Chem. Soc.*, **89**, 6477 (1967).

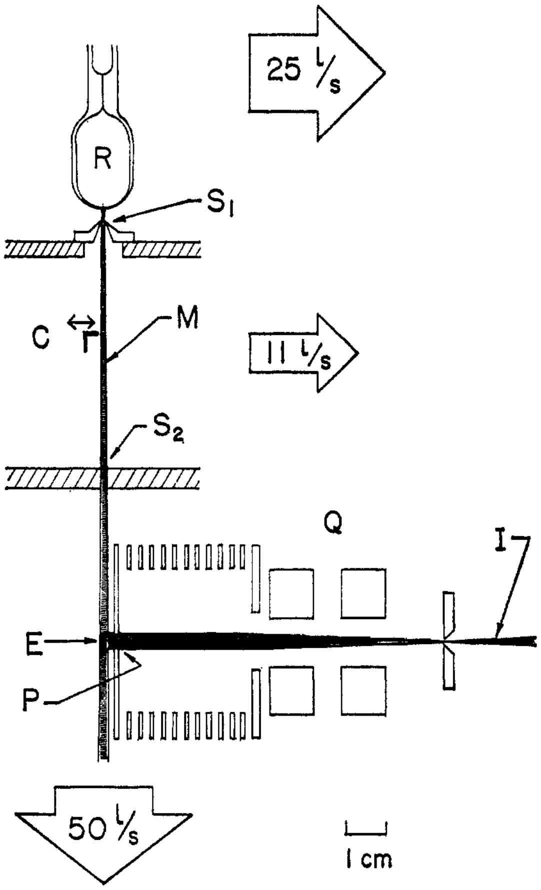

Figure 1. Schematic drawing of the beam system. C is the mechanical chopper. E is the electron-beam cross section (0.8 × 3.8 mm). I is the ion beam and M is the molecular beam. P is the ion exit hole (3.8 × 6.8 mm). Q is the quadrupole lens and R is the reactor. S_1 is a beam-defining orifice (0.56-mm diameter) and S_2 is the final beam slit (1 × 4 mm filled with five corrugations of 0.025-mm tantalum foil).

composes further in a surface reaction to give tetraatomic phosphorus and phosphine. These initial studies clearly indicate that the phosphorus–phosphorus bond in diphosphine-4 has a bond energy greater than 40 kcal/mole and that the apparent instability of diphosphine-4 is due to the availability of this surface-catalyzed path.

We have also reported briefly on the formation of another intermediate, triphosphine-5, which was tentatively identified in the low-pressure pyrolysis of diphosphine-4 in a quartz tubular flow reactor.[2] Quantities of pure triphosphine-5 can be obtained by the photolysis of diphosphine-4,[3] and we now present a report of the low-pressure pyrolysis of triphosphine-5, the second intermediate in the thermal decomposition of diphosphine-4. This study includes the identification of products of the reaction, the reaction order, stoichiometry, and reaction rates. It also shows the value of this technique in elucidating the initial steps in a complex reaction.

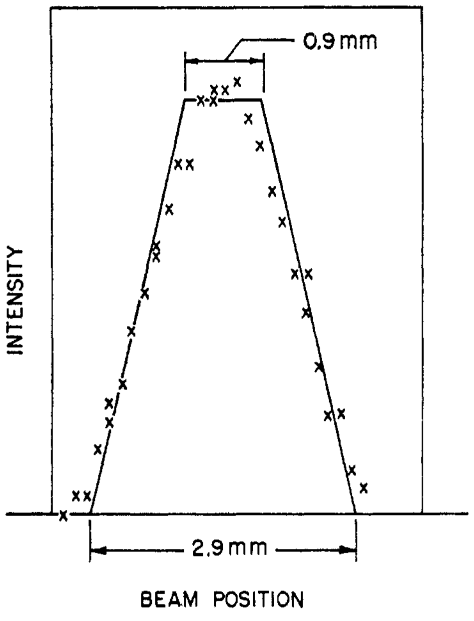

Figure 2. Beam profile at the detector. The solid line is the profile estimated from the beam geometry and the detector width.

Experimental Section

The reactor used in these studies is identical with the reactor that was employed to study the pyrolysis of diphosphine-4.[1] As before, mass spectrometry was used as the analytical tool, and the products from the reactor were sampled using a modulated molecular beam sampling technique.[4] The spectrometer and beam system used in the present study have been modified and are shown schematically in Figure 1. The length of the molecular beam has been increased to 11.5 cm and the molecular beam, electron beam, and ion beam are now mutually perpendicular. The ion beam is focused using a quadrupole ion lens,[5] mass analyzed in a 60°, 14-cm radius of curvature magnetic sector spectrometer, and detected using electron multiplier detection. The spectrometer slits were adjusted for unit resolution at m/e 200 and scanning can be done either electrically or magnetically. The real current sensitivity of the spectrometer is 0.1/torr.[6] A species at a pressure of 0.1 mtorr in the reactor, corresponding to a calculated beam intensity at the detector of 10^{10} molecules/sec, can be detected with a signal-to-noise ratio of 1 at a time constant of 3 sec and with an electron beam density of 0.1 mA/cm^2. The pressure in the spectrometer chamber during operation was 1.5×10^{-8} torr. The neutral beam was generally modulated at 160 Hz using a stable, variable-frequency chopper,[7] and the output of the electron multiplier was amplified by a narrow band amplifier locked into the frequency and phase of the chopper. In the newly modified instrument, not only could the chemical reactor be scanned across the beam-forming system, but the electron beam could also be scanned across the molecular beam. This allowed one to easily maximize the signal intensity and to observe the actual beam profile at the detector. An example of the beam profile is shown in Figure 2. The observed profile agrees well with that estimated from the geometry of the system.

As has been shown recently, beam modulation provides a convenient means for the qualitative identification of the neutral products effusing from the reactor.[8,9] A measurement of the relative phase of an ion signal with respect to the phase of a reference signal is equivalent to a measurement of the difference in the average velocities of the neutral species from which these ions were produced. As the relationship between the signal intensity and phase

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(2) T. P. Fehlner, *J. Amer. Chem. Soc.*, **88**, 2613 (1966); see also M. Baudler, H. Ständeke, M. Borgardt, H. Strabel, and J. Dobbers, *Naturwissenschaften*, **53**, 106 (1966), and references therein; and P. Royen, C. Rocktäschel, and W. Mosch, *Angew. Chem.*, **76**, 860 (1964).

(3) T. P. Fehlner, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968; *J. Amer. Chem. Soc.*, in press.

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

(5) C. S. Lu and H. E. Carr, *Rev. Sci. Instrum.*, **33**, 823 (1962).

(6) The real current sensitivity is the ion current at the first dynode divided by the product of the electron beam current times the pressure.

(7) S. G. Andresen, *Rev. Sci. Instrum.*, **37**, 974 (1966).

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

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

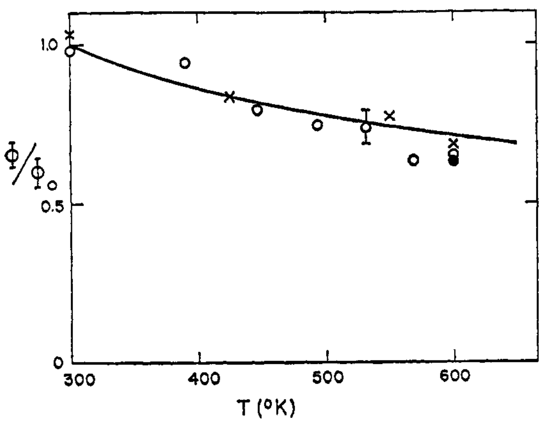

Figure 3. Variation in the phase of the *m/e* 28 ion peak from nitrogen as a function of reactor temperature: ○, 9 mtorr; ×, 14 mtorr; ●, 28 mtorr.

angle is essentially sinusoidal,[8,9] it is convenient to measure the phase angle at zero intensity. Differences in this zero intercept distinguish ions produced by molecular progenitors differing in molecular mass. The present arrangement is a compromise between useful phase measurements and convenient ion intensities, and, although the mass resolution of the method is not very good, these simple measurements are very helpful in identifying molecular products (see below). In addition, one can use this method to obtain a measure of the average gas temperature and compare it to the independently measured wall temperature of the reactor. Figure 3 shows this comparison for this particular reactor, and it is seen that within experimental error the gas temperature equals the wall temperature.

Triphosphine-5 was prepared by the photolysis of diphosphine-4 in a grease-free and mercury-free circulation system. This preparation and the purification of triphosphine-5 have been reported earlier[3] and will be reported in more detail later. Triphosphine-5 was evaporated from a reservoir which was kept at a selected constant low temperature. It was then transferred to the reactor at low pressure through a dark mercury-free vacuum line. The main impurity was diphosphine-4, and consequently the *m/e* 66 ion peak intensity was used as a criterion of purity as the relative intensity of this ion from triphosphine-5 is very small. The triphosphine-5 was better than 95% pure. Sensitivity calibration for phosphine, diphosphine-4, and triphosphine-5 was accomplished as described previously.[1] The accuracy of the pressure measurement is not better than 10%.

Results

Identification of Products. The observed ion spectrum allows the neutral product composition in the ion source of the mass spectrometer to be determined. From this composition one must deduce the composition in the chemical reactor. In these experiments the beam composition is representative of the reactor composition, and, as the beam molecules are labeled with a particular frequency and phase, there is a well-established relationship between the observed ion signals and the composition in the reactor.[1] The products of the decomposition of triphosphine-5 were identified as follows. Triphosphine-5 was introduced into the reactor at a given flow rate and the mass spectrum was obtained. The temperature of the reactor was first increased and then decreased in a stepwise fashion, and the mass spectrum was obtained at each temperature after allowing sufficient time for temperature equilibration. Changes in the following ion intensities were observed: P_4^+, $P_3H_x^+$ ($x = 0, 1, 2, 3, 4, 5$), $P_2H_x^+$ ($x = 0, 1, 2, 3, 4$), PH_x^+ ($x = 0, 1, 2, 3, 4$). No ions containing hydrogen and four phosphorus atoms were observed in these experiments.

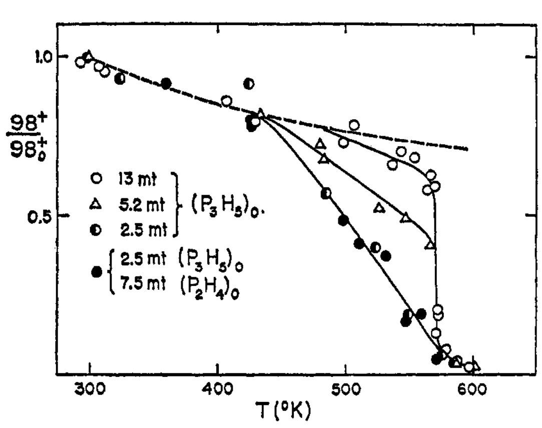

Figure 4. Variation in the *m/e* 98 ion intensity with reactor temperature for various initial pressures.

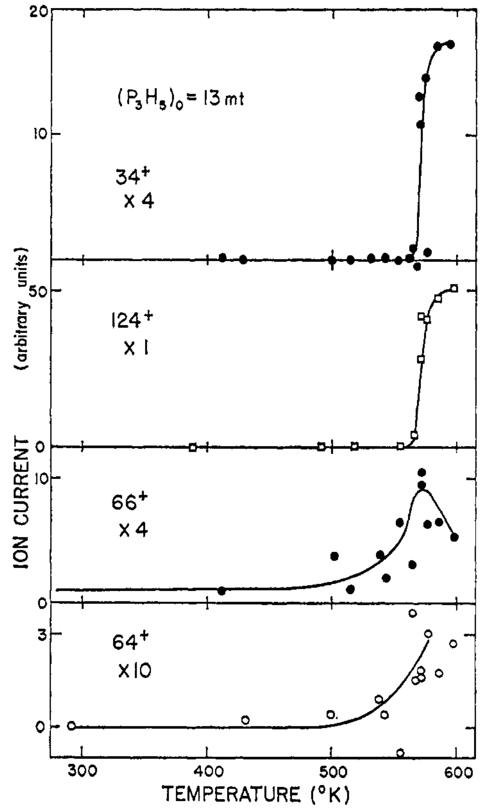

Figure 5. Variation in the *m/e* 34, 124, 66, and 64 ion intensities with reactor temperature. The contribution of triphosphine-5 to *m/e* 34 and the contributions of triphosphine-5 and diphosphine-4 to *m/e* 64 have been removed.

The variations of selected ion intensities with reactor temperature are shown in Figures 4 and 5. Figure 4 illustrates the loss of triphosphine-5 for three different initial pressures. It is evident from this figure that one type of decomposition sets in at about 440°K and another type at about 565°K. Changes in ion intensities representative of the products formed in the 13-mtorr run are shown in Figure 5. The *m/e* 34 and 64 curves have been corrected for the contributions due to fragmentation of triphosphine-5 and diphosphine-4. The change in the *m/e* 124 ion peak is due to the formation of tetraatomic phosphorus. Assignment of the change in the *m/e* 34^+ ion peak to the formation of phosphine is also straightforward as one sees the appearance of the characteristic fragmentation pattern of

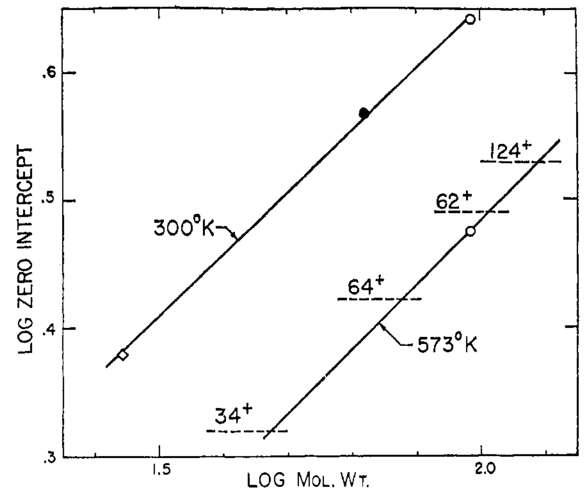

Figure 6. A plot of log of the zero intercept (relative phase) *vs.* log of the molecular weight of the neutral progenitor of the ion: ○, triphosphine-5; ●, diphosphine-4; ◇, nitrogen. The horizontal dashed lines are values of the relative phase measured for the indicated ion mass.

phosphine.[10] The change in the m/e 66$^+$ ion peak has been assigned to the formation of diphosphine-4. The appearance potential of this ion peak was characteristic of the ionization potential of diphosphine-4;[10] however, this is not too meaningful as diphosphine-4 was the main impurity in the reactant. The peak definitely did increase and went through a maximum value at 575°K, the temperature at which diphosphine-4 begins to decompose.[1] Finally the change in the m/e 64 ion peak has been assigned to the formation of diphosphine-2. The precision of measurement of this peak is very bad because both the contributions of triphosphine-5 and diphosphine-4 had to be removed. The appearance potential of this ion was indicative of the presence of diphosphine-2,[1,11] and consequently this change in ion intensity is taken to be real.

Significant changes in ion intensities can result from changes in fragmentation patterns with temperature,[12,13] and thus the confirmation of the identity of these products from the observation of the relative phase of the ion signals is important. An example of the use of these observations is shown in Figure 6. The slope of the line formed by the plot of log of the zero intercept *vs.* log of the molecular weight is the same at 300°K as at the operating temperature. A measurement on an ion peak from a single known molecular progenitor (in this case m/e 98 from triphosphine-5) yields the position of the line at the higher temperature. Thus an "apparent molecular weight" for any other ion peak is obtained from a measurement of the zero intercept. Results from the m/e 34, 62, 64, and 124 ion peaks are shown. By inspection it is evident that these ions are due, at least in part, to different molecular progenitors. In the case of m/e 34, which is due to phosphine and triphosphine-5, it is possible to calculate from the apparent phase the fraction of phosphine in the beam.[9] The value calculated is 0.75 which can be compared with a value of 0.71 calculated from the relative ion intensities and sensitivities for phosphine and triphosphine-5. Although the m/e 124 ion peak clearly results from tetraatomic phosphorus, it is not possible to quantitatively resolve the other ion peaks as they are the result of more than two contributors. Qualitatively, however, the apparent phase of the m/e 64 ion peak is consistent with its formation from triphosphine-5 and diphosphine-4 and -2; and the phase of m/e 62 is consistent with its formation from tetraatomic phosphorus, triphosphine-5, and diphosphine-4 and -2. The products of the decomposition of triphosphine-5, then, are tetraatomic phosphorus, diphosphine-4, diphosphine-2, and phosphine.

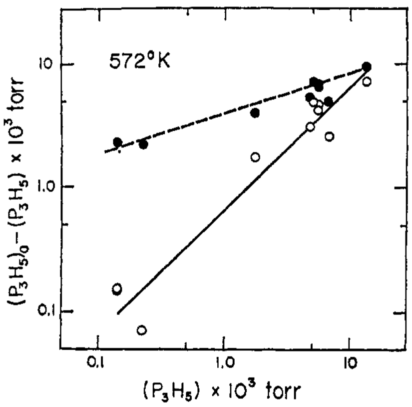

Figure 7. A plot of log BP_0 *vs.* log $(1 - B)P_0$, where B is the reactor yield. The solid circles are the experimental data and the dashed line has a slope of 0.33. The open circles refer to the reactor yield due to the first-order reaction. The solid line has a slope of 1.0.

Rate of Loss of Triphosphine-5. The procedure used previously to treat the results for the thermal decomposition of diphosphine-4 is used here.[1,14-17] Figure 4 indicates that this reaction is complex; however, if the data are treated as normal and a plot of log BP_0 *vs.* log $(1 - B)P_0$[18] is constructed at a single temperature, a straight line having a slope of 0.33 results (Figure 7). Because of scatter in the data this plot does not exhibit the curvature expected of a complex reaction, and thus care must be exercised in interpreting these plots. From inspection of Figure 4 it is clear that there are two reactions of different order taking place. In fact, the plot in Figure 7 can be resolved into a zero-order term and a first-order term, the first order being shown in Figure 7 (open circles). Below 550°K the reaction is mainly zero order and $h(T)$ is given by $h_0(T) = g_0B/v_m$. By examining $h_0(T)$ as a function of temperature in this region at constant g_0, it was found that $h_0(T)$ could be expressed by the equation

$$\log h_0(T) = 16.0 - 1660/T \text{ molecules cm}^{-2}$$

This reaction path was not inhibited by diphosphine-4 (see Figure 4) and appears to be very similar to the zero-order decomposition path for diphosphine-4.[1]

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

(11) T. P. Fehlner, *J. Amer. Chem. Soc.*, **88**, 1819 (1966).

(12) A. Cassuto, "Mass Spectrometry," R. I. Reed, Ed., Academic Press Inc., New York, N. Y., 1965, p 283.

(13) H. Ehrhardt and O. Osberghaus, *Z. Naturforsch., A*, **13**, 16 (1958).

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

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

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

(17) An alternative treatment of reactions in this type of reactor is given in S. W. Benson and G. N. Spokes, *J. Amer. Chem. Soc.*, **89**, 2525 (1967).

(18) B is the reactor yield (see ref 1).

With the zero-order path established, $h_0(T)$ can be subtracted from the net reaction at the higher temperatures. The remainder is due to the first-order reaction and $h_1(T) = B/[(1 - B)v_m]$ can be calculated and is expressed by $\log h_1(T) = 52.4 - 32{,}400/T$. The question that immediately arises is whether the reaction is homogeneous or heterogeneous. There is one observation which tempts one to assign the reaction as homogeneous. Figure 4 shows that the "residual" $(1 - B)$[19] is much lower here (*ca.* 0.02) than it was for the zero-order diphosphine-4 decomposition (*ca.* 0.2).[1] One possible explanation is that, as there are a number of gas–gas collisions under the reaction conditions,[20] these collisions can enhance the reactor efficiency in a homogeneous process. Now if this were a unimolecular homogeneous reaction, the probability of reaction per collision, $h_1(T)$, can be estimated using a treatment similar to that suggested by Benson and Spokes.[17] The calculated $h_1(T)$ has a much smaller preexponential factor and activation energy than does the measured $h_1(T)$. This discrepancy can only be explained if the reaction is complex. In other words, the experimental $h_1(T)$ is not an expression of a rate constant for a single reaction, and a chain-type process is suggested. On the other hand, as diphosphine-4 decomposed on a small fraction of the available sites,[1] the lower "residual" $(1 - B)$ could just as well be due to a complex heterogeneous reaction on all the available sites (see below).

Rate of Formation of Products. Product formation is complicated by several factors. Diphosphine-2 decomposes in a reaction which is inhibited by phosphorus hydrides and, above 575°K, diphosphine-4 decomposes into phosphine and diphosphine-2.[1] Consequently, we observe the following behavior. At fairly high reactant pressures (Figure 5), diphosphine-4 and diphosphine-2 appear to be the initial products formed, phosphine and tetraatomic phosphorus appearing only when the first-order reaction sets in. Apparently, diphosphine-4 and diphosphine-2 are the products of the zero-order reaction while phosphine is the product of the first-order reaction. The tetraatomic phosphorus is produced in increasing amounts by the decomposition of diphosphine-2 as the total pressure of phosphorus hydrides falls off. On the other hand, if one looks at the products being produced in a low-pressure run, then phosphine and tetraatomic phosphorus are also observed initially. In this case the total pressure of phosphorus hydrides is low enough so that some of the diphosphine-2 produced in the zero-order reaction decomposes. Clear evidence for this interpretation is obtained by varying the reactant pressure at a given temperature (*e.g.*, 570°K). As the pressure is increased, the reactor yield increases (Figure 7), but the tetraatomic phosphorus produced decreases. The amount of diphosphine-4 produced remains about constant while the phosphine produced increases but does not "track" the loss in triphosphine-5. As we believe that tetraatomic phosphorus results only from the reaction

$$P_2H_2 \longrightarrow \tfrac{2}{3}PH_3 + \tfrac{1}{3}P_4$$

it is a measure of the diphosphine-2 lost. Consequently, as the pressure is increased, the increase in phosphine from the first-order reaction is offset by the decrease in the decomposition of diphosphine-2. The result is that the formation of phosphine does not simply correspond to the loss of triphosphine-5, and the simple treatment of product formation used previously is not very valuable. However, using the measured relative sensitivities for phosphine, diphosphine-4, and triphosphine-5, one can show that about 1 mole of diphosphine-4 is formed per mole of triphosphine-5 lost by the zero-order path and that about 1 mole of phosphine is formed per mole of triphosphine-5 lost by the first-order path when the amount of tetraatomic phosphorus formed is small. With a single diphosphine-2 sensitivity, a self-consistent mass balance for the hydrogen-containing products can be calculated. However, because of the scatter in the data, this calculation is not too meaningful. It is concluded that the products of the zero-order path are diphosphine-4 and diphosphine-2, and that the products of the first-order path are phosphine and diphosphine-2.

Discussion

The reaction scheme

$$\begin{tikzcd} & P_2H_4 + \tfrac{1}{2}P_2H_2 & P_2H_2 \xrightarrow{3} \tfrac{2}{3}PH_3 + \tfrac{1}{3}P_4 \\ P_3H_5 \arrow[ur, "1"] \arrow[dr, "2"'] & & \\ & PH_3 + P_2H_2 & P_2H_4 \xrightarrow{4} PH_3 + \tfrac{1}{2}P_2H_2 \end{tikzcd}$$

accounts for the thermal decomposition of triphosphine-5 in a Pyrex vessel over the pressure range of 0.2–10 mtorr. Reaction 1 is zero order in triphosphine-5 while reaction 2 is first order in triphosphine-5. Reactions 3 and 4 have been discussed before,[1] and the reactions of interest here are steps 1 and 2.

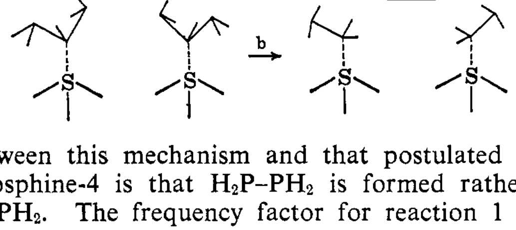
As zero-order kinetics were found previously for diphosphine-4 decomposition (reaction 4), it was not much of a surprise to find similar kinetics for reaction 1. However, this observation again requires the postulaion of a surface reaction taking place on a very limited number of sites which are saturated with respect to triphosphine-5. The mechanism can be represented as

$$2P_3H_5 + 2S \xrightarrow{a} 2P_3H_5\cdot S$$

$$2P_3H_5\cdot S \xrightarrow{b} 2P_2H_4\cdot S + P_2H_2$$

$$2P_2H_4\cdot S \xrightarrow{c} 2P_2H_4 + 2S$$

where the first step is the adsorption of two molecules of triphosphine-5 on adjacent sites. Pictorially one might view the reaction as in eq I. The only difference



(I)

between this mechanism and that postulated for diphosphine-4 is that $H_2P{-}PH_2$ is formed rather than $H{-}PH_2$. The frequency factor for reaction 1 is substantially lower than that for reaction 4,[1] and this may indicate that there are fewer available sites for

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[19] When the probability of reaction per collision on the surface approaches 1, $1 - B$ gives the fraction of molecules that do not collide with the reactive surface (see ref 1).

[20] At the highest pressures used there are about four times as many gas–gas collisions as gas–surface collisions.

reaction 1 as opposed to reaction 4. The latter may explain why diphosphine-4 does not inhibit reaction 1. The activation energy for reaction 1 is much lower than that for 4, however, and this difference more than compensates for the lower frequency factor.

The observed activation energy for reaction 4 is only slightly (3 kcal/mole) greater than the heat of reaction.[21] By analogy, a similar situation for reaction 1 might well obtain, and thus the reaction is close to being thermoneutral as the activation energy for 1 is 7.6 kcal/mole. This allows one to estimate the heat of formation of triphosphine-5 as 14 to 18 kcal/mole. This also means that the activation energy for the reverse reaction

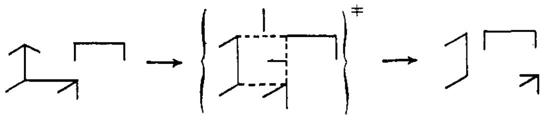
$$P_2H_2 + 2P_2H_4 \cdot S \xrightarrow{-b} 2P_3H_5 \cdot S$$

is not very large and may be a path for the formation of triphosphine-5. In fact, this reaction can account for our earlier observations of triphosphine-5[2] as follows. The original studies were carried out in a tubular diffusive flow reactor. As pointed out by LeGoff,[22] the products of reaction in the hot zone of the reactor can diffuse out into the spectrometer or back into the reactant supply line. The molecules undergoing the latter process spend a characteristic length of time in the supply line before reentering the reactor; and, if the back-diffusing species are reactive, they can be destroyed by reaction in the supply line. As reaction −b appears to have a low activation energy, diphosphine-2 diffusing back into the supply line would react with surface diphosphine-4 to produce triphosphine-5. Once produced, some triphosphine-5 would be expected to pass through the hot zone and into the mass spectrometer without decomposition. In the reactor used for the present studies back-diffusion is inhibited, and no triphosphine-5 was observed as a product of diphosphine-4 pyrolysis.[1]

Reaction 2 is the first-order path and, for the reasons given above, is not a simple unimolecular elimination of phosphine. The reaction is complex but still must be first order in triphosphine-5 and zero order in diphosphine-4. The reaction

$$P_2H_2 + P_3H_5 \longrightarrow PH_3 + 2P_2H_2$$

can explain the observed order. In addition, as this reaction is autocatalytic, it can explain the strong dependence of $h_1(T)$ on the temperature. That is, reaction 2 is first order in triphosphine-5 and first order in diphosphine-2 and thus, as the temperature is increased, there will be an acceleration in the rate due to the concentration factor in addition to that due to the increased temperature. Additional acceleration is due to the fact that in the region where reaction 2 sets in, diphosphine-4 also starts to decompose to yield more diphosphine-2. For reaction 2 to start there must be an initial amount of diphosphine-2. This is supplied by reaction 1. One might picture this reaction as shown in eq II, where diphosphine-2 aids the hydrogen-atom transfer. There is negative evidence that indicates that this reaction is heterogeneous. Because of the low density of collisions in this reactor, any bimolecular reaction observed must have a low activation energy (*ca.* 5 kcal). Using the heat of formation of triphosphine-5 estimated above, the heat of reaction for 2 is 9–13 kcal/mole. In addition, phosphine is not observed as a product of triphosphine-5 decomposition at lower temperatures and higher pressures. Consequently, this is probably a heterogeneous reaction but one that takes place on a majority of the available sites (see above).


(II)

As was the case with diphosphine-4, the apparent instability of triphosphine-5 is due in part to the availability of a surface-catalyzed reaction. The bonding in this molecule, as reflected in the heat of formation estimated above, appears normal. A value of 9 kcal/mole for the heat of formation of triphosphine-5 can be estimated from the heats of formation of phosphine and diphosphine-4. Once again it is interesting to note that substitution of a single trifluoromethyl on each phosphorus removes the surface-catalyzed pathway and results in a much less reactive molecule from the standpoint of thermal decomposition.[23]

In the course of these studies it also became apparent that reaction 1 is not the only efficient decomposition path available to triphosphine-5. This compound also decomposes in the inlet line of the mass spectrometer and in the liquid phase. The products of reaction in the inlet line appear to be diphosphine-4 and tetraphosphine-6. The features of this reaction will be described in more detail elsewhere.

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[21] A value of 26 kcal/mole is used for the heat of formation of diphosphine-2 (see ref 10).

[22] A. Pentenero and P. LeGoff, "Mass Spectrometry," R. I. Reed, Ed., Academic Press Inc., New York, N. Y., 1965, p 305.

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