

### Conclusions

The alkali halide pressed disks of infrared spectroscopy are convenient systems in which unstable chemical species can be trapped for spectroscopic studies. These unstable species can be formed directly in the matrices by carrying out chemical reactions in them. In the present work, chemical reactions were initiated thermally, but other methods of initiation such as irradiation appear possible. Events occurring in the disks may be followed spectroscopically and by chemical means since the disks can be dissolved in liquids,

ground under liquids and gases, or subjected to chemical analysis. Quantitative studies of solid-state reactions in these disks also are possible. Examples of such studies will be presented in subsequent reports.

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## Mass Spectrometric Study of Phosphine and Diphosphine<sup>1</sup>

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The appearance potentials of the principal positive ions in the mass spectra of phosphine, diphosphine, and phosphine and diphosphine containing various numbers of deuterium atoms are reported. Assignments of the probable processes of ionization and dissociation are made, consistent with the observed energetics. The molecular ionization potentials of phosphine and diphosphine are found to be 10.2 and 8.7 e.v., respectively. Based on the appearance potential of the  $P_2H_3^+$  ion, it is suggested that the vapor phase decomposition of diphosphine, to give  $PH_3$  and a solid of approximate composition  $P_2H$ , proceeds through the intermediate  $P_2H_3$ .

### Introduction

Only a relatively few phosphorus compounds have been studied mass spectrometrically. In an attempt to learn more of the properties of the gaseous ions containing phosphorus and their origin in electron impact experiments, we have studied the two hydrides,  $PH_3$  and  $P_2H_4$ . It has been found that because of the ease of decomposition of diphosphine, the  $P_2H_3^+$  and  $PH_2^+$  ions are not formed by simple dissociative ionization of diphosphine. Further, some evidence is presented which leads us to believe that the thermal decomposition of diphosphine may proceed through the intermediate  $P_2H_3$ .

### Experimental

The samples of phosphine and diphosphine were prepared by hydrolyzing calcium phosphide in a vacuum system.<sup>2</sup> The impure phosphine gas generated by the hydrolysis was dried by passing it through a soda-lime column. The diphosphine present was separated from the phosphine by condensing it in a  $CO_2$ -acetone trap. White, crystalline phosphine was trapped out at liquid nitrogen temperature and was purified by repeated sublimations. The diphosphine trapped in the  $CO_2$ -acetone bath was then repeatedly distilled at low temperatures until a reasonably pure sample was obtained. Low voltage mass spectrometry was used to judge the approximate purities of the samples prepared and used. The samples of deuteriophosphine

and deuteriodiphosphine were prepared in similar manner, but deuterium oxide was used in the hydrolysis.

Only fresh samples were used in our studies. Particular care was taken to do so in the case of diphosphine, since decomposition is known to occur.<sup>2</sup> After several hours, yellow deposits were easily observable on the walls of the sample flasks, so that the individual studies with diphosphine samples were necessarily hurried.

The ionization and appearance potentials were determined using a time-of-flight mass spectrometer, described previously.<sup>3</sup> The experimental ionization efficiency curves for the phosphine study were interpreted using the extrapolated voltage differences method<sup>4</sup> and the method of Lossing, Tickner, and Bryce.<sup>5</sup> The results were checked using the energy compensation technique.<sup>6</sup> The voltage scale was calibrated using krypton (ionization potential = 14.00 e.v.) mixed intimately with the sample. For the diphosphine study, we used only the energy compensation technique, since we wished to obtain the results quickly, before serious decomposition of the samples occurred. To partially compensate for lack of precision in the determinations, repeated measurements were made, using a fresh sample each time.

### Results

The mass spectral cracking patterns and appearance potentials for ions from the phosphines and diphosphines are given in Tables I to IV. The relative abundances are reported for 70-e.v. electrons. The probable processes shown in Tables I and II were arrived at from considerations of the energetics, as is indicated in the Discussion. The heats of formation of

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

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TABLE I  
 RELATIVE ABUNDANCES AND APPEARANCE POTENTIALS OF THE PRINCIPAL IONS IN THE MASS SPECTRUM OF PHOSPHINE

<i>m/e</i>	70-e.v. relative abundance		Appearance potential, e.v.		Probable process	$\Delta H_f^+$ , kcal./mole
	This work	Others	This work	Others		
31	24.1	26.4, <sup>a</sup> 40.2 <sup>b</sup>	17.2 ± 0.2	16.7, <sup>a</sup> 16.5 <sup>b</sup>	PH <sub>3</sub> → P <sup>+</sup> + H + H <sub>2</sub>	346
32	100.0	100.0, <sup>a</sup> 100.0 <sup>b</sup>	13.3 ± 0.2	12.0, <sup>a</sup> 12.4 <sup>b</sup>	PH <sub>3</sub> → PH <sup>+</sup> + H <sub>2</sub>	308
33	21.8	27.6, <sup>a</sup> 25.4 <sup>b</sup>	13.2 ± 0.2	13.9, <sup>a</sup> 14.4 <sup>b</sup>	PH <sub>3</sub> → PH <sub>2</sub> <sup>+</sup> + H	254
34	75.2	85.0, <sup>a</sup> 68.0 <sup>b</sup>	10.2 ± 0.2	10.0, <sup>a</sup> 11.5 <sup>b</sup>	PH <sub>3</sub> → PH <sub>3</sub> <sup>+</sup>	237

<sup>a</sup> See ref. 8. <sup>b</sup> See ref. 9.

 TABLE II  
 RELATIVE ABUNDANCES AND APPEARANCE POTENTIALS OF THE PRINCIPAL IONS IN THE MASS SPECTRUM OF DIPHOSPHINE

<i>m/e</i>	70-e.v. relative abundance		Appearance potential, e.v.		Probable process	$\Delta H_f^+$ , kcal./mole
	This work	Others <sup>a</sup>	This work	Others <sup>a</sup>		
31	65.3	1.2	(17.3)	16.7		
32	100.0	0.2	(13.4)			
33	21.3	5.1	(13.2)			
34	52.0	0.4	(10.1)			
62	57.3	100.0	12.2	13.7	P <sub>2</sub> H <sub>4</sub> → P <sub>2</sub> <sup>+</sup> + 2H <sub>2</sub>	286
63	44.0	5.6	13.2	13.6	P <sub>2</sub> H <sub>4</sub> → P <sub>2</sub> H <sup>+</sup> + H + H <sub>2</sub>	257
64	50.7	5.8	10.5	12.7	P <sub>2</sub> H <sub>4</sub> → P <sub>2</sub> H <sub>2</sub> <sup>+</sup> + H <sub>2</sub>	247
65	9.3	1.3	9.1	11.3		
66	74.6	8.4	8.7 ± 0.3	10.6	P <sub>2</sub> H <sub>4</sub> → P <sub>2</sub> H <sub>4</sub> <sup>+</sup>	206

<sup>a</sup> See ref. 10.

phosphine and diphosphine are 1.3 and 5.0 kcal./mole, respectively.<sup>7</sup>

Omitted from Table II are the processes for the formation of and the heats of formation of the ions observed at *m/e* = 31, 32, 33, and 34. The appearance potentials for these ions, which are enclosed in parentheses, give strong indication that they are due to phosphine either desorbed from the interior surfaces of the sample introductory system or formed by chemical decomposition in the ion source.

Tables III and IV indicate the results of our studies of mixtures of deuterated phosphines and mixtures of deuterated diphosphines, respectively. These results are seen to agree with those presented in Tables I and II.

## Discussion

**Relative Abundances.**—The relative abundance of the ions in the 70-e.v. mass spectrum of phosphine agree reasonably well both with those determined by Neuert and Clasen<sup>8</sup> at 100 e.v. and with the 60 e.v. spectrum reported by Saalfeld and Svec.<sup>9</sup>

Our experimental determination of the mass spectrum of diphosphine differs drastically from that recently reported by Saalfeld and Svec.<sup>10</sup> The relative abundances of the *m/e* = 31, 32, 33, and 34 ions which were observed in the mass spectrum of diphosphine were unexpectedly high. Further, the appearance potentials measured for these ions are essentially the same as for the same ions from phosphine. We believe, therefore, that the major portion of the intensities which we observed for these four ions derives from phosphine formed *via* the decomposition of diphosphine.

TABLE III

RELATIVE ABUNDANCES AND APPEARANCE POTENTIALS OF IONS FROM A MIXTURE OF PHOSPHINE AND DEUTERATED PHOSPHINES

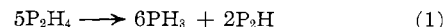
<i>m/e</i>	70-e.v. relative abundance	Appearance potential, e.v.	Ionic species
31	39.8	17.1 ± 0.3	P <sup>+</sup>
32	85.8	13.3 ± 0.2	PH <sup>+</sup>
33	100.0	13.1 ± 0.2	PD <sup>+</sup> or PH <sub>2</sub> <sup>+</sup>
34	33.8	10.1 ± 0.2	PH <sub>3</sub> <sup>+</sup>
35	58.0	10.1 ± 0.2	PDH <sub>2</sub> <sup>+</sup>
36	47.8	10.2 ± 0.2	PD <sub>2</sub> H <sup>+</sup>
37	22.9	10.1 ± 0.2	PD <sub>3</sub> <sup>+</sup>

TABLE IV

RELATIVE ABUNDANCES AND APPEARANCE POTENTIALS OF IONS FROM A MIXTURE OF DIPHOSPHINE AND DEUTERATED DIPHOSPHINES

<i>m/e</i>	70-e.v. relative abundance	Appearance potential, e.v.	Ionic species
31	39.9	(17.4)	P <sup>+</sup>
32	73.6	(13.3)	PH <sup>+</sup>
33	28.3	(13.2)	PD <sup>+</sup> or PH <sub>2</sub> <sup>+</sup>
34	37.5	(10.3)	PH <sub>3</sub> <sup>+</sup>
35	19.0	(10.4)	PDH <sub>2</sub> <sup>+</sup>
62	100.0	12.4	P <sub>2</sub> <sup>+</sup>
63	63.3	12.5	P <sub>2</sub> H <sup>+</sup>
64	83.1	10.8	P <sub>2</sub> H <sub>2</sub> <sup>+</sup>
65	30.8	8.9	P <sub>2</sub> H <sub>3</sub> <sup>+</sup>
66	93.4	8.2 ± 0.3	P <sub>2</sub> H <sub>4</sub> <sup>+</sup>
67	42.0	8.4 ± 0.3	P <sub>2</sub> DH <sub>3</sub> <sup>+</sup>
68	7.5	8.2 ± 0.5	P <sub>2</sub> D <sub>2</sub> H <sub>2</sub> <sup>+</sup>

The over-all decomposition of diphosphine may be expressed<sup>2</sup> by the equation



and since the decomposition of P<sub>2</sub>H<sub>4</sub> occurs rather readily,<sup>2,7</sup> we believe the ions of PH<sub>x</sub><sup>+</sup>, where *x* = 0, 1, 2, and 3, observed from the diphosphine sample, originate from the phosphine formed as the product of the decomposition rather than directly from ionization and dissociation of diphosphine.

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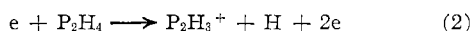
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**Ionization Potentials.**—The ionization potentials of phosphine and diphosphine were determined to be  $10.2 \pm 0.2$  and  $8.7 \pm 0.3$  e.v., respectively. Because the energy compensation technique was used to determine  $I(\text{P}_2\text{H}_4)$ , we have had to estimate a probable error value in this case. The value of  $I(\text{PH}_3)$  determined by us compares favorably with that measured by Neuert and Clasen.<sup>8</sup> However, we find that the results of Saalfeld and Svec<sup>9,10</sup> are in poor agreement with the ionization potential determinations we report here. Saalfeld and Svec<sup>9</sup> noted in passing that the value of  $I(\text{PH}_3)$  which they determined was rather high compared to that determined by Neuert and Clasen.<sup>8</sup> A satisfactory explanation for their different findings was not given by Saalfeld and Svec.

It is noted that the ionization potential of ammonia is 10.15–10.5 e.v.<sup>11–13</sup> and that of hydrazine is  $9.00 \pm 0.1$  e.v.<sup>14</sup> From a comparison of ammonia and phosphine, and of hydrazine and diphosphine, one would expect  $I(\text{P}_2\text{H}_4) \leq 9.0$  e.v., in agreement with our experimental measurements.

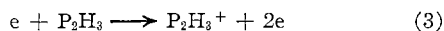
We believe that the appearance potentials of 8.9–9.1 e.v. measured for  $\text{P}_2\text{H}_3^+$  do not represent the threshold energy for the reaction



but rather that this value is the ionization potential of the  $\text{P}_2\text{H}_3$  species. Our reasoning for this is presented in the following paragraphs.

Cottrell<sup>15</sup> indicates  $E(\text{P-H})$  in  $\text{PH}_3$  is about 77 kcal./mole. From the data in Table I,  $D(\text{H-PH}_2)$  in the  $\text{PH}_3^+$  ion is 3.0 e.v., or 69 kcal./mole. Similarly,  $D(\text{H-PH})$  in the  $\text{PH}_2^+$  ion and  $D(\text{H-P})$  in the  $\text{PH}^+$  ion are 106 and 90 kcal./mole, respectively. Thus,  $E(\text{P-H})$  in the  $\text{PH}_x^+$  ions ( $x = 2, 3$ ) is 88 kcal./mole. This is somewhat greater than that for the uncharged molecule.

Then in the  $\text{P}_2\text{H}_4$  molecule, and the  $\text{P}_2\text{H}_x^+$  ions ( $x = 1, 2, 3$ , or 4), one might expect  $E(\text{P-H}) \simeq 70\text{--}75$  kcal./mole. Taking  $E(\text{P-H}) = 75$  kcal./mole for the ions,  $AP(\text{P}_2\text{H}_2^+) \simeq 8.7 + 6.5 - 4.5 = 10.7$  e.v. In fact, 10.5 e.v. was determined. Similarly,  $AP(\text{P}_2\text{H}^+) \simeq 8.7 + 9.7 - 4.5 = 13.9$  e.v.; 13.2 e.v. was measured. However, upon attempting this for the  $\text{P}_2\text{H}_3^+$  ion,  $AP(\text{P}_2\text{H}_3^+) \simeq 8.7 + 3.2 - 0 = 11.9$  e.v.; 9.1 e.v. was observed. We believe, therefore, that the value of 9.0 e.v. represents the threshold energy for the reaction



Further comments on the significance of this conclusion are discussed later.

**Appearance Potentials.**—From a comparison of the data in Tables I and III it is seen that both the deuterated phosphine and phosphine lead to the same results for the appearance potentials. This is also true of the data determined for diphosphine and deuterated diphos-

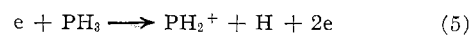
phines. The heats of formation for the various  $\text{PH}_x^+$  and  $\text{P}_2\text{H}_x^+$  species are summarized in Tables I and II.

With the exception of the  $m/e = 63$  ion, the appearance potentials determined for the  $\text{P}_2\text{H}_x^+$  ions from diphosphine are consistently and significantly lower than those determined by Saalfeld and Svec.<sup>10</sup> Saalfeld and Svec used the linear extrapolation method in interpreting their ionization efficiency curves (with data points taken at the large intervals of 0.5 e.v.). It is known both that the linear extrapolation method is one of the poorest methods available among a large variety of interpretative techniques and that the linear extrapolation method consistently yields appearance potentials which are too large, particularly for fragment ions. Therefore we conclude that our results approach the true values more satisfactorily than do the data presented by Saalfeld and Svec.

Recently the P-P bond dissociation energy in  $\text{P}_2\text{Cl}_4$  was determined.<sup>16</sup> It would be of interest also to determine this quantity from other compounds of the general formula  $\text{P}_2\text{X}_4$ . The simplest of the  $\text{P}_2\text{X}_4$  compounds is the hydride, diphosphine. If the process of



could have been studied, it would provide information about  $D(\text{H}_2\text{P-PH}_2)$ , but it has already been indicated that the  $AP(\text{PH}_2^+)$  which was determined in the diphosphine mass spectrum is due to the process



where the  $\text{PH}_3$  is formed from the decomposition of the diphosphine. This prevents us from determining  $D(\text{H}_2\text{P-PH}_2)$  in this study.

We indicated above that the  $AP(\text{P}_2\text{H}_3^+)$  is for the process given by eq. 3. This precludes a direct calculation of  $\Delta H_f(\text{P}_2\text{H}_3^+)$ . However, we may infer a value of  $\Delta H_f(\text{P}_2\text{H}_3^+)$  by an analogy drawn between the  $\text{N}_2\text{H}_x$  and  $\text{P}_2\text{H}_x$  molecules and ions. From the study of Dibeler, Franklin, and Reese,<sup>14</sup>  $\Delta H_f(\text{N}_2\text{H}_4^+) \simeq \Delta H_f(\text{N}_2\text{H}_3^+)$  and  $\Delta H_f(\text{N}_2\text{H}_2^+) \simeq \Delta H_f(\text{N}_2\text{H}^+)$ . From Table II,  $\Delta H_f(\text{P}_2\text{H}_2^+) \simeq \Delta H_f(\text{P}_2\text{H}^+)$ , and so by analogy we estimate  $\Delta H_f(\text{P}_2\text{H}_3^+) \simeq \Delta H_f(\text{P}_2\text{H}_4^+) = 206$  kcal./mole. Taking  $\Delta H_f(\text{P}_2\text{H}_3^+) = 210$  kcal./mole and  $I(\text{P}_2\text{H}_3) = 9.0$  e.v., one calculates  $D(\text{H-P}_2\text{H}_3) \geq 50$  kcal./mole. Probably this value of  $D(\text{H-P}_2\text{H}_3)$  is somewhat low, suggesting  $I(\text{P}_2\text{H}_3)$  is actually slightly less than 9.0 e.v.

Alternatively,  $\Delta H_f(\text{P}_2\text{H}_3^+)$  may be estimated as follows<sup>17</sup>:  $E(\text{P-H}) \simeq 70\text{--}75$  kcal./mole was noted above for both the  $\text{P}_2\text{H}_x$  molecules and ions. Taking  $E(\text{P-H}) = 70$  kcal./mole for the diphosphine molecule,  $\Delta H_f(\text{P}_2\text{H}_3) = 23$  kcal./mole. Then  $\Delta H_f(\text{P}_2\text{H}_3^+) = 227$  kcal./mole. The value of  $E(\text{P-H}) = 70$  kcal./mole appears to us to be more reasonable than a lower value near 50 kcal./mole. Consequently,  $\Delta H_f(\text{P}_2\text{H}_3^+) = 227$  kcal./mole is considered to be the better value, although both results are obviously speculative.

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**Decomposition of Diphosphine.**—If  $P_2H_3^+$  is not formed by the process given in eq. 2, then it is formed by simple ionization of the  $P_2H_3$  radical (eq. 3). Therefore this radical could well be an intermediate in the thermal decomposition of diphosphine. Such a conclusion is not unreasonable, for the  $N_2H_3$  radical has been postulated in mechanisms for the decomposition of hydra-

zine.<sup>18,19</sup> If  $P_2H_3$  is an intermediate, as suggested by our study, the convictions of Evers and Street<sup>2</sup> concerning the active species in the room temperature decomposition of diphosphine may have to be revised.

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## Positional and *cis-trans* Isomeric Dimethylaminotriphosphonitriles. The Use of $H^1$ Nuclear Magnetic Resonance in Configurational Analysis

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Through aminolysis with dimethylamine, arylation with benzene or xylene in the presence of aluminum chloride, and a combination of both, a series of derivatives of trimeric phosphonitrilic chloride has been made.  $H^1$  nuclear magnetic resonance spectra were obtained for these compounds and used to determine both their positional and *cis-trans* configurations. The structural analysis is based on consideration of the number of chemical shifts and the values of the coupling constants.

### Introduction

Although complete substitution of the halogen atoms on the lower cyclic phosphonitrilic chlorides,  $(NPCL_2)_{3,4}$ , has received considerable study in the past several years,<sup>1-3</sup> it is only quite recently that attention has been focused on progressive replacement of halogens with elucidation of the positions at which such replacement occurs.<sup>4-9</sup> Trimeric phosphonitrilic chloride is an essentially planar ring,<sup>10,11</sup> with the chlorine atoms lying above and below the plane of the ring. Compounds such as  $P_3N_2A_2B_4$ ,  $P_3N_3A_3B_3$ , and  $P_3N_3A_2B_2C_2$  can, therefore, be formed as positional and *cis-trans* isomers.

Becke-Goehring and co-workers<sup>4,5</sup> found that treatment of  $(NPCL_2)_3$  with strong nucleophiles such as methyl- and dimethylamine in amounts less than required for full replacement of chlorine gave di- and trisubstituted products in which each amino group was attached to a separate phosphorus atom. This was an important and somewhat surprising finding because it had been generally assumed that replacement reactions to give  $P_3N_3A_4B_2$  compounds resulted in geminal substitution of B for A. This assumption was based almost entirely on the fact that treatment of

$(NPCL_2)_3$  with  $C_6H_6$  in the presence of  $AlCl_3$  gave  $P_3N_3Cl_4(C_6H_5)_2$  with the phenyls both attached to the same phosphorus.<sup>12</sup> Recently we have shown that even Friedel-Crafts phenylation can give nongeminal substitution.<sup>13</sup>

Subsequent to Becke-Goehring's report there have been several publications on the reactions of  $(NPCL_2)_3$  with restricted amounts of amines to give  $P_3N_3Cl_4A_2$ ,  $P_3N_3Cl_3A_3$ , and  $P_3N_3Cl_2A_4$  derivatives (A representing an amino group). In several cases two compounds of the same composition but differing melting point were obtained. Disregarding the possibility of boat and chair configurations, these represent positional and/or *cis-trans* isomers. A compilation of such compounds is given in a recent review.<sup>3</sup>

Even more clear-cut evidence for *cis-trans* isomers was found for the lower cyclic phenylchlorophosphonitriles,  $[(C_6H_5)(Cl)PN]_{3,4}$ , obtained by the action of  $NH_4Cl$  on  $(C_6H_5)_3PCl_4$ . Two trimeric<sup>14,15</sup> species and three tetrameric<sup>15</sup> species have been reported. However, despite the isolation of a fair number of isomers of aminochloro- and phenylchlorophosphonitriles, there are only two reports in which *cis-trans* configuration has been indicated. Our own report<sup>13</sup> is one; the other is by Moeller and Nannelli<sup>16</sup> and reports identification of the *cis* and *trans* forms for each of two isomers of  $P_3N_3(C_6H_5)_3(n-C_3H_7NH)_3$  and  $P_3N_3(C_6H_5)_3(n-C_4H_9NH)_3$ . In both cases assignment was based on proton magnetic resonance data. Recently,<sup>17</sup> Moeller

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