reported techniques.[4–6,13–15] Raman spectra were obtained with crystalline samples using a Cary Model 81 spectrophotometer equipped with an He–Ne laser source. Infrared spectra were measured on a Beckman IR-11 far-infrared spectrophotometer using Nujol mulls and polyethylene windows.

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Study of Ion–Molecule Reactions in Phosphine by Ion Cyclotron Resonance[1]

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Although numerous mass spectrometric investigations of phosphine have been reported,[3–7] only two groups[3,6] have investigated the ion–molecule chemistry of PH_3, and their work concentrated solely on the formation of the phosphonium cation, PH_4^+. Halmann and Platzner[6] concluded from appearance potential measurements that the PH_4^+ ion was produced by the reaction

$$PH_3^+ + PH_3 \longrightarrow PH_4^+ + PH_2 \text{ (or } PH_4^+ + PH + H) \quad (1)$$

They were unable to detect any contribution to the formation of PH_4^+ from ion–molecule reactions involving PH_2^+ or PH^+.

Since ion cyclotron single- and double-resonance techniques have proven to be useful methods for the identification of gas-phase ion–molecule reactions,[8–10] these techniques were used to study the reactions which produce PH_4^+. During the course of the investigation, a variety of previously unreported ionic species and ion–molecule reactions occurring in PH_3 were discovered.

Experimental Section

The ion cyclotron resonance (icr) spectra in this study were obtained at room temperature using a Varian ICR-9 ion cyclotron resonance spectrometer, described in previous literature,[9] utilizing the electron energy modulation scheme described by Henis and Frasure.[11] Gaseous phosphine (Matheson Co., Inc.) was used without further purification, while acetone and acetaldehyde (reagent grade) were purified by repetitive freeze–pump–thaw cycles. PD_3 was prepared by exchange between PH_3 and acidified 99.8% D_2O (Stohler Isotope Chemicals Co., Azusa, Calif. 91702) in excess, as reported by Weston and Bigeleisen.[12]

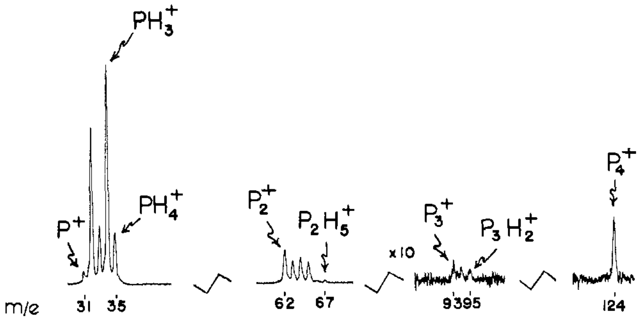

Figure 1.—Icr single-resonance spectrum of positive ions in PH_3 at 2×10^{-5} Torr and 23-eV peak ionizing electron energy.

Results and Discussion

Figure 1 shows an icr single-resonance spectrum of PH_3 at 2×10^{-5} Torr and 23-eV peak ionizing energy. The parent ion, PH_3^+, as well as all three fragment ions PH_2^+, PH^+, and P^+ may be observed. In addition to the *m/e* 35 PH_4^+ product ion, a large number of other ions, attributable to ion–molecule reactions in PH_3, appear in the higher mass regions. These include $P_2H_n^+$ (n = 0–5), $P_3H_n^+$ (n = 0–2), and P_4^+. With the exception of PH_4^+, none of the higher mass ions has been reported previously as an ion–molecule reaction product in gaseous PH_3. Analogous species have, however, been observed as ion–molecule reaction products in the congener of phosphine, ammonia.[13,14] Derwish, *et al.*, reported formation of the species $N_2H_n^+$ (n = 1–5) in gaseous ammonia.

Using ion cyclotron double-resonance techniques, the ion–molecule reactions listed in Table I were identified. With the exception of reaction 1, none of these reactions has been reported previously. The sign of the icr double-resonance signal, given in Table I for each reaction, depends on the sign of $(\mathrm{d}k/\mathrm{d}E_{\text{ion}})^0$, where k is the reaction rate constant, E_{ion} is the translational energy of the irradiated ion, and the derivative is evaluated in the limit of vanishing field strength of the irradiating oscillator.[15] General observations in this and previous icr studies are that $(\mathrm{d}k/\mathrm{d}E_{\text{ion}})^0$ is (1) negative for exothermic reactions other than charge transfer and (2) positive for exothermic charge-transfer reactions. A reaction which gives a negative double-resonance signal must be occurring at thermal energies and must therefore be exothermic or thermoneutral. A reaction which gives a positive double-resonance signal may be either endothermic or exothermic, but an endothermic reaction must give a

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TABLE I
ION-MOLECULE REACTIONS IN PHOSPHINE CONFIRMED BY DOUBLE RESONANCE (NEUTRALS ASSUMED)

	Reaction	$(dk/dE_{ion})^0$
1.	$PH_3^+ + PH_3 \rightarrow PH_4^+ + PH_2$	−
2.	$PH_3^+ + PH_3 \rightarrow P_2H^+ + 2H_2 + H$	+
3.	$PH_3^+ + PH_3 \rightarrow P_2H_3^+ + H_2 + H$	+
4.	$PH_3^+ + PH_3 \rightarrow P_2H_4^+ + H_2$	+
5.	$PH_3^+ + PH_3 \rightarrow P_2H_5^+ + H$	−
6.	$PH_2^+ + PH_3 \rightarrow PH_3^+ + PH_2$	+
7.	$PH_2^+ + PH_3 \rightarrow P_2H^+ + 2H_2$	−
8.	$PH_2^+ + PH_3 \rightarrow P_2H_3^+ + H_2$	−
9.	$PH^+ + PH_3 \rightarrow PH_4^+ + P$	+
10.	$PH^+ + PH_3 \rightarrow PH_3^+ + PH$	+
11.	$PH^+ + PH_3 \rightarrow PH_2^+ + PH_2$	+
12.	$PH^+ + PH_3 \rightarrow P_2^+ + 2H_2$	−
13.	$PH^+ + PH_3 \rightarrow P_2H_2^+ + H_2$	−
14.	$PH^+ + PH_3 \rightarrow P_2H_3^+ + H$	−
15.	$P^+ + PH_3 \rightarrow PH_3^+ + P$	+
16.	$P^+ + PH_3 \rightarrow P_2H^+ + H_2$	−
17.	$P_2^+ + PH_3 \rightarrow P_3H^+ + H_2$	−
18.	$P_2^+ + PH_3 \rightarrow P_3H_2^+ + H$	−
19.	$P_2H^+ + PH_3 \rightarrow P_3H_2^+ + H_2$	−

positive double-resonance signal near threshold. Thus, observation of a positive double-resonance signal for a reaction does not necessarily imply that it occurs when the parent ion is not irradiated.

All double-resonance spectra were recorded in the limit of low irradiating field intensities to minimize the occurrence of spurious results as first mentioned by Gray[16] and more recently by Clow and Futrell.[17]

The absence of any observable reactions producing the P_4^+ ion suggests that it may result from electron impact ionization of a P_4 impurity in PH_3 or from pyrolysis on the electron-emitting filament. Reaction 1 in Table I indicates that the PH_4^+ ion is produced by the parent ion, PH_3^+. Additionally, reaction 9 indicates that PH^+ is also a possible reactant. However, the positive $(dk/dE_{ion})^0$ for reaction 9 suggests that it may be endothermic and thus may not contribute significantly to the formation of PH_4^+ at thermal ion energies. This explanation is also consistent with Halmann and Platzner's failure to detect reaction 9, since conventional mass spectrometric determinations detect only exothermic reactions.

Many of the reactions reported in Table I have exact analogies in the gaseous ammonia system, as reported by Derwish, *et al.*,[13] and Melton.[14] In fact, with the exception of reaction 7, all of the reactions in Table I which have a negative $(dk/dE_{ion})^0$ and thus are assumed exothermic have exact analogies in the NH_3 system, except those which would involve N_2^+. Formation of N_2^+ by a reaction analogous to reaction 12 in Table I is calculated to be exothermic by 12 kcal/mol for ground-state ions[18] and thus is not precluded by energetic considerations. However, charge transfer *via* the reaction

$$N_2^+ + NH_3 \longrightarrow NH_3^+ + N_2 \qquad (20)$$

is calculated to be exothermic by 125 kcal/mol for ground-state ions; thus, for the pressures at which the experiments of Derwish, *et al.*,[13] and Melton[14] were conducted, reaction 20 could remove N_2^+ ions from observation. This may explain why the species N_2^+ and any reactions in which it might be involved were not observed in gaseous NH_3, while P_2^+ and its reactions were seen in the present study.

The proton affinity of PH_3 ($PA(PH_3)$) has been determined using the methods outlined by Beauchamp and Buttrill.[15] Reactions which limit the proton affinity of PH_3 are

$$CH_3CHOH^+ + PH_3 \longrightarrow PH_4^+ + CH_3CHO \qquad (21)$$

$$PH_4^+ + (CH_3)_2C{=}O \longrightarrow (CH_3)_2C{=}OH^+ + PH_3 \qquad (22)$$

Reaction 21 implies that $PA(PH_3)$ is greater than that of acetaldehyde (185 ± 3 kcal/mol) while reaction 22 implies $PA(PH_3)$ is less than that of acetone (186 ± 3 kcal/mol). These considerations lead to a value of 186 ± 3 kcal/mol for the proton affinity of PH_3 at room temperature and a value of 181 ± 3 kcal/mol for $\Delta H_f(PH_4^+)$.[19]

This value for $PA(PH_3)$ is in excellent agreement with that reported by Holtz and Beauchamp,[20] determined by the same method to be 185 ± 4 kcal/mol, and with that reported by Haney and Franklin of 186 ± 1 kcal/mol.[21] The proton affinity of ammonia has been reported by Haney and Franklin[22] to be 207 kcal/mol, some 21 kcal/mol higher than that of phosphine. The higher basicity of NH_3 relative to PH_3 in the gas phase parallels the differences between the two in aqueous solutions, where one may estimate a difference of approximately 20 p*K* units in their relative basicities.[23]

Studies of PD_3–PH_3 mixtures using icr single- and double-resonance techniques indicate that reaction 1 can proceed by both a proton transfer and a hydrogen abstraction mechanism. Icr double-resonance spectra of approximately 1:1 PD_3–PH_3 mixtures indicate that both PD_3^+ and PH_3^+ contribute to the formation of PH_3D^+ and that both precursors also contribute to the formation of PD_3H^+.

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