

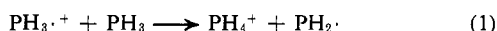
# Acidity, Basicity, and Ion-Molecule Reactions of Phosphine in the Gas Phase by Ion Cyclotron Resonance Spectroscopy

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**Abstract:** The ion-molecule reactions of phosphine, both pure and in binary mixtures with several other molecules, have been investigated by ion cyclotron resonance spectroscopy. Reaction pathways, product distributions, and rate constants have been determined for a wide variety of ion-molecule reactions for both positive and, to a lesser extent, negative ions. Phosphine fragment ions condense with neutral PH<sub>3</sub> to generate ions containing two and, on further reaction, three atoms of phosphorus. In the process of condensation, one or two molecules of H<sub>2</sub> are expelled, whereas hydrogen atom loss occurs only when the reactant ion is a radical species such as PH<sub>2</sub><sup>·+</sup>. The formation of PH<sub>4</sub><sup>+</sup> occurs primarily from PH<sub>3</sub><sup>·+</sup> which does not undergo condensation reactions to any significant extent. Observation of a mixture of PH<sub>3</sub> and PD<sub>3</sub> indicated that proton transfer is 1.2 times more important than hydrogen abstraction as a means of forming PH<sub>4</sub><sup>+</sup> from PH<sub>3</sub><sup>·+</sup>. Where possible, thermodynamic data have been determined, including the gas-phase acidity, PA(PH<sub>2</sub><sup>-</sup>) = 362 ± 11 kcal/mol, and basicity, PA(PH<sub>3</sub>) = 185 ± 4 kcal/mol, of PH<sub>3</sub>. The implications of these results are discussed and the ion-molecule reactions of PH<sub>3</sub> are compared with those of other hydrides. Interestingly, the condensation reactions of PH<sub>3</sub> are most like those observed for CH<sub>4</sub>.

Numerous mass spectrometric studies of the important hydride phosphine have been reported.<sup>2-17</sup> Few investigations of the gas-phase ion-molecule chemistry of PH<sub>3</sub> have been attempted, however. Giardini-Guidoni and Volpi<sup>12</sup> and later Halmann and Platzner<sup>13</sup> studied the reaction



More recently, Platzner<sup>14</sup> reported the formation of small amounts (0.05–0.5%) of PO<sup>·+</sup>, PO<sub>2</sub><sup>+</sup>, and PO<sub>3</sub><sup>·+</sup> from ion-molecule reactions in PH<sub>3</sub>–H<sub>2</sub>O mixtures. In the present paper we report a systematic study by ion cyclotron resonance (icr) of the gas-phase ion chemistry of PH<sub>3</sub>, alone and in mixtures with other molecular species. A wide variety of ion-molecule reactions, most reported here for the first time, are delineated. While our study emphasizes the chemistry of positive ions, several reactions of negative ions generated from PH<sub>3</sub> have also been investigated. Where possible, kinetic and thermodynamic data have been

determined, including the proton affinity of PH<sub>3</sub> and the electron affinity of the PH<sub>2</sub><sup>·</sup> radical.

## Experimental Section

The instrumentation and experimental techniques associated with ion cyclotron resonance spectroscopy have been previously described in detail.<sup>18-25</sup> An icr cell with overall dimensions of 2.54 × 1.27 × 12.7 cm was employed. Such a "flat" cell is found to give more reproducible spectral intensities and derived rate constants<sup>20</sup> than those recorded with the "square" cell with dimensions 2.54 × 2.54 × 12.7 cm.<sup>23</sup> An MKS Model 90H1-E capacitance manometer calibrated as previously described<sup>24</sup> was used to determine pressures above 10<sup>-5</sup> Torr. Such calibration is believed to be accurate to within ±0.2 × 10<sup>-5</sup> Torr.<sup>24</sup> Below 10<sup>-5</sup> Torr pressures were determined from the ion pump current which was assumed to be linear with pressure and was calibrated against the capacitance manometer in the 10<sup>-5</sup> Torr pressure region. Electron energies were measured with a digital voltmeter and are correct to ±0.5 eV. Filament emission currents were typically in the range 10<sup>-8</sup>–10<sup>-9</sup> A, a value low enough to minimize the possibility of pyrolysis reactions and also avoid both ion trapping in the electron beam, which would affect reaction rate determinations, and spurious effects due to ion-ion interactions in double-resonance experiments.<sup>26</sup> The formation of small amounts (≤3% of the total ion current) of P<sub>4</sub><sup>·+</sup>, P<sub>5</sub><sup>·+</sup>, and P<sub>6</sub><sup>·+</sup> was observed with some PH<sub>3</sub> samples when high filament currents were employed. Presumably these ions are formed by pyrolysis of PH<sub>3</sub> on the hot rhenium filament employed for primary ionization by electron impact. The P<sub>4</sub><sup>·+</sup>, P<sub>5</sub><sup>·+</sup>, and P<sub>6</sub><sup>·+</sup> ions disappeared when lower filament emission currents were used. The possibility that other products observed in the present study resulted from pyrolysis reactions<sup>27</sup> was rejected on the basis that P<sub>2</sub>H<sub>n</sub><sup>+</sup> and P<sub>3</sub>H<sub>n</sub><sup>+</sup> ions were shown by double-resonance experiments to be formed from ions containing one less

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**Table I.** Summary of Product Distributions, Reaction Rates, Thermochemical Changes, and Pulsed-Double-Resonance Experiments for the Principal Ion-Molecule Reactions of Phosphine

Reaction <sup>a-c</sup>	$\Delta H$ , <sup>d</sup> kcal/mol	Product distribution <sup>e</sup>	$k_i$ / <sup>f</sup>	$\Sigma k_i$ / <sup>f</sup>
$P^+ + PH_3 \rightarrow P_2H^+ + H_2$	-72	1.00	8.2	8.2
$PH^+ + PH_3 \rightarrow$ $\begin{cases} P_2^+ + 2H_2 \\ P_2H^+ + H_2 + H \\ P_2H_2^+ + H_2 \\ P_2H_3^+ + H \end{cases}$	+2	0.43	4.0	9.3
	+21	0.04	0.3	
	-41	0.35	3.2	
	-22	0.19	1.8	
$PH_2^+ + PH_3 \rightarrow$ $\begin{cases} P_2H^+ + 2H_2 \\ P_2H_3^+ + H_2 \end{cases}$	0	0.74	6.2	8.4
	-43	0.26	2.2	
$PH_3^+ + PH_3 \rightarrow$ $\begin{cases} PH_4^+ + PH_3 \\ P_2H_4^+ + H_2 \\ P_2H_5^+ + H \end{cases}$	-18	0.97	10.5	10.8
	-26	0.01	0.1	
			0.02	

<sup>a</sup> Except as noted, all reactions listed gave a negative pulsed-double-resonance response, which normally is indicative of an exothermic reaction.<sup>21</sup> <sup>b</sup> Reaction pathways for the formation of ions containing three P atoms are outlined in reactions 12-15, and were identified by pulsed double resonance. <sup>c</sup> A positive pulsed-double-resonance response was observed for  $P^+$ ,  $PH^+$ , and  $PH_2^+$  contributing to the formation of  $PH_3^+$ , and  $PH^+$  contributing to the formation of  $PH_4^+$ . None of these processes is important at thermal ion energies, as shown by the constancy of the ratio of  $PH_4^+/PH_3^+$  when the electron energy is varied. <sup>d</sup> Large errors may be present in these values owing to poorly known heats of formation for many relevant ions. Thermochemical data employed in calculating  $\Delta H$  were taken from J. L. Franklin and J. G. Dillard; H. M. Rosenstock, J. T. Herron, and K. Draxl; and F. H. Field, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS 26, U. S. Government Printing Office, Washington, D. C., 1969. <sup>e</sup> Total product distribution normalized to unity for each reactant ion. <sup>f</sup>  $\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} \times 10^{10}$ .

phosphorus atom. Thus only  $PH_3$  and those ions formed from  $PH_3$  by electron impact or ion-molecule reactions are important to the chemistry reported in this paper. All icr experiments were performed at ambient temperature.

Spectral intensities reported in tables and figures are the measured single-resonance peak heights. However, spectral intensities used to derive rate and product distribution data have been normalized by dividing by the square of the ion mass (see below, eq 21). Relative rates and product distributions for reactions observed in phosphine and phosphine in mixture with other species were determined by two methods. The first method, frequency sweep ion ejection, has been described elsewhere.<sup>19</sup> The second method segregates different reaction pathways by a variation of the electron energy.<sup>28</sup> At a low electron energy ( $\sim 13$  eV) the reaction  $PH_3^+ + PH_3 \rightarrow PH_4^+ + PH_2$  (reaction 1) is the only one observed. With increasing electron energy new primary and secondary ions appear. A simple comparison of the percentage of conversion of reactants to products for specific reaction pathways (always kept below 15%), taking into account differences in concentrations of neutral reactants (for mixtures) and differences of reaction residence times in the icr cell of primary reactants, gives the relative rates of reaction for the various pathways. Absolute rates were assigned by using as a standard the conversion of  $PH_3^+$  to  $PH_4^+$  (reaction 1) for which we have determined a rate constant of  $1.05 \pm 0.2 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ . In cases where more than one primary ion contributes to a given secondary ion the contribution of the primary ion with the lower appearance potential was determined at an electron energy where the second primary ion was absent. The contribution of the second primary ion was then determined at a higher electron energy by subtracting out the contribution of the first primary ion, which was assumed not to change with electron energy. The assumption that reaction rates are invariant with electron energy was verified in one case: the reaction forming  $PH_4^+$  from  $PH_3^+$  (reaction 1). Relative rates determined with the above methodologies are presented in Tables I and IV.

A critical parameter for the accurate determination of relative rates in mixtures is the sample composition. Sample compositions were determined manometrically and also by measuring by icr the total ionization of each species in the mixture at pressures low enough to avoid ion-molecule reactions. Utilizing the known ionization cross section<sup>29</sup> of  $PH_3$  and the species with which it was admixed permitted the determination of the composition of the mixture under investigation. Spectral intensities were corrected to ion abundance by dividing the measured icr single resonance intensity by ion mass.<sup>20</sup> Determinations of sample composition by the two methods differed by as much as 30%. The composition determined by ionization, under conditions similar to those of the

kinetic experiments, was used in calculating rate constants. Surface adsorption phenomena and differences in leak rates into the vacuum chamber for different species make manometric compositions suspect.

Phosphine was generated *in vacuo* by transferring water onto excess magnesium aluminum phosphide,  $Mg_3P_2 \cdot 2AlP$ .<sup>30</sup> Purification was achieved by bulb-to-bulb fractionation at  $-80^\circ$ . Mass spectrometric examination at 70 eV showed the phosphine to contain less than 0.1% impurities and in particular no water or diphosphine. Phosphine- $d_3$  was prepared and purified in a similar manner employing 99.8 atom %  $D_2O$  and  $Ca_3P_2$  (Alfa Inorganics). Mass spectrometric examination at 70 eV revealed 8%  $PD_2H$ , but no other significant impurities. For studies involving negative ions or  $PH_3$ - $PD_3$  mixtures commercial phosphine (Matheson, 99.5%) was used without further purification. Mass spectrometric examination at 30 eV indicated a small peak at  $m/e$  124 ( $P_4^+$ ) as the only impurity. All other chemicals were reagent grade commercial samples utilized as supplied except for degassing with freeze-pump-thaw cycles. Purities as ascertained by mass spectrometric analysis were acceptable.

### III. Results

**A. Positive Ion Chemistry of Phosphine. Identification of Reactions.** Electron bombardment (70 eV) of  $PH_3$  at low pressure ( $10^{-7}$  Torr) yields a single-resonance spectrum with ion intensities of  $PH_3^+$ ,  $PH_2^+$ ,  $PH^+$ , and  $P^+$  in agreement with the known<sup>5,9</sup> mass spectrum of  $PH_3$  (Figure 1a and Table I). As the  $PH_3$  pressure is raised, ion-molecule reactions occur to form  $PH_4^+$  in addition to condensation products containing two ( $P_2^+$ ,  $P_2H^+$ ,  $P_2H_2^+$ ,  $P_2H_3^+$ ,  $P_2H_4^+$ ,  $P_2H_5^+$ ) and three ( $P_3^+$ ,  $P_3H^+$ ,  $P_3H_2^+$ ) phosphorus atoms (Figure 1b and 1c and Table I). At the highest pressures employed ( $\sim 10^{-3}$  Torr) all ions react to ultimately give only  $PH_4^+$ . The variation of ion single-resonance intensities with pressure at 70 eV is illustrated in Figure 2.

Reaction pathways were investigated by three methods: observing the relative variation of single-resonance intensities as a function of the ionizing electron energy (appearance potential method),<sup>28</sup> and the icr techniques of frequency sweep ion ejection<sup>19</sup> and pulsed double resonance.<sup>18</sup> All three methods are capable of establishing reaction pathways. As described in the Experimental Section the appearance potential and

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(30) The authors gratefully acknowledge the gift of a sample of  $Mg_3P_2 \cdot 2AlP$  from Rocky Mountain Research, Inc., Denver, Colo.

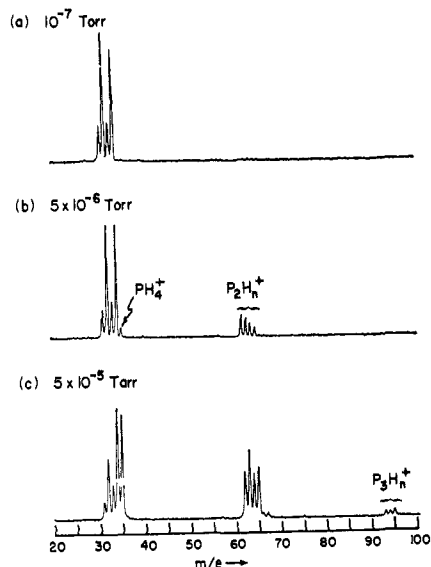
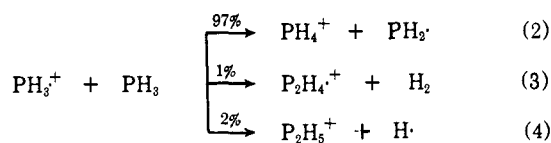


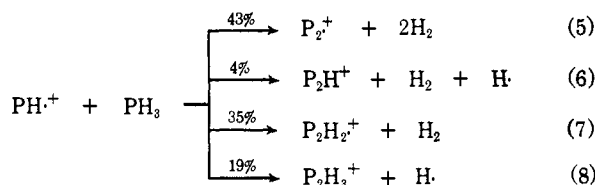
Figure 1. Single-resonance spectra of  $\text{PH}_3$  at 70 eV and various pressures: (a)  $10^{-7}$  Torr, (b)  $5 \times 10^{-6}$  Torr, (c)  $5 \times 10^{-5}$  Torr. Electron energy modulation yields the absorption presentation.

frequency sweep ion ejection methods also allow for the determination of relative reaction rates and product distributions.

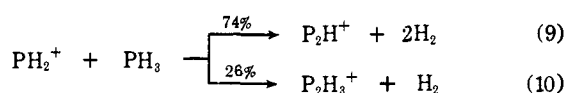
For example, below 13 eV,  $\text{PH}_3^+$  is the only ion formed by electron impact. As the  $\text{PH}_3$  pressure is increased,  $\text{PH}_4^+$ ,  $\text{P}_2\text{H}_4^+$ , and  $\text{P}_2\text{H}_5^+$  appear, the latter two condensation products occurring only to a minor extent, indicating reactions 2–4. At 14.5 eV the fragment ion  $\text{PH}_2^+$  appears. With increasing  $\text{PH}_3$  pressure this ion leads to product species at  $m/e$  values corresponding



to  $\text{P}_2^+$ ,  $\text{P}_2\text{H}^+$  (minor),  $\text{P}_2\text{H}_2^+$ , and  $\text{P}_2\text{H}_3^+$ , indicating reactions 5–8. At 18 eV the fragment  $\text{PH}_2^+$  appears. The ratios of  $\text{P}_2^+$  and  $\text{P}_2\text{H}_2^+$  to  $\text{PH}_2^+$  at 18 eV are



identical with the ratios observed at 14.5 eV. The intensities of  $\text{P}_2\text{H}^+$  and  $\text{P}_2\text{H}_3^+$  relative to  $\text{PH}_2^+$  exhibit an increase, however, indicating the occurrence of reactions 9 and 10.



At higher electron energies the remaining minor fragment ion,  $\text{P}^+$ , appears, causing an increase in the  $\text{P}_2\text{H}^+$  intensity relative to the intensity of the other condensation products and thus identifying reaction 11. The

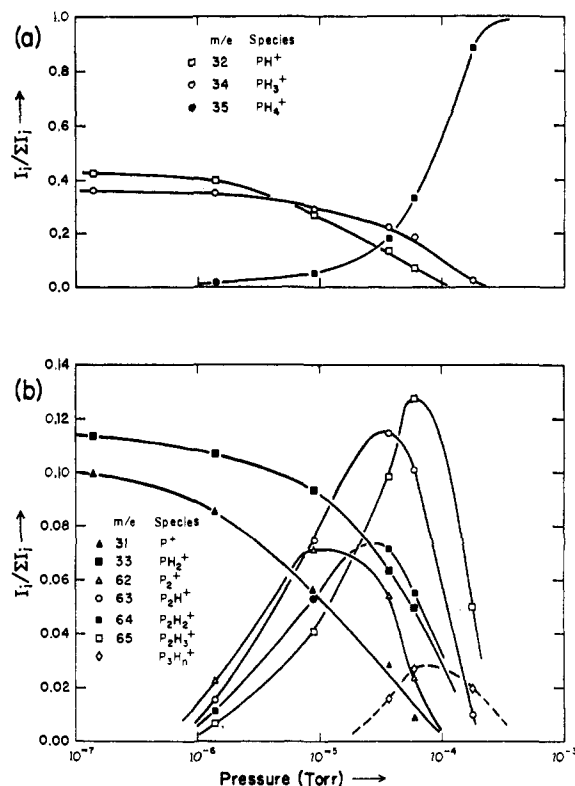
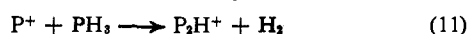
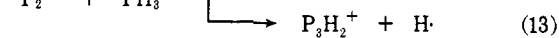
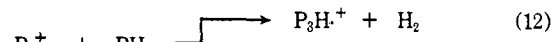


Figure 2. Variation of ion single-resonance intensities with pressure for  $\text{PH}_3$  at 70 eV: (a) major ions, (b) minor ions. The intensities of the minor  $\text{P}_3\text{H}_n^+$  ( $n = 0-2$ ) products are summed.

reaction rates and product distributions for the above reactions determined by analyzing the variation of the spectra with electron energy are summarized in Table I.

The results of pulsed-double-resonance experiments performed on the ions  $\text{PH}_4^+$ ,  $\text{P}_2\text{H}_n^+$  ( $n = 0-3$ ), and  $\text{P}_3\text{H}_n^+$  ( $n = 0-2$ ) confirm and amplify conclusions derived from the variation of electron energy. Results from both methods are presented in Table I. It is to be emphasized that the methods for determining reaction pathways are complementary. The facile identification by double-resonance techniques of reactions 12–15, which lead to the formation of the tertiary ions  $\text{P}_3\text{H}_n^+$  ( $n = 0-2$ ), could be accomplished only with difficulty by the appearance potential method. On the

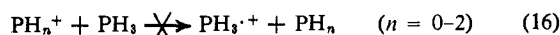


other hand, pulsed double resonance gives no information regarding product distributions, the spectral intensities reflecting instead the energy dependence of the reaction rates.<sup>21, 31</sup>

As is evident in Figure 2 all reaction pathways eventually lead to the production of  $\text{PH}_4^+$ . All secondary and tertiary ions are thus reactive toward  $\text{PH}_3$  in that they undergo either proton transfer to the parent neutral or react in condensation sequences which eventually result in the production of  $\text{PH}_4^+$  as an ionic product.

(31) M. T. Bowers, D. D. Elleman, and J. L. Beauchamp, *J. Phys. Chem.*, **72**, 3599 (1968).

The formation of protonated phosphine,  $\text{PH}_4^+$ , was studied in some detail. As mentioned above, at 13 eV  $\text{PH}_3^{\cdot+}$  is the only ion formed by electron impact reacting with neutral  $\text{PH}_3$  to form mainly (97%)  $\text{PH}_4^+$ . When the electron energy is varied between 13 and 70 eV, at a pressure such that the conversion of primary to secondary ions is low, many other fragment and product ions appear, but the ratio of the intensity of  $\text{PH}_4^+$  to  $\text{PH}_3^{\cdot+}$  remains constant to within  $\pm 3\%$ . This suggests that  $\text{PH}_4^+$  is formed solely *via* reaction 2 and is not generated to any extent as a *secondary* ion by any of the remaining  $\text{PH}_3$  fragment ions. Furthermore, it is unlikely that charge exchange processes such as the generalized reaction 16 are important, as this would lead to a decrease in the ratio of  $\text{PH}_4^+$  to  $\text{PH}_3^{\cdot+}$  with increasing electron energy. Halmann and Platzner,<sup>13</sup> on the basis of similar experiments, reached the same conclusion concerning the production of  $\text{PH}_4^+$ .



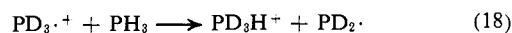
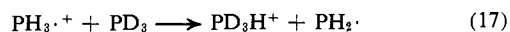
More intimate details of the formation of  $\text{PH}_4^+$  from  $\text{PH}_3^{\cdot+}$  (reaction 1) were obtained by examining an equimolar mixture of  $\text{PH}_3$  and  $\text{PD}_3$ . Conventional pulsed double resonance was employed to establish reactant-product relationships. Frequency sweep ion ejection was used to determine product distributions.<sup>19</sup> The results are presented in Table II, and indicate that pro-

**Table II.** Relative Rates of Isotopic Phosphonium Ion Formation in an Equimolar Mixture of  $\text{PH}_3$  and  $\text{PD}_3$  at 13.5 eV<sup>a,b</sup>

Reaction	Rel rate
$\text{PH}_3^{\cdot+} + \text{PD}_3 \rightarrow \left\{ \begin{array}{l} \text{PH}_3\text{D}^+ + \text{PD}_2^{\cdot} \\ \text{PH}_2\text{D}_2^+ + \text{PHD}^{\cdot} \\ \text{PD}_3^+ + \text{PH}_3 \\ \text{PD}_3\text{H}^+ + \text{PH}_2 \end{array} \right\}$	(1.0)
	0.6 <sup>c</sup>
	1.4
$\text{PD}_3^{\cdot+} + \text{PH}_3 \rightarrow \left\{ \begin{array}{l} \text{PD}_3\text{H}^+ + \text{PH}_2 \\ \text{PH}_2\text{D}_2^+ + \text{PHD}^{\cdot} \\ \text{PH}_3\text{D}^+ + \text{PD}_2^{\cdot} \end{array} \right\}$	1.2
	<sup>d</sup>
	1.4

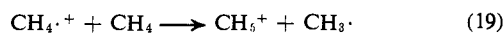
<sup>a</sup> Determined employing frequency sweep ion ejection techniques: J. L. Beauchamp and R. C. Dunbar, *J. Amer. Chem. Soc.*, **92**, 1477 (1970). <sup>b</sup> Corrected for 8%  $\text{PD}_2\text{H}$  impurity in the sample of  $\text{PD}_3$  used. <sup>c</sup> No assessment of the relative importance of the two reaction pathways can be made since both product ions have the same mass. <sup>d</sup> The relative rate for this reaction pathway cannot be determined since reactant and product ion both have the same mass.

ton transfer (reaction 17) is favored over hydrogen abstraction (reaction 18) by a ratio of  $1.4/1.2 = 1.17$ ; deuteron transfer exceeds deuterium abstraction by  $1.4/1.0 = 1.40$ . The observation of the minor product



$\text{PH}_2\text{D}_2^+$  indicates that a less favored reaction pathway is the formation of a reaction complex,  $\text{P}_2\text{H}_3\text{D}_3^+$ , having a lifetime sufficient for H-D scrambling to occur.

Confidence in our experimental techniques was gained by determining the isotopic product distributions for reaction 19 in a mixture of  $\text{CH}_4$  with  $\text{CD}_4$ . This



reaction has been independently studied by tandem mass spectrometry by Abramson and Futrell.<sup>32</sup> The quanti-

(32) F. P. Abramson and J. H. Futrell, *J. Chem. Phys.*, **45**, 1925 (1966).

**Table III.** Relative Rates of Isotopic Protonated Methane Formation in an Equimolar Mixture of  $\text{CH}_4$  and  $\text{CD}_4$  at 15 eV

Reaction	—Rel rate— This work <sup>a</sup> Lit. <sup>b</sup>
$\text{CH}_4^{\cdot+} + \text{CD}_4 \rightarrow \left\{ \begin{array}{l} \text{CH}_3\text{D}^+ + \text{CD}_3^{\cdot} \\ \text{CD}_3\text{H}^+ + \text{CH}_3 \end{array} \right\}$	(1.0) (1.0)
	2.3 2.3
$\text{CD}_4^{\cdot+} + \text{CH}_4 \rightarrow \left\{ \begin{array}{l} \text{CD}_3\text{H}^+ + \text{CH}_3 \\ \text{CH}_3\text{D}_2^+ + \text{CD}_2\text{H}^{\cdot} \\ \text{CH}_4\text{D}^+ + \text{CD}_3^{\cdot} \end{array} \right\}$	0.9 (1.0)
	0.2 0.25
	2.0 1.9

<sup>a</sup> Determined employing frequency sweep ion ejection techniques.

<sup>b</sup> Determined by tandem mass spectrometry at 0.3 eV relative energy: F. P. Abramson and J. H. Futrell, *J. Chem. Phys.*, **45**, 1925 (1966).

tative agreement of our results with those obtained previously is presented in Table III.

**Determination of Reaction Rates.** Procedures for determining reaction rates utilizing ion cyclotron resonance techniques have been discussed in detail by Buttrill.<sup>20</sup> His analysis<sup>20</sup> can be greatly simplified by neglecting the variation of the power absorption of an ion with the time which the ion spends in the cell when integrating over the ions present under conditions where reactions are occurring. For the generation of secondary from primary ions this leads in the limit of low conversion to the expression given by eq 20 for the rate of formation of the *i*th product in the case that several products result from a single reactant ion. In eq 20

$$k_i = \frac{2I_{st}/m_{st}^2}{n(\tau_p + \tau_p') \left[ \sum_s I_{st}/m_{st}^2 + I_p/m_p^2 \right]} \quad (20)$$

the quantities  $I_p$ ,  $I_s$ ,  $m_p$ , and  $m_s$  are the single-resonance intensities and masses of the primary and secondary ions,  $n$  is the number density of the neutral species, and  $\tau_p$  and  $\tau_p'$  are the respective times at which the primary ion enters and leaves the resonance region of the cell. The factors appearing in eq 20 have the following interpretation. Dividing the single-resonance intensity by mass yields the true ion current.<sup>20</sup> Multiplying the product ion intensity by  $m_p/m_s$  corrects for the variation of the extent of reaction with magnetic field strength, which results from the fact that the ion-drift velocity decreases with increasing magnetic field strength.<sup>20, 31</sup> The quantity  $(\tau_p + \tau_p')/2$  is simply the time at which the reactant ion reaches the center of the resonance region of the cell; this corresponds to the time at which the system is "sampled."

Rates calculated by means of eq 20 give values lower than, but within 10% of those derived from computer analysis using Buttrill's equations.<sup>33</sup> Errors of this magnitude are inherent in rate determinations by icr owing to uncertainties in pressure measurement, and more importantly, errors in the accurate estimation of  $\tau_p$  and  $\tau_p'$ . In view of these problems, the use of eq 20 for calculating reaction rates by icr seems adequate.

Care must be exercised if accurate and reproducible rate constants are desired. We find it necessary to clean the icr cell in an ultrasonic bath and to bake the spectrometer vacuum system immediately before use in order to obtain reproducible rate constants which are in agreement with literature values. With the above precautions we obtain<sup>33</sup> a value of  $1.1 \pm 0.1 \times 10^{-9}$

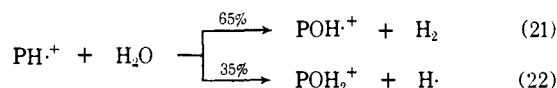
(33) P. G. Miasek and J. L. Beauchamp, unpublished results.

$\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$  for the rate constant associated with reaction 19 in methane, in good agreement with previous determinations.<sup>34</sup> After prolonged use of the spectrometer a somewhat lower rate is obtained, the deviation probably resulting from unpredictable surface potentials. In spite of these difficulties it is always possible to measure *relative* reaction rates reproducibly and accurately. Accordingly, using reaction 19 as a standard, the rate of reaction 1 was found to be  $1.05 \pm 0.2 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$  ( $6.0 \pm 1.2 \times 10^{11} \text{ M}^{-1} \text{ sec}^{-1}$ ). The remainder of the rate constants for the formation of secondary ions in phosphine were then determined relative to the rate of formation of  $\text{PH}_4^+$  by methods outlined in the Experimental Section. The data obtained are summarized in Table I. The rate constant for the generation of  $\text{PH}_4^+$  from  $\text{PH}_3^+$  is in good agreement with the values of  $0.93 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$  reported by Giardini-Guidoni and Volpi<sup>12</sup> and  $0.98 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$  reported by Halmann and Platzner.<sup>13</sup> These authors did not report the formation of the condensation products  $\text{P}_2\text{H}_n^+$  ( $n = 0-5$ ) and  $\text{P}_3\text{H}_m^+$  ( $m = 0-2$ ).

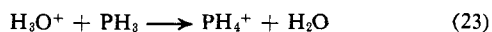
**B. Condensation Reactions in Mixtures of Phosphine with Other Hydrides.** The extensive condensation reactions observed between  $\text{PH}_3$  and its ionic fragments led us to investigate the occurrence of condensation reactions in mixtures of  $\text{PH}_3$  with the important hydrides,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , and  $\text{CH}_4$ .

**Phosphine and Water.** The variation with pressure at 70 eV of the single-resonance intensities for a 1.8:1 mixture of  $\text{H}_2\text{O}$  and  $\text{PH}_3$  is illustrated in Figure 3. Besides reactions occurring in the pure components alone, new condensation products corresponding to ions of empirical formula  $\text{POH}^+$  and  $\text{POH}_2^+$  are observed. In direct analogy to the behavior observed for the condensation products in  $\text{PH}_3$  alone, with increasing pressure the  $\text{POH}^+$  and  $\text{POH}_2^+$  single-resonance intensities pass through a maximum in reacting to form  $\text{PH}_4^+$  which is the only ion remaining at high pressure ( $\sim 10^{-3}$  torr, Figure 3). Platzner<sup>14</sup> has previously observed the  $\text{POH}^+$  and  $\text{POH}_2^+$  ions, *in much lower abundance*, in  $\text{PH}_3$ - $\text{H}_2\text{O}$  mixtures, as well as ions corresponding to  $\text{PO}_2\text{H}_m^+$ ,  $\text{PO}_3\text{H}_m^+$ , and  $\text{PO}_4\text{H}_m^+$  ( $m = 0-3$ ). We did not observe any ion species containing more than one oxygen.

Variation of ion abundances with electron energy as well as pulsed-double-resonance experiments identify  $\text{PH}^+$  as the precursor to both  $\text{POH}^+$  and  $\text{POH}_2^+$  indicating reactions 21 and 22. The rates of the condensation reactions 21 and 22 are reported in Table IV.



At electron energies low enough such that only the parent ions are generated ( $\sim 13 \text{ eV}$ ), there are no condensation products observed. The protonated parents are generated and with increasing pressures reaction 23 is observed, leading to  $\text{PH}_4^+$  as the only remaining ionic



species at high pressure ( $10^{-3}$  Torr). As described in more detail below, this result indicates that the proton affinity of  $\text{PH}_3$ ,  $\text{PA}(\text{PH}_3)$ , is greater than  $\text{PA}(\text{H}_2\text{O})$ .

(34) S. K. Gupta, E. G. Jones, A. G. Harrison, and J. J. Myher, *Can. J. Chem.*, **45**, 3107 (1967).

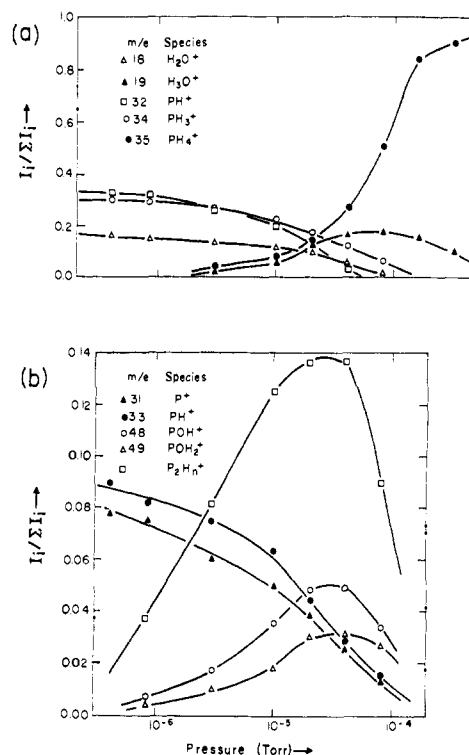


Figure 3. Variation of ion single-resonance intensities with pressure for a 1.8:1 mixture of  $\text{H}_2\text{O}$  and  $\text{PH}_3$  at 70 eV: (a) major ions, (b) minor ions.

**Phosphine and Ammonia.** The variation with pressure at 70 eV of the single-resonance intensities for a 1.8:1 mixture of  $\text{NH}_3$  and  $\text{PH}_3$  is illustrated in Figure 4. The ion chemistry observed is similar to that described above for  $\text{H}_2\text{O}$  and  $\text{PH}_3$ . Thus, cross-condensation

Table IV. Rates Determined for Various Reactions Observed in Binary Mixtures of Phosphine with Water, Ammonia, and Methane<sup>a</sup>

Reaction	Rate constant, $\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} \times 10^{10}$	$\Sigma k_i$
$\text{PH}^+ + \text{H}_2\text{O} \begin{cases} \text{POH}^+ + \text{H}_2 \\ \text{POH}_2^+ + \text{H} \end{cases}$	4.4 2.4	6.8
$\text{PH}^+ + \text{NH}_3 \begin{cases} \text{PNH}_2^+ + \text{H}_2 \\ \text{PNH}_3^+ + \text{H} \end{cases}$	5.2 6.9	12.1
$\text{PH}^+ + \text{CH}_4 \begin{cases} \text{PCH}_3^+ + \text{H}_2 \\ \text{PCH}_4^+ + \text{H} \end{cases}$	7.3 1.5	8.8
$\text{CH}_3^+ + \text{PH}_3 \begin{cases} \text{PCH}_3^+ + 2\text{H}_2 \\ \text{PCH}_4^+ + \text{H}_2 \end{cases}$	7.0 <sup>b</sup> 4.1 <sup>c</sup>	11.1

<sup>a</sup> Determined by the appearance potential method, as described in the Experimental Section, except for the reactions of  $\text{CH}_3^+$ , which were determined by the frequency sweep ion ejection method.<sup>19</sup>  
<sup>b</sup>  $\Delta H = -14 \text{ kcal/mol}$ . <sup>c</sup>  $\Delta H = -54 \text{ kcal/mol}$ .

product ions of empirical formula  $\text{PNH}^+$  (minor),  $\text{PNH}_2^+$ , and  $\text{PNH}_3^+$  are observed; the intensities of these condensation products decrease at higher pressure, leading to the eventual formation of  $\text{NH}_4^+$  as the sole remaining ion.

The primary ion  $\text{PH}^+$  was identified as the reactant leading to the production of  $\text{PNH}_2^+$  and  $\text{PNH}_3^+$ , in-

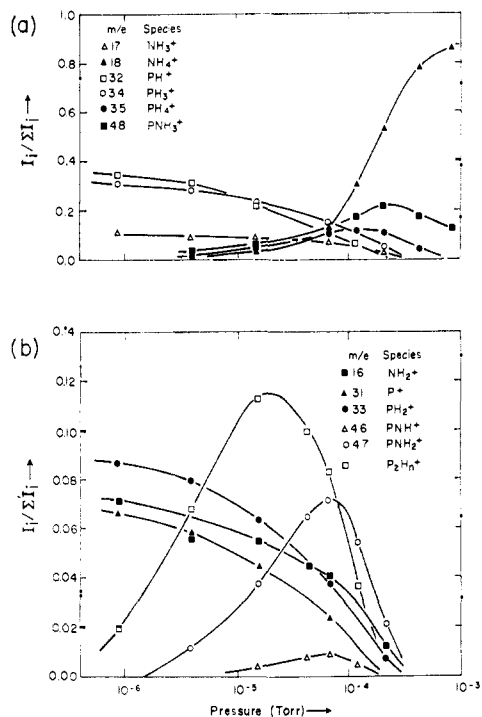
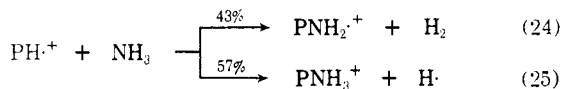
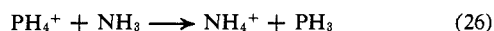


Figure 4. Variation of ion single-resonance intensities with pressure for a 1.8:1 mixture of  $\text{NH}_3$  and  $\text{PH}_3$  at 70 eV: (a) major ions, (b) minor ions.

dicating reactions 24 and 25. The rates of reaction 24 and 25 are given in Table IV.



As previously reported,<sup>35</sup> at low electron energy (12 eV) only the parent ions  $\text{NH}_3^+$  and  $\text{PH}_3^+$  are observed in addition to the reaction products  $\text{NH}_4^+$  and  $\text{PH}_4^+$ . As the pressure is raised, all ions, and in particular  $\text{PH}_4^+$ , react to give  $\text{NH}_4^+$  (reaction 26). As discussed below, this result indicates  $\text{PA}(\text{NH}_3) \geq \text{PA}(\text{PH}_3)$ .



**Phosphine and Methane.** The variation with pressure at 70 eV of the single-resonance intensities for a 3.2:1 mixture of  $\text{CH}_4$  and  $\text{PH}_3$  is illustrated in Figure 5. Pulsed-double-resonance experiments are summarized in Table V. Besides reactions occurring in the pure

Table V. Summary of Pulsed-Double-Resonance Experiments in a 3.2:1  $\text{CH}_4$ - $\text{PH}_3$  Mixture<sup>a</sup>

Ion	Source of ion pulsed double resonance <sup>b</sup>
$\text{PCH}_2^+$	$\text{P}^+$ , $\text{CH}_3^+$ ( $\text{PH}_2^+$ , $\text{PH}^+$ ) <sup>c</sup>
$\text{PCH}_3^+$	$\text{PH}^+$
$\text{PCH}_4^+$	$\text{PH}_2^+$ , $\text{CH}_3^+$ ( $\text{PH}^+$ ) <sup>c</sup>
$\text{P}_2\text{CH}^+$	No signal above noise
$\text{P}_2\text{CH}_3^+$	$\text{PCH}_2^+$
$\text{P}_2\text{CH}_4^+$	$\text{PCH}_3^+$
$\text{P}_3\text{CH}_5^+$	$\text{PCH}_4^+$ , $\text{PCH}_3^+$
$\text{PH}_3^+$	$(\text{CH}_4^+, \text{CH}_3^+)^d$
$\text{PH}_4^+$	$\text{C}_2\text{H}_5^+$ , $\text{CH}_5^+$ , $\text{CH}_4^+$

<sup>a</sup> 70 eV and pressures of 4 and  $10 \times 10^{-5}$  Torr. <sup>b</sup> Unless indicated otherwise, negative pulsed-double-resonance signals were observed. <sup>c</sup> Minor contribution. <sup>d</sup> Positive pulsed-double-resonance response observed.

(35) D. Holtz and J. L. Beauchamp, *J. Amer. Chem. Soc.*, 91, 5913 (1969).

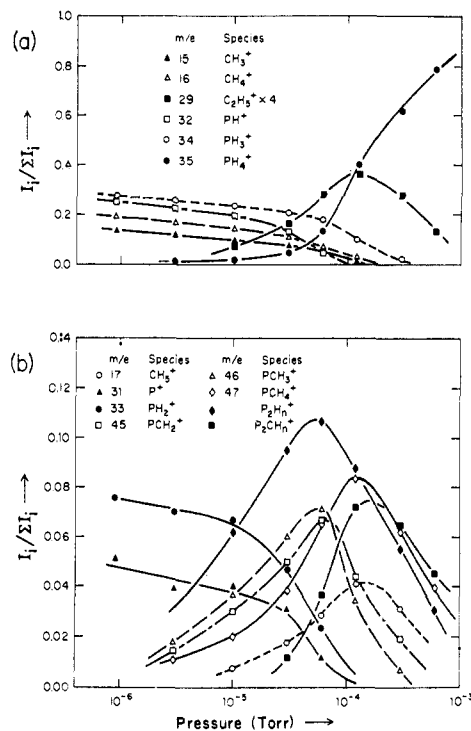
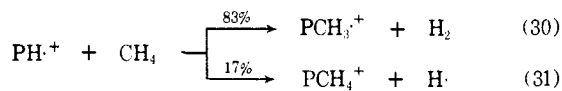
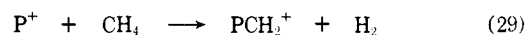
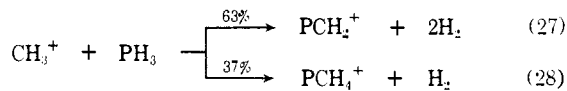


Figure 5. Variation of ion single-resonance intensities with pressure for a 3.2:1 mixture of  $\text{CH}_4$  and  $\text{PH}_3$  at 70 eV: (a) major ions, (b) minor ions.

components alone, new condensation products corresponding to ions of empirical formula  $\text{PCH}_n^+$  ( $n = 2-4$ ) and  $\text{P}_2\text{CH}_n^+$  ( $n = 1, 3-5$ ) are observed. As indicated by reactions 27-32 both  $\text{CH}_3^+$  and fragments derived from  $\text{PH}_3$  react to generate the  $\text{PCH}_n^+$  species.



The rate constants determined for these processes are presented in Table IV. It is interesting to note that reactions 30 and 31 are analogous to reactions 21 and 22 as well as 24 and 25 observed for the  $\text{PH}^+$  ion in  $\text{PH}_3$ - $\text{H}_2\text{O}$  and  $\text{PH}_3$ - $\text{NH}_3$  mixtures, respectively.

No ions of composition  $\text{PC}_2\text{H}_n^+$  are observed. Thus the species  $\text{PCH}_n^+$  react further only with  $\text{PH}_3$ , being unreactive toward  $\text{CH}_4$ . At the highest pressures observed ( $\sim 10^{-3}$  Torr), all ions, and it is especially to be noted  $\text{CH}_5^+$  and  $\text{C}_2\text{H}_5^+$ , react to form  $\text{PH}_4^+$  (Figure 5). As discussed below, this result implies that  $\text{PA}(\text{PH}_3) \geq \text{PA}(\text{C}_2\text{H}_5)$  and  $\text{PA}(\text{CH}_4)$ .

**C. Basicity of Phosphine.** One of the original purposes of the present study was to determine the gas-phase basicity of  $\text{PH}_3$ , which has been reported in a preliminary communication.<sup>33</sup> The enthalpy change for the gas-phase reaction  $\text{MH}^+ \rightarrow \text{M} + \text{H}^+$  is known as the proton affinity (PA) of the species, M, and is a quantitative measure of the basicity of M. Since gas-

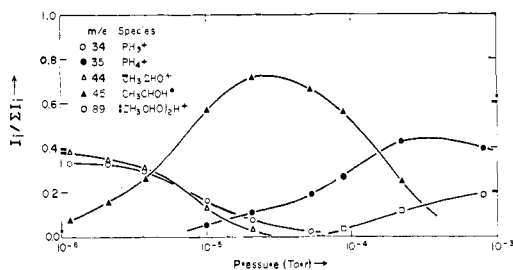


Figure 6. Variation of ion single-resonance intensities with pressure for a 2.3:1 mixture of  $\text{CH}_3\text{CHO}$  and  $\text{PH}_3$  at 12.5 eV. Note that at higher pressures  $\text{CH}_3\text{CHOH}^+$  transfers a proton to  $\text{PH}_3$ , forming  $\text{PH}_4^+$  and indicating that  $\text{PA}(\text{PH}_3) \geq \text{PA}(\text{CH}_3\text{CHO})$ .

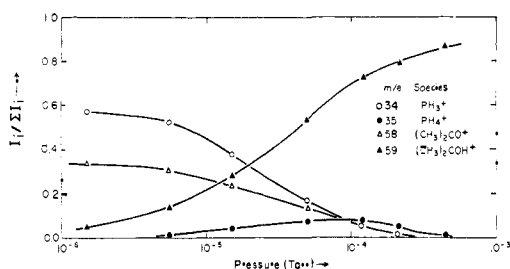
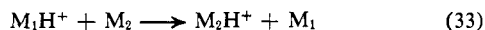


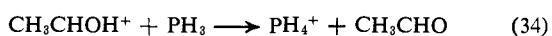
Figure 7. Variation of ion single-resonance intensities with pressure for a 0.8:1 mixture of  $\text{CH}_3\text{COCH}_3$  and  $\text{PH}_3$  at 13 eV. Note that at higher pressures  $\text{PH}_4^+$  transfers a proton to  $\text{CH}_3\text{COCH}_3$ , forming  $(\text{CH}_3)_2\text{COH}^+$  and indicating that  $\text{PA}(\text{CH}_3\text{COCH}_3) \geq \text{PA}(\text{PH}_3)$ .

phase ion-molecule reactions are assumed to proceed with negligible activation energy,<sup>28, 36-38</sup> the observation of a process such as reaction 33 is usually interpreted as indicating that  $\text{PA}(\text{M}_2) \geq \text{PA}(\text{M}_1)$ . Ion



cyclotron resonance is ideally suited for identifying the occurrence and direction of reaction 33. By examining suitable mixtures, the proton affinity of most molecules can be estimated to an accuracy of better than  $\pm 5$  kcal/mol. Thus, from the chemistry of the several mixtures reported above (Figures 3-5), it is evident that  $\text{PA}(\text{PH}_3)$  is greater than  $\text{PA}(\text{H}_2\text{O}) = 165$ ,  $\text{PA}(\text{C}_2\text{H}_4) = 158$ , and  $\text{PA}(\text{CH}_4) = 124$  kcal/mol.<sup>35</sup> On the other hand, as demonstrated by reaction 26,  $\text{PA}(\text{PH}_3)$  is less than  $\text{PA}(\text{NH}_3) = 207$  kcal/mol.<sup>35</sup>

In order to provide somewhat narrower limits for  $\text{PA}(\text{PH}_3)$ , mixtures of phosphine with acetone and phosphine with acetaldehyde were examined. In both mixtures, at low electron energy and low pressures, the parent ions are the major species present. As the pressure is raised, the protonated parent ions appear. Further reaction of these species as evidenced by the variation of the single-resonance intensities with pressure (Figures 6 and 7) indicates the occurrence of the proton-transfer reactions 34 and 35. Confirmation of these



processes is illustrated by the double-resonance spectra, taken in the limit of low oscillator irradiating field (30 mV), presented in Figures 8 and 9. In Figures 8b

(36) A. Cassuto, *Advan. Mass Spectrom.*, **2**, 296 (1963).

(37) V. L. Tal'roze, *Pure Appl. Chem.*, **5**, 455 (1962).

(38) F. W. Lampe, J. L. Franklin, and F. H. Field, *Progr. React. Kinet.*, **1**, 67 (1961).

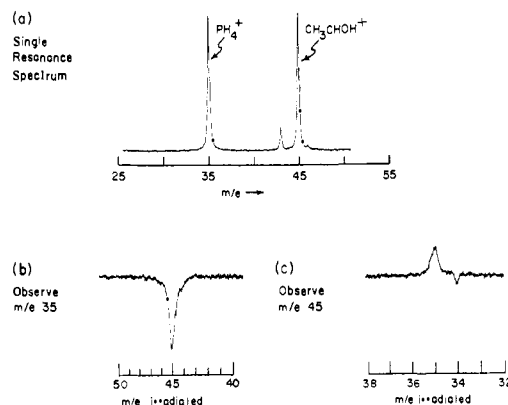


Figure 8. (a) Single-resonance spectrum of a 2.3:1 mixture of  $\text{CH}_3\text{CHO}$  and  $\text{PH}_3$  at 12.5 eV and  $2 \times 10^{-4}$  Torr. (b) Pulsed-double-resonance spectrum of  $\text{PH}_4^+$  ( $m/e$  35) with an irradiating field of 30 mV. (c) Pulsed-double-resonance spectrum of  $\text{CH}_3\text{CHOH}^+$  ( $m/e$  45) with an irradiating field of 30 mV. Note that the results indicate that  $\text{PA}(\text{PH}_3) \geq \text{PA}(\text{CH}_3\text{CHO})$ .

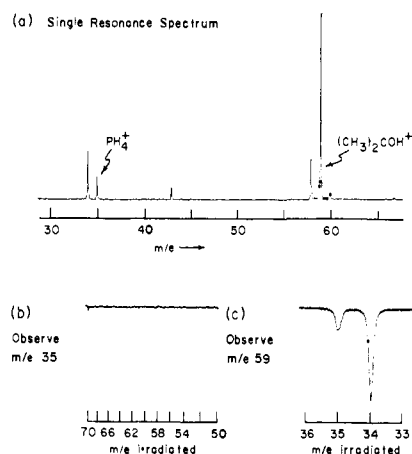


Figure 9. (a) Single-resonance spectrum of a 0.8:1 mixture of  $\text{CH}_3\text{COCH}_3$  and  $\text{PH}_3$  at 13 eV and  $7 \times 10^{-6}$  Torr. (b) Pulsed-double-resonance spectrum of  $\text{PH}_4^+$  ( $m/e$  35) at an irradiating field of 30 mV. The failure to observe a signal strongly indicates that  $\text{PH}_4^+$  does not transfer a proton to  $\text{CH}_3\text{COCH}_3$ . (c) Pulsed-double-resonance spectrum of  $(\text{CH}_3)_2\text{COH}^+$  ( $m/e$  59) at 30 mV irradiating field. Note that the results indicate that  $\text{PA}(\text{CH}_3\text{COCH}_3) \geq \text{PA}(\text{PH}_3)$ .

and 9c, respectively, the negative pulsed-double-resonance response indicates that the rate constants for reactions 34 and 35 decrease with increasing ion energy, a characteristic feature of exothermic proton-transfer reactions.<sup>21</sup> Reaction 35 proceeds only as written, with no detectable reaction in the reverse direction (Figure 9b). For reaction 34, however, proton transfer is observed to occur in both directions (Figure 8b and 8c). The positive double-resonance response observed at low irradiating power for the reverse of reaction 34 indicates, however, that the rate constant increases with increasing ion energy, as would be required of an endothermic process.<sup>21</sup> The double-resonance results are thus consistent with the variation of single-resonance intensities with pressure, indicating that reactions 34 and 35 are exothermic as written. The results bracket the proton affinity of phosphine,  $\text{PA}(\text{PH}_3): 182$  kcal/mol =  $\text{PA}(\text{CH}_3\text{CHO}) \leq \text{PA}(\text{PH}_3) \leq \text{PA}(\text{CH}_3\text{COCH}_3) = 189$  kcal/mol. Thus, we have reported  $\text{PA}(\text{PH}_3) = 185 \pm 4$  kcal/mol.<sup>35, 39</sup> Recent experiments of Haney

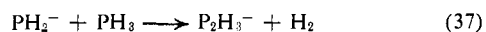
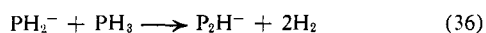
(39) J. R. Eyler, *Inorg. Chem.*, **9**, 981 (1970).

and Franklin have confirmed this value.<sup>40</sup> It is of interest to note that although Figure 6 indicates that  $\text{CH}_3\text{CHOH}^+$  transfers a proton to  $\text{PH}_3$ , the formation of  $\text{PH}_3^+$  levels off at high pressure and actually decreases in favor of the proton bound dimer of acetaldehyde,  $(\text{CH}_3\text{CHO})_2\text{H}^+$ . Such behavior suggests that the proton is more strongly bound by two molecules of acetaldehyde than one molecule of phosphine. The proton bound dimer, however, is formed with excess energy and thus requires collisional stabilization (third-order process) to remain intact. The energy of the proton bond in binary clusters of oxygenated species is fairly strong<sup>41,42</sup> ( $\sim 35$  kcal/mol), as has been demonstrated by the decisive role it plays in certain gas-phase bimolecular reactions.<sup>43</sup>

The spectra of the mixtures of  $\text{PH}_3$  with acetaldehyde and acetone at 70 eV exhibited no products that could be attributed to ionic condensation reactions.

**Negative Ion Chemistry of Phosphine.** Cross sections for production of negative ions *via* dissociative electron capture are typically of the order of  $10^3$  less than cross sections for formation of positive ions *via* electron impact.<sup>44</sup> For this reason, observation of negative ions with the icr spectrometer is more difficult than observation of positive ions. The employment of high pressures ( $>10^{-5}$  Torr) and emission currents ( $\sim 1$   $\mu\text{A}$ ) is required. Despite these limitations we were able to detect negative ions in gaseous phosphine, observe reaction products, and determine the gas-phase acidity<sup>45</sup> of  $\text{PH}_3$  by studying proton-transfer reactions between negative ions in mixtures of phosphine with other species.

In contrast to the multitude of fragment ions and condensation products observed for the positive ion chemistry of phosphine, relatively few negative ion species are observed. At 7.3 eV and  $10^{-5}$  Torr only peaks at  $m/e$  31, 32, 33, 63, and 65 appear in the single resonance spectrum. The peaks at  $m/e$  31, 32, and 33 correspond to the primary ions  $\text{P}^-$ ,  $\text{PH}^-$ , and  $\text{PH}_2^-$ ; the peaks at  $m/e$  63 and 65 are the condensation products  $\text{P}_2\text{H}^-$  and  $\text{P}_2\text{H}_3^-$  formed by reactions 36 and 37. At 9.6 eV



(Table VI) the relative intensities of  $\text{P}^-$  and  $\text{PH}^-$  have greatly increased, but no additional condensation products are observed. Further, the amount of  $\text{P}_2\text{H}^-$  and  $\text{P}_2\text{H}_3^-$  relative to  $\text{PH}_2^-$  remains the same, indicating that only  $\text{PH}_2^-$  reacts to form these condensation products, a result confirmed by double-resonance experiments.

An estimate of the rates of reaction 36 and 37 may be made. Comparison of the relative intensities of  $\text{P}_2\text{H}^-$  and  $\text{PH}_2^-$  with those of  $\text{P}_2\text{H}_3^+$  and  $\text{PH}_3^+$  at comparable pressures and ion residence times in the icr cell indicate that reaction 36 has a rate no greater than that of reaction 4 for which a rate constant of  $\sim 2 \times 10^{-11}$   $\text{cm}^3$

(40) M. A. Haney and J. L. Franklin, *J. Phys. Chem.*, **73**, 4329 (1969).

(41) P. Kebarle, S. K. Searles, A. Zolla, J. Scarborough, and M. Arshadi, *J. Amer. Chem. Soc.*, **89**, 6393 (1967).

(42) P. Kebarle, R. N. Haynes, and J. G. Collins, *ibid.*, **89**, 5793 (1967).

(43) J. L. Beauchamp, *J. Amer. Chem. Soc.*, **91**, 5925 (1969).

(44) R. W. Kiser, ref 29, p 192.

(45) J. I. Brauman and L. K. Blair, *J. Amer. Chem. Soc.*, **90**, 5636 (1968).

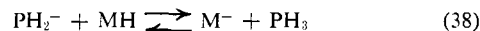
**Table VI.** Negative Ionic Species Observed in  $\text{PH}_3^a$

$m/e$	Species	Rel intensity	
		7.2 eV	9.6 eV
31	$\text{P}^-$	4	8
32	$\text{PH}^-$	2	69
33	$\text{PH}_2^-$	100	100
63	$\text{P}_2\text{H}^-$	$\sim 1$	$\sim 1$
65	$\text{P}_2\text{H}_3^-$	$< 1$	$< 1$

<sup>a</sup>  $10^{-5}$  Torr.

molecule<sup>-1</sup> sec<sup>-1</sup> has been determined (Table I). Thus an upper limit of  $10^{-11}$   $\text{cm}^3$  molecule<sup>-1</sup> sec<sup>-1</sup> may be placed on the rate constants associated with reactions 36 and 37.

**Acidity of Phosphine.** A quantitative estimate of the gas-phase acidity of  $\text{PH}_3$ ,  $\text{PA}(\text{PH}_2^-)$ , was obtained by determining the course of reaction 38 for binary mixtures of  $\text{PH}_3$  with appropriate compounds MH. Com-



pounds MH employed were those for which the proton affinity of the corresponding anion  $\text{M}^-$ ,  $\text{PA}(\text{M}^-)$ , could be calculated from existing thermochemical data (Table VII). Such compounds included  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{ONO}(\text{CH}_3\text{O}^-)$ ,  $\text{C}_2\text{H}_5\text{OH}$ ,  $n\text{-C}_3\text{H}_7\text{OH}$ ,  $\text{H}_2\text{S}$ , and  $\text{HCN}$ . Both ion intensity *vs.* pressure studies and pulsed-double-resonance techniques were employed in determining the course of the reactions reported. Results are summarized in Table VII and allow assignment of  $\text{PA}(\text{PH}_2^-) = 362 \pm 11$  kcal/mol.

**Table VII.** Proton-Transfer Reactions Observed among Negative Ions in Phosphine Mixtures at 7 eV

Reaction observed	$\text{PA}(\text{PH}_2^-)^{a,b}$
$\text{NH}_2^- + \text{PH}_3 \rightarrow \text{PH}_2^- + \text{NH}_3$	$\leq 389$
$\text{OH}^- + \text{PH}_3 \rightarrow \text{PH}_2^- + \text{H}_2\text{O}$	$\leq 390$
$\text{CH}_3\text{O}^- + \text{PH}_3 \rightarrow \text{PH}_2^- + \text{CH}_3\text{OH}$	$\leq 385$
$\text{C}_2\text{H}_5\text{O}^- + \text{PH}_3 \rightarrow \text{PH}_2^- + \text{C}_2\text{H}_5\text{OH}$	$\leq 376^c$
$n\text{-C}_3\text{H}_7\text{O}^- + \text{PH}_3 \rightarrow \text{PH}_2^- + n\text{-C}_3\text{H}_7\text{OH}$	$\leq 373^c$
$\text{PD}_2^- + \text{H}_2\text{S} \rightarrow \text{HS}^- + \text{PD}_2\text{H}$	$\geq 350^{c,d}$
$\text{PH}_2^- + \text{HCN} \rightarrow \text{CN}^- + \text{PH}_3$	$\geq 344$

<sup>a</sup> All values in kcal/mol. <sup>b</sup> Calculated from eq 40 using the following bond strengths and electron affinities:  $D(\text{CH}_3\text{O}-\text{H}) = 102^e$ ,  $D(\text{C}_2\text{H}_5\text{O}-\text{H}) = 102^e$ ,  $D(n\text{-C}_3\text{H}_7\text{O}-\text{H}) = 103^e$ ,  $D(\text{H}-\text{CN}) = 119^g$ ,  $\text{EA}(\text{CH}_3\text{O}^-) = 30$ , <sup>g</sup>  $\text{EA}(\text{C}_2\text{H}_5\text{O}^-) = 39^h$ ,  $\text{EA}(n\text{-C}_3\text{H}_7\text{O}^-) = 43^h$ ,  $\text{EA}(\text{CN}^-) = 88^i$ ,  $\text{IP}(\text{H}^\cdot) = 313$ , and relevant values presented in Table X. <sup>c</sup>  $\text{CH}_3\text{ONO}$  ( $\sim 25\%$ ) added to these binary mixtures to increase negative ion formation. <sup>d</sup>  $\text{PD}_3$  employed because  $\text{PH}_2^-$  and  $\text{HS}^-$  have the same  $m/e$  ratio. <sup>e</sup> J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966). <sup>f</sup> V. H. Dibeler and S. K. Liston, *J. Chem. Phys.*, **48**, 4765 (1968). <sup>g</sup> P. Kriemler and S. E. Buttrill, Jr., *J. Amer. Chem. Soc.*, **92**, 1123 (1970). <sup>h</sup> J. M. Williams and W. H. Hamill, *J. Chem. Phys.*, **49**, 4467 (1968). <sup>i</sup> R. S. Berry, *Chem. Rev.*, **69**, 533 (1969).

The generation of negative ions in high yield was the major difficulty in the above study. For the binary mixtures of  $\text{PH}_3$  with  $\text{C}_2\text{H}_5\text{OH}$ ,  $n\text{-C}_3\text{H}_7\text{OH}$ , and  $\text{H}_2\text{S}$  negative ion intensities were enhanced by addition of  $\sim 25$  mol % of methyl nitrite,  $\text{CH}_3\text{ONO}$ , which readily forms abundant quantities of  $\text{CH}_3\text{O}^-$  upon electron impact.<sup>46</sup> The addition of  $\text{CH}_3\text{ONO}$  to the above mix-

(46) K. Jaeger and A. Henglein, *Z. Naturforsch. A*, **22**, 700 (1967), report a large cross section for the formation of  $\text{C}_2\text{H}_5\text{O}^-$  from  $\text{C}_2\text{H}_5\text{ONO}$ . We find a similar large cross-section for the formation of  $\text{CH}_3\text{O}^-$  from  $\text{CH}_3\text{ONO}$ . We thank Dr. M. A. Haney for suggesting the described procedure.



**Table VIII.** Summary of Reaction Rates and Thermochemical Changes for the Principal Ion-Molecule Reactions of Ammonia<sup>a</sup>

Reaction	$\Delta H_f^b$ kcal/mol	Rate constant, cm <sup>3</sup> molecule <sup>-1</sup> sec <sup>-1</sup> × 10 <sup>10</sup>			$\Sigma k_i$
		Harrison <sup>c</sup> $k_i$	Melton <sup>d</sup> $k_i$	Volpi <sup>e</sup> $k_i$	
$N^+ + NH_3 \rightarrow \begin{cases} NH_3^+ + N \cdot \\ N_2H^+ + H_2 \end{cases}$	$\begin{matrix} -101 \\ -200 \end{matrix}$		0.6	0.26	14
$NH^+ + NH_3 \rightarrow \begin{cases} NH_3^+ + NH \\ N_2H^+ + H_2 + H_2 \\ N_2H_2^+ + H_2 \\ N_2H_3^+ + H \cdot \end{cases}$	$\begin{matrix} -69 \\ -80 \\ -95 \\ -102 \end{matrix}$		0.03	$\begin{matrix} 0.21 \\ 0.18 \\ 0.08 \end{matrix}$	16
$NH_2^+ + NH_3 \rightarrow \begin{cases} NH_3^+ + NH_2 \cdot \\ NH_4^+ + NH \\ N_2H_3^+ + H_2 \\ N_2H_4^+ + H \cdot \end{cases}$	$\begin{matrix} -29 \\ -66 \\ -78 \\ -93 \end{matrix}$	6.5 <sup>f</sup>	19.0	17.0	18
$NH_3^+ + NH_3 \rightarrow \begin{cases} NH_4^+ + NH_3 \cdot \\ N_2H_5^+ + H \cdot \end{cases}$	$\begin{matrix} -23 \\ \end{matrix}$	10.0 <sup>f</sup>	15	$\begin{matrix} 13 \\ \sim 0.003 \end{matrix}$	13

<sup>a</sup> Except where noted, rates were determined for ions with kinetic energy of up to several electron volts. Some reaction rates may be a function of ion energy; therefore caution should be exercised in comparing the above rates with rates determined by icr at thermal ion energies. <sup>b</sup> See footnote *d*, Table I. <sup>c</sup> S. K. Gupta, E. G. Jones, A. G. Harrison, and J. J. Myher, *Can. J. Chem.*, **45**, 3107 (1967), correcting rates reported in A. G. Harrison and J. C. J. Thynne, *Trans. Faraday Soc.*, **62**, 2804 (1966). <sup>d</sup> C. E. Melton, *J. Chem. Phys.*, **45**, 4414 (1966). <sup>e</sup> G. A. W. Derwish, A. Galli, A. Giardini-Guidoni, and G. G. Volpi, *ibid.*, **39**, 1599 (1963). Included is the total reaction rate of each reactant ion derived from the rate of its disappearance. The ions  $N^+$  and  $NH^+$  are likely to be reacting to form one of the major primary ions, probably  $NH_3^+$ . <sup>f</sup> Determined at thermal ion energies.

tures greatly facilitated the study of the course of reaction 38, since proton-transfer reactions between  $CH_3O^-$  and the more acidic species present produced higher intensities of  $PH_2^-$ ,  $C_2H_3O^-$ ,  $n-C_3H_7O^-$ , and  $HS^-$  than could be obtained by electron impact on the binary mixtures alone.

## Discussion

The ion chemistry of phosphine is exceedingly rich. For example, at 70 eV and pressures above  $10^{-6}$  Torr, condensation reactions in phosphine generate ions containing two and three atoms of phosphorus. Such reaction products make up  $\sim 35\%$  of the total single resonance intensity at  $5 \times 10^{-5}$  Torr. Reaction pathways are summarized in Table I. To generalize, the most common reaction occurring in ionized  $PH_3$  is the condensation of an ion with neutral  $PH_3$ , with the subsequent expulsion of one or two molecules of  $H_2$ . Hydrogen atom loss occurs only when the reactant ion is a radical species such as  $PH_2^+$ , as in the case of reactions 6 and 8. Although considerable uncertainties exist in many of the heats of formation of relevant ions, the enthalpy change, where data are available, is given for each of the reactions listed in Table I. All but two of the reactions observed are calculated to be exothermic. Only reaction 6, which represents a minor contribution to the total reactivity of  $PH_2^+$ , is significantly endothermic, indicating that internal excitation in the reactant ion is probably necessary for the process to be observed.

The ion-molecule reactions observed in phosphine are in marked contrast to those found in ammonia, which are surveyed in Table VIII. While product ions containing two atoms of nitrogen, analogous to the secondary ions observed in the case of  $PH_3$ , are formed, such ions in no case represent more than 0.1% of the total ionization. It is important to note, however, that fragment ions in  $PH_3$  and  $NH_3$  have comparable reactivities (Tables I and VIII). Fragment ions in ammonia react with the neutral parent to generate  $NH_3^+$  and  $NH_4^+$  by charge-exchange and proton-transfer processes in preference to participating in ionic condensation reactions (Table VIII). Such behavior is also

characteristic of water and its fragments.<sup>47</sup> As noted above, fragment ions in phosphine do not participate in the generation of  $PH_3^+$  and  $PH_4^+$ . In view of the dissimilarity between the ion-molecule chemistry of  $PH_3$  and  $NH_3$ , it is of interest to note that the condensation of phosphine with its fragment ions follows qualitatively the reactivity pattern of methane with its fragment ions (Table IX). The ion chemistry of arsine is also qualitatively similar to that of phosphine.<sup>48</sup>

**Table IX.** Comparison of Fragment Ion Condensation Reactions in Phosphine and Methane

Reactant ion	Product distribution, <sup>a</sup> %			
	$P_2^+$	$P_2H^+$	$P_2H_2^+$	$P_2H_3^+$
$PH_2^+$	0	74	0	26
$PH_2^+$	43	4	35	19
$P^+$	0	100	0	0
	$C_2H_2^+$	$C_2H_3^+$	$C_2H_4^+$	$C_2H_5^+$
$CH_3^+$	0	4.1	0	96
$CH_2^+$	21	25	37	27
$CH^+$	13	82	5	0

<sup>a</sup> Values for phosphine are from Table I. Values for methane are from F. P. Abramson and J. H. Futrell, *J. Chem. Phys.*, **45**, 1925 (1966).

The rates of several reaction processes in  $PH_3$  and in mixtures of  $PH_3$  with other hydrides have been measured and are summarized in Tables I and IV. Rate measurements by icr at pressures of  $\sim 10^{-5}$  Torr have an uncertainty of  $\pm 20\%$  with our current instrumentation. We feel, however, that the present determinations are at least of comparable quality to determinations of reaction rates by other mass spectrometric methods. The major advantage of kinetic measurements by icr is that rate constants are determined at near thermal ion energies and involve no extrapolations to correct for excess kinetic energy and also do not require the assumption of a theoretical model to convert experimental phenomenological cross sections into rate constants.<sup>49</sup>

(47) A. G. Harrison and J. C. J. Thynne, *Trans. Faraday Soc.*, **62**, 2804 (1966).

(48) D. Holtz, R. H. Wyatt, and J. L. Beauchamp, unpublished results.

It is gratifying to note, however, that our determination of the rate constant for reaction 1,  $1.05 \pm 0.2 \times 10^{-9}$  cm<sup>3</sup> molecule<sup>-1</sup> sec<sup>-1</sup>, compares favorably with previous literature values.<sup>12,13</sup>

**Basicity of Phosphine.** The proton affinity of phosphine, PA(PH<sub>3</sub>), has been determined above to be  $185 \pm 4$  kcal/mol. The implications of this interesting result have been presented in a recent publication<sup>35</sup> and will not be further discussed here. We wish to stress the validity of our results, however.

As mentioned above the enthalpy of the gas-phase reaction  $MH^+ \rightarrow M + H^+$  is known as the proton affinity (PA) of the species, M, and is a quantitative measure of the basicity of M. Since gas-phase ion-molecule reactions are assumed to proceed with negligible activation energy,<sup>28,36-38</sup> the observation of a process such as reaction 33 is usually interpreted as indicating that  $PA(M_2) \geq PA(M_1)$ . One of the major criticisms<sup>50</sup> of the determination of thermodynamic quantities on the basis of the occurrence (or nonoccurrence) of ion-molecule reactions is that the possibility exists that a reaction occurs not because it is exothermic but rather because the reactant ion is in an excited state or possesses excess kinetic energy. For example, our estimate that  $PA(PH_3) \geq 182$  kcal/mol is based on the fact that  $PA(CH_3CHO) = 182$  kcal/mol and that reaction 35 is observed to proceed to the right. However, if  $CH_3CHOH^+$  possesses excess internal or translational energy, then the lower limit on  $PA(PH_3)$  will be less than 182 kcal/mol by the amount of excess energy involved and available for reaction.

We have minimized the possibility of observing the reactions of excited ions by following the course of relevant proton-transfer reactions over a wide range of pressure (Figures 6 and 7). As the pressure is increased, both reactant and product ions suffer many collisions before observation; at  $10^{-3}$  Torr an ion suffers on the average  $\sim 100$  collisions with other molecules in the icr cell. Under such conditions, particularly when thermoneutral proton transfers can occur, any excess energy should be relaxed and processes that are observed should be characteristic of ground state ions with thermal kinetic energy. To remove the possibility of observing excited ions it is important that the assignment of proton affinities be based, if possible, on pressure plots such as Figures 6 and 7. In the present study pulsed-double-resonance experiments performed with a minimum oscillator irradiating field have confirmed the relative proton affinities as determined from an examination of the reaction kinetics.

**Acidity of Phosphine.** The gas-phase acidity of a species MH is in principle determined in the same manner as the gas-phase basicity.<sup>45</sup> The enthalpy of the reaction  $MH \rightarrow M^- + H^+$  is the proton affinity of the anion, M<sup>-</sup>, and is a measure of the acidity of MH. The determination of gas-phase acidities is more difficult than the corresponding basicities because of the problems associated with forming negative ions in the gas phase and also because the meager number of species for which reliable electron affinities have been determined<sup>51</sup> limits the availability of comparison

(49) J. H. Futrell and T. O. Tiernan, "Fundamental Processes in Radiation Chemistry," P. Ausloos, Ed., Wiley, New York, N. Y., 1968, Chapter 4.

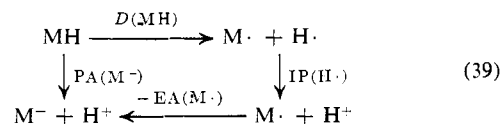
(50) M. DePas, J. J. Leventhal, and L. Friedman, *J. Chem. Phys.*, **49**, 5543 (1968).

standards, MH, necessary for the determination of relative proton affinities from the observation of reaction 38. Nevertheless, the examination of the course of reaction 38 for binary mixtures of phosphine with appropriate standards has allowed a determination of  $PA(PH_2^-) = 362 \pm 11$  kcal/mol and  $EA(PH_2\cdot) = 35 \pm 11$  kcal/mol ( $1.4 \pm 0.5$  eV) for the electron affinity of the radical species  $PH_2\cdot$ . Several recent estimates of  $EA(PH_2\cdot)$  are available. Goode and Page,<sup>52</sup> employing a magnetron, have determined  $EA(PH_2\cdot) = 37$  kcal/mol. Halmann and Platzner,<sup>17</sup> from mass spectrometric appearance potentials, have reported  $EA(PH_2\cdot) \geq 37$  kcal/mol. Smyth and Brauman,<sup>53</sup> from observation of photodetachment processes in an icr spectrometer,<sup>54</sup> have obtained  $EA(PH_2\cdot) = 28$  kcal/mol.

The absolute value of our determination of  $PA(PH_2^-)$  should be accepted with caution owing to uncertainties in the values of the electron affinities used in calculating the proton affinities of the standards employed (Table VII). Thus Brauman and Blair<sup>55</sup> have shown, employing icr methods, that  $PA(NH_2^-) > PA(OH^-)$ , an ordering opposite from that obtained employing available thermochemical data (Table VII). However, our determination of the relative acidity order (in order of decreasing acidity)  $HCN > H_2S > PH_3 > n-C_3H_7OH, CH_3CH_2OH, CH_3OH, H_2O, NH_3$  should be reliable. Previous work by Brauman and Blair<sup>55,56</sup> allows a "greater than" symbol,  $>$ , to be placed wherever a comma appears in the above list.

The relative acidities determined in the gas phase,  $PH_3 > NH_3$ , agrees with studies performed in solution. Birchall and Jolly<sup>57</sup> have found  $AsH_3 > PH_3 > NH_3$  in liquid ammonia. Weston and Bigeleisen<sup>58</sup> have estimated the  $pK_a$  of  $PH_3$  as 29 in aqueous solution based on isotope exchange kinetics. Unfortunately, quantitative data on the solution acidity of other group V hydrides are lacking.

An examination of the energetics of ionization is worthwhile. The gas-phase acidity of a molecule can be divided into three thermodynamic components: bond dissociation energy (to a radical and a hydrogen atom), ionization potential of the hydrogen atom (to a proton), and electron affinity of the radical (to an anion). The thermodynamic cycle is illustrated schematically in eq 39. Thus the gas-phase acidity of MH,



$PA(M^-)$ , is given by eq 40. The difference in acidity of

$$PA(M^-) = D(MH) + IP(H\cdot) - EA(M\cdot) \quad (40)$$

two species  $M_2H$  and  $M_1H$  is simply the difference in their respective bond strengths and electron affinities

(51) R. S. Berry, *Chem. Rev.*, **69**, 533 (1969).

(52) F. M. Page and G. C. Goode, "Negative Ions and the Magnetron," Wiley-Interscience, London, 1969, p 138.

(53) J. I. Brauman and K. C. Smyth, private communication.

(54) J. I. Brauman and K. C. Smyth, *J. Amer. Chem. Soc.*, **91**, 7778 (1969).

(55) J. I. Brauman and L. K. Blair, *ibid.*, **91**, 2126 (1969).

(56) J. I. Brauman and L. K. Blair, *ibid.*, **90**, 6561 (1968).

(57) T. Birchall and W. L. Jolly, *Inorg. Chem.*, **5**, 2177 (1966).

(58) R. E. Weston and J. Bigeleisen, *J. Amer. Chem. Soc.*, **76**, 3074 (1954).

$$\Delta\text{acidity}(\text{M}_2\text{H}, \text{M}_1\text{H}) = \text{PA}(\text{M}_2^-) - \text{PA}(\text{M}_1^-) = [D(\text{M}_2\text{H}) - D(\text{M}_1\text{H})] - [\text{EA}(\text{M}_2\cdot) - \text{EA}(\text{M}_1\cdot)] \quad (41)$$

The bond strengths, electron affinities, and gas-phase acidities of several group V, VI, and VII hydrides, where available, are presented in Table X. Inspection of Table X reveals that the greater acidity of  $\text{PH}_3$  relative

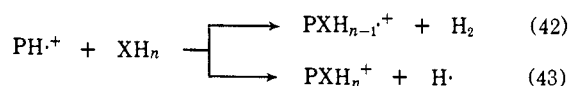
**Table X.** Some Thermochemical Quantities Related to the Acidity of the Group V, VI, and VII Hydrides<sup>a,b</sup>

Species	Bond strength	EA (radical)	PA (anion) <sup>c</sup>
$\text{NH}_3$	109 <sup>d</sup>	33	389
$\text{PH}_3$	84 <sup>e</sup>	35 <sup>f</sup>	362 <sup>f</sup>
$\text{H}_2\text{O}$	119	42	390
$\text{H}_2\text{S}$	90	53	350
$\text{HF}$	136	79	370
$\text{HCl}$	103	83	333
$\text{HBr}$	88	78	323
$\text{HI}$	71	71	313

<sup>a</sup> All values in kcal/mol. <sup>b</sup> Except where noted, bond strengths are taken from S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965); electron affinities are taken from R. S. Berry, *Chem. Rev.*, **69**, 533 (1969). <sup>c</sup> Calculated from eq 40, employing  $\text{IP}(\text{H}\cdot) = 313$ . <sup>d</sup> S. W. Benson and H. E. O'Neil, "Kinetic Data on Gas Phase Unimolecular Reactions," NSRDS-NBS 21, U. S. Government Printing Office, Washington, D. C., 1970, p 35. <sup>e</sup> T. McAllister and F. P. Lossing, *J. Phys. Chem.*, **73**, 2996 (1969). <sup>f</sup> This work.

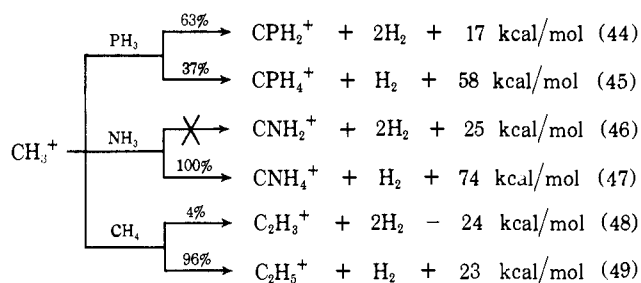
to its congener  $\text{NH}_3$  results primarily from bond strength differences. This phenomenon appears to be general; *within a given group differences in bond strengths seem to be the major factor in determining acidity in the gas phase.*

**Reactivity in Mixtures.** Condensation reactions account for only 3% of the reactivity of the phosphine parent ion  $\text{PH}_3\cdot^+$  in pure phosphine. Similarly,  $\text{PH}_3\cdot^+$  is not observed to condense with other neutrals in any of the phosphine mixtures examined. The principle condensation process observed in mixtures of  $\text{PH}_3$  with  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , and  $\text{CH}_4$  involves  $\text{PH}\cdot^+$  as reactant and is generalized in reactions 42 and 43. The rates for these



reactions are summarized in Table IV. Unfortunately, with the exception of several of the ion species  $\text{PCH}_n^+$ , data are not available to evaluate the thermochemical changes attending these condensation reactions.

The  $\text{PH}_3$ - $\text{CH}_4$  mixture is the only one in which an ionic fragment of another hydride molecule is observed to condense with neutral phosphine. The condensation of methyl cation with  $\text{PH}_3$ ,  $\text{NH}_3$ , and  $\text{CH}_4$  is compared in reactions 44-49. It is interesting to note that in the case of methane and ammonia, reaction 46 does not occur,<sup>59</sup> even though it is calculated to be 25 kcal/mol exothermic, and the analogous process, reaction 44, is observed to occur in methane and phosphine.



We are currently studying the ion chemistry of other volatile hydrides of the first-, second-, and third-row elements in order to elucidate further the factors which govern the reactivity of these important and interesting species.

**Acknowledgment.** This work was supported in part by the United States Atomic Energy Commission under Grant No. AT(04-3) 767-8 awarded to J. L. Beauchamp (California Institute of Technology), by the National Science Foundation under Grant No. NSF-GP-4924-X, and the National Aeronautics and Space Administration under Grant No. NGL-02-020-S1 awarded to John D. Baldeschwieler (Stanford University), and by the Center for Materials Research (Stanford University).

(59) W. T. Huntress, Jr., and D. D. Elleman, *J. Amer. Chem. Soc.*, **92**, 3565 (1970).