

Basicities and Ion-Molecule Reactions of the Methylphosphines in the Gas Phase by Ion Cyclotron Resonance Spectroscopy

Ralph H. Staley and J. L. Beauchamp*¹

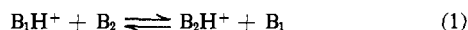
Contribution No. 4823 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91109.

Received February 8, 1974

Abstract: The gas phase ion chemistry of the methylphosphines, $(\text{CH}_3)_n\text{PH}_{3-n}$ ($n = 1-3$), has been investigated using ion cyclotron resonance spectroscopy. Reaction pathways, product distributions, and rate constants have been determined using trapped ion techniques complemented by the more usual method of examining the variation of ion abundance with pressure. Reaction of the parent ion to give protonated parent was observed for methyl- and dimethylphosphine only. Condensation reaction of the parent ion and neutral with loss of methyl radical occurs in all three phosphines. Condensation reactions of prominent fragment ions with loss of various small molecules or radicals were also studied. Values of 187.9, 206.9, 218.9, and 228.0 kcal/mol have been determined for the proton affinities of phosphine and methyl-, dimethyl-, and trimethylphosphine from investigations of proton transfer equilibria. Adiabatic ionization potentials measured by photoelectron spectroscopy are combined with these results to yield values of 104.0, 103.6, 100.7, and 99.2 kcal/mol for the respective BH^+ homolytic bond dissociation energies for the conjugate acids of the methylphosphines. Factors affecting proton affinities and homolytic bond dissociation energies are discussed in a comparison of the results for the phosphines to those for the congeneric amines. The proton affinity results are also combined with enthalpies of protonation in HSO_3F to obtain a measure of solvation effects.

It is only recently that studies of the thermochemistry of protonation reactions in the gas phase have led to an understanding and quantification of the relationship between intrinsic base strengths and other molecular parameters such as ionization potentials, electron affinities, and bond dissociation energies.²⁻¹² While the full impact which these results will have on interpreting properties and reactivity in condensed phases has not yet been realized, it is clear that a detailed understanding of the role which solvation plays in modifying base strengths can be derived from a comparison of the energetics of protonation in the gas phase and in solution.

Exemplifying these studies are recently determined gas phase basicities for a large number of alkyl and aromatic nitrogen bases.³⁻¹² The results allow the evaluation of intrinsic (gas phase) substituent effects and, in combination with solution basicities, the quantitative thermodynamic analysis of the effects of solvation.⁴ Equilibrium constants for proton transfer in the gas phase, reaction 1, have been determined by ion cyclotron



(1) Camille and Henry Dreyfus Teacher-Scholar, 1971-1976.

(2) J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971).

(3) W. G. Henderson, M. Taagepera, D. Holtz, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *J. Amer. Chem. Soc.*, **94**, 4728 (1972).

(4) E. M. Arnett, F. M. Jones, III, M. Taagepera, W. G. Henderson, J. L. Beauchamp, D. Holtz, and R. W. Taft, *J. Amer. Chem. Soc.*, **94**, 4724 (1972).

(5) M. Taagepera, W. G. Henderson, R. T. C. Brownlee, J. L. Beauchamp, D. Holtz, and R. W. Taft, *J. Amer. Chem. Soc.*, **94**, 1369 (1972).

(6) R. W. Taft, M. Taagepera, K. D. Summerhays, and J. Mitsky, *J. Amer. Chem. Soc.*, **95**, 3811 (1973).

(7) M. T. Bowers, D. H. Aue, H. M. Webb, and R. T. McIver, Jr., *J. Amer. Chem. Soc.*, **93**, 4314 (1971).

(8) D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Amer. Chem. Soc.*, **94**, 4726 (1972).

(9) D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Amer. Chem. Soc.*, **95**, 2699 (1973).

(10) J. I. Brauman, J. M. Riveros, and L. K. Blair, *J. Amer. Chem. Soc.*, **93**, 3914 (1971).

(11) J. P. Briggs, R. Yamdagni, and P. Kebarle, *J. Amer. Chem. Soc.*, **94**, 5128 (1972).

resonance (icr) techniques^{3,7,8} and high-pressure mass spectrometry^{11,12} yielding accurate (± 0.2 kcal/mol) relative free energies of protonation of nitrogen bases. Temperature dependence is observed to be slight,^{11,12} confirming the expectation that ΔS° is small for reaction 1 and can likely be attributed to changes in symmetry numbers.¹³

The proton affinity of an n-donor base B, $\text{PA}(\text{B})$, defined as the standard enthalpy change for reaction 2, is a



quantitative measure of gas phase basicity. Beginning with ammonia in the methylamine series, for example, successive increases in proton affinity of 9.3, 6.1, and 4.2 kcal/mol are observed for substitution of the first, second, and third methyl groups. In solution, this systematic behavior is largely canceled by an opposite systematic effect of methyl substitution, namely loss of specific strong hydrogen bonds between solvent molecules and acidic hydrogen (protonic binding sites) in BH^+ .⁴ Combination of these effects leads to the well-known "anomalous order" of amine basicities in solution.⁴ Detailed thermodynamic analysis of this behavior has been carried out for substituted pyridines,⁵ anilines,⁶ and other alkylamine series⁴ in addition to the methylamines.

The homolytic bond dissociation energy $D(\text{B}^+-\text{H})$, the enthalpy change for reaction 3, is related to proton



$$\text{PA}(\text{B}) - D(\text{B}^+-\text{H}) = \text{IP}(\text{H}\cdot) - \text{IP}(\text{B}) \quad (4)$$

affinity by eq 4. Homolytic bond dissociation energies are useful in correlating and predicting gas phase basicities. It is generally observed for a homologous series that $D(\text{B}^+-\text{H})$ remains approximately constant, leading to a linear relation between $\text{PA}(\text{B})$ and $\text{IP}(\text{B})$. For example, all primary aliphatic amines, RNH_2 , are found

(12) R. Yamdagni and P. Kebarle, *J. Amer. Chem. Soc.*, **95**, 3504 (1973).

(13) S. W. Benson, *J. Amer. Chem. Soc.*, **80**, 5151 (1958).

to have $D(\text{B}^+-\text{H}) = 109 \pm 1$ kcal/mol.³ Homolytic BH^+ bond dissociation energies do not remain constant when factors affecting the stability of B^+ relative to BH^+ are altered. Methyl substitution directly on nitrogen, for example, leads to hyperconjugative delocalization of charge in B^+ but not BH^+ . Thus $D(\text{B}^+-\text{H})$ for primary amines is 19 kcal/mol lower than for ammonia. Further methyl substitution in the amine series leads to smaller effects: 11 kcal/mol for dimethylamine compared to methylamine and 5 kcal/mol for trimethylamine compared to dimethylamine.³ Stabilization of the B^+ radical cation may also result from resonance delocalization of charge among interacting lone pair sites. For example, the radical cation of the symmetric diamine 1,4-diazabicyclo[2.2.2]octane has recently been shown to be stabilized by a substantial 14 kcal/mol.¹⁴ As a final example, destabilization of B^+ relative to BH^+ has been noted for ring systems in which the radical cation is constrained from relaxing to its preferred planar configuration.¹⁴

In view of the fact that the pK_a scale in aqueous solution allows for determination and comparison of amine base strengths, it is logical that the amines were selected as a class of compounds for initial studies in the gas phase. Quantitative data for the basicity of other series of weak organic bases in aqueous solution have been lacking, and even relative basicities are often controversial.¹⁵ However, recent determinations of heats of protonation in fluorosulfuric acid (HSO_3F) have extended the range of accurately known solution basicities to include a large number of nitrogen, oxygen, sulfur, and phosphorus bases.^{16,17}

Available gas phase and solution data for oxygen, sulfur, and phosphorus bases, while less complete than data for the amines, have led to some expectations about the general nature of the results for these series. Approximate values for gas phase basicities of the simple methyl substituted oxygen and sulfur compounds are known.^{2,18} Addition of the first methyl group increases $\text{PA}(\text{B})$ by about 16 kcal/mol in both cases, which is substantially greater than the effect of the second substitution. Solution basicities in the oxygen series¹⁵⁻¹⁷ are approximately constant as in the amines due to the canceling effect of loss of hydrogen bonding when methyl replaces hydrogen. For the sulfur series, however, basicities in solution appear to directly reflect gas phase basicities, indicating that hydrogen bonding to protonic binding sites in the conjugate acids of sulfur bases is relatively weak compared to oxygen bases.^{16,17} A similar result is expected in comparing methyl substituent effects on the basicities of nitrogen and phosphorus bases.^{16,17}

This paper reports an investigation of the basicities, homolytic BH^+ bond dissociation energies, and gas phase ion chemistry of the methylphosphine series $[(\text{CH}_3)_n\text{PH}_{3-n}]$, $n = 1-3$ for the purpose of comparison to the congeneric methylamines. While the gas phase ion chemistry of the methyl phosphines has not previously been reported in detail, the reactions of phosphine both alone and in mixtures with other molecular

species have been extensively investigated by Holtz, Beauchamp, and Eyler using icr techniques¹⁹⁻²¹ and at much higher pressures by Long and Franklin using single source mass spectrometric methods.²² The icr studies included an examination of the basicity of PH_3 , the value $\text{PA}(\text{PH}_3) = 185 \pm 4$ kcal/mol being obtained. A related study of the basicity of trimethylphosphine by McDaniel, Coffman, and Strong²³ reports that its proton affinity lies between that of trimethylamine, 226.6 kcal/mol,^{3,4} and triethylamine, 233.3 kcal/mol,⁴ indicating a value of 230 ± 3 kcal/mol. However, in their study of protonation in HSO_3F , Arnett and Wolf question this result and suggest on the basis of correlations in other series that $\text{PA}(\text{Me}_3\text{P})$ may be lower by 11 kcal/mol.¹⁶

Experimental Section

Methylphosphine and dimethylphosphine were available from previous studies.²⁴ Trimethylphosphine was obtained from Strem Chemicals, Inc. Azomethane was prepared in this laboratory by M. S. Foster. Other chemicals were obtained from commercial sources. The phosphines were stored in metal containers or frozen on glass surfaces at 77°K except during transfers to minimize exposure to vacuum grease. Chemicals were degassed with freeze-pump-thaw cycles before use, and purities as ascertained by mass spectrometric analysis were acceptable.

The general features and operating characteristics of icr instrumentation have been previously described in detail.² All experiments were performed at ambient temperature in a modified Varian V-5900 icr spectrometer utilizing a flat cell equipped for trapped ion studies.^{2,25} The control unit for the icr spectrometer has been redesigned to incorporate pulse circuitry for performing trapped ion experiments.²⁵ This circuitry, which allows for switching between trapped ion and normal drift modes of operation, will be described in detail elsewhere.²⁶

Spectral intensities reported in tables and figures have been corrected to ion abundance by dividing the measured icr single resonance peak heights by ion mass.^{2,25} In the case of trapped ion experiments this represents an exact ion abundance.²⁵ The same procedure for drift operation yields an approximate ion abundance depending on the operating pressure.²

Trapped ion experiments are generally performed in the pressure range 10^{-7} – 10^{-5} Torr.²⁵ To accurately measure absolute pressures, a Schulz-Phelp type gauge has been installed adjacent to the icr cell in the magnetic field. This gauge is calibrated for a given emission current (10 μA) and magnetic field (usually 6 kG) against an MKS Instruments Baratron Model 90H1-E capacitance manometer. A linear variation of ion gauge current with pressure is observed over three decades (10^{-6} – 10^{-3} Torr). The major error in rate constants (estimated to be $\pm 10\%$) arises from uncertainties in absolute pressure determination. Gas mixtures were prepared directly in the instrument using two sample inlets and the calibrated Schulz-Phelp gauge.

Photoelectron spectra were obtained using a newly constructed photoelectron spectrometer employing a He(I) resonance lamp and cylindrical 127° electrostatic analyzer. Calibration was with respect to an internal Ar standard.

Results

Reactions of the Parent Ions. Electron bombardment of methylphosphine at low electron energy (9–12

(19) D. Holtz, J. L. Beauchamp, and J. R. Eyler, *J. Amer. Chem. Soc.*, **92**, 7045 (1970).

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

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

(22) J. W. Long and J. L. Franklin, *J. Amer. Chem. Soc.*, **96**, 2320 (1974).

(23) D. H. McDaniel, N. B. Coffman, and J. M. Strong, *J. Amer. Chem. Soc.*, **92**, 6697 (1970).

(24) G. M. Whitesides, J. L. Beauchamp, and J. D. Roberts, *J. Amer. Chem. Soc.*, **85**, 2665 (1963).

(25) T. B. McMahon and J. L. Beauchamp, *Rev. Sci. Instrum.*, **43**, 509 (1972).

(26) T. B. McMahon, M. S. Foster, and J. L. Beauchamp, to be submitted for publication.

(14) R. H. Staley and J. L. Beauchamp, *J. Amer. Chem. Soc.*, **96**, 1604 (1974).

(15) E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 223 (1963).

(16) E. M. Arnett and J. F. Wolf, *J. Amer. Chem. Soc.*, **95**, 978 (1973).

(17) E. M. Arnett, *Accounts Chem. Res.*, **6**, 404 (1973).

(18) M. A. Haney and J. L. Franklin, *J. Phys. Chem.*, **73**, 4328 (1969).

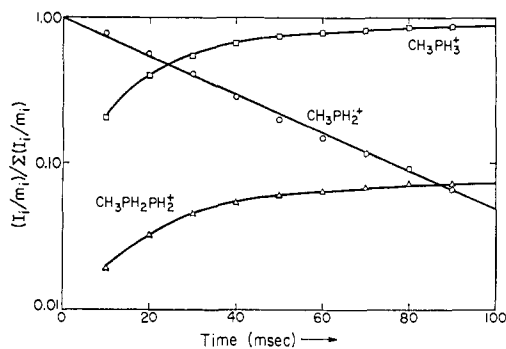


Figure 1. Variation of ion abundance with time for methylphosphine at 12 eV and 1.0×10^{-6} Torr with a 10-msec electron beam pulse.

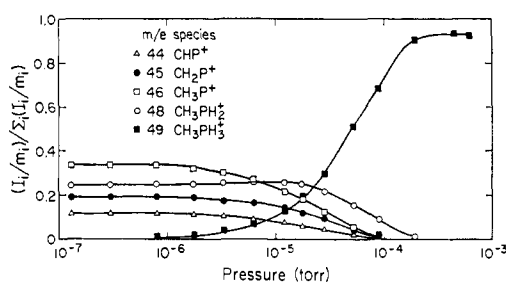
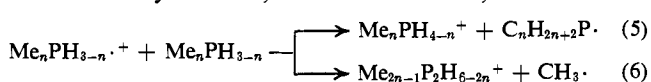


Figure 2. Variation of ion abundance with pressure at 70 eV for the major ions in methylphosphine.

eV) and low pressure (10^{-7} Torr) yields a single resonance icr spectrum which contains only the parent ion, m/e 48. Raising the pressure and/or trapping the ions for long times (up to several seconds) results in the appearance of reaction products in the spectrum. Variation of ion abundance with time for methylphosphine at 12 eV and 1.0×10^{-6} Torr is illustrated in Figure 1. Under these conditions only the parent ion is generated. This species reacts to give protonated methylphosphine in addition to a condensation product resulting from loss of methyl radical, reactions 5 and 6, $n = 1$. The



parent ion decay rate directly yields the total reaction rate constant. The product distribution is constant with time and is used to extract the individual reaction rate constants. Similar results are obtained for dimethylphosphine, reactions 5 and 6, $n = 2$. For trimethylphosphine ($n = 3$) only reaction 6 is significant. Rate constants for reactions of parent ions in phosphine²⁰ and all of the methylphosphines are summarized in Table I. The most reasonable structure for the product of reaction 2 is an appropriately substituted diphosphine. The reason for this choice is discussed below.

Ion-Molecule Reactions in Methylphosphine. Low-pressure icr spectra of methylphosphine at 70 eV are in good agreement with previously reported mass spectra.^{27, 28} At higher pressures a variety of product ions appear in the spectra, Figures 2 and 3. Slight increases in parent, CH_3PH_2^+ (m/e 48), and parent minus hydrogen, CH_4P^+ (m/e 47), abundances indicate the occur-

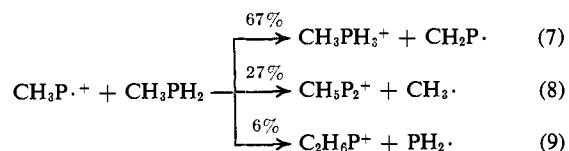
Table I. Rate Constants for Ion-Molecule Reactions of Parent Ions in Phosphine^a and the Methylphosphines^b

Reaction ^c	k_2^d	Σk_i^d
$\text{PH}_3^+ + \text{PH}_3 \begin{cases} \rightarrow \text{PH}_4^+ + \text{PH}_2 \cdot \\ \rightarrow \text{P}_2\text{H}_4^+ + \text{H}_2 \\ \rightarrow \text{P}_2\text{H}_5^+ + \text{H} \cdot \end{cases}$	10.5	10.8
	0.1	
	0.2	
$\text{MePH}_2^+ + \text{MePH}_2 \begin{cases} \rightarrow \text{MePH}_3^+ + \text{CH}_3\text{P} \cdot \\ \rightarrow \text{MePH}_2\text{PH}_2^+ + \text{CH}_3 \cdot \end{cases}$	8.8	9.5
	0.7	
$\text{Me}_2\text{PH}^+ + \text{Me}_2\text{PH} \begin{cases} \rightarrow \text{Me}_2\text{PH}_2^+ + \text{C}_2\text{H}_5\text{P} \cdot \\ \rightarrow \text{Me}_2\text{PHPHMe}^+ + \text{CH}_3 \cdot \end{cases}$	6.0	6.3
	0.3	
$\text{Me}_3\text{P}^+ + \text{Me}_3\text{P} \rightarrow \text{Me}_3\text{PPMe}_2^+ + \text{CH}_3 \cdot$	5.9	5.9

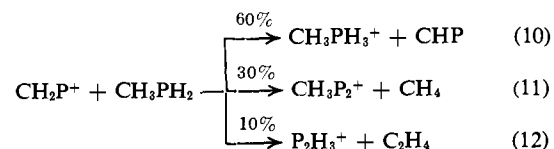
^a Results for phosphine are from ref 20. ^b All data for the methylphosphines from trapped ion studies at 12 eV where only the parent ion is present; see text. Product distributions were found to be constant with time and in agreement with those obtained in studies done at higher pressures using trapping voltage modulation. ^c All reactions listed gave a negative double resonance response which normally is indicative of an exothermic reaction: J. L. Beauchamp and S. E. Buttrill, Jr., *J. Chem. Phys.*, **48**, 1783 (1968). ^d 10^{-10} cm³ molecule⁻¹ sec⁻¹. Accuracy in total rate constant estimated to be $\pm 20\%$ due to uncertainties in pressure measurement.

rence of charge transfer and hydride abstraction reactions. Reactions of the parent ion are detailed above and yield the observed 4% abundance of protonated methylphosphine, $\text{CH}_3\text{PH}_2\text{PH}_2^+$ (m/e 81), as well as contributing to production of the protonated parent, CH_3PH_3^+ (m/e 49). The hydride abstraction product as well as all other hydrogen containing fragments react at least in part to give protonated parent as revealed by double resonance results. Protonated parent constitutes 93% of the ionization above 2×10^{-4} Torr and does not readily undergo further reactions.

Condensation reactions of fragment ions give rise to four product ions which appear at intermediate pressures, 10^{-5} to 10^{-4} Torr. The base peak in the mass spectrum, CH_3P^+ (m/e 46) an odd electron species, yields, in addition to protonated parent, two products, CH_5P_2^+ (m/e 79) and $\text{C}_2\text{H}_6\text{P}^+$ (m/e 61), corresponding to condensation with loss of the radicals $\text{CH}_3 \cdot$ or $\text{PH}_2 \cdot$, reactions 7-9. Similarly, the even electron fragment,



CH_2P^+ (m/e 45), condenses with loss of small molecules, reactions 10-12. The ionic condensation products all



undergo further reaction as evidenced by their decreasing abundance at high pressures. Double resonance experiments identify the most abundant of these, CH_5P_2^+ (m/e 79), as reacting to give protonated parent.

Ion-Molecule Reactions in Dimethylphosphine. Variation of ion abundance with pressure at 70 eV for dimethylphosphine is illustrated in Figures 4 and 5. Relative ion abundances at low pressure are in good

(27) Y. Wada and R. W. Kiser, *J. Phys. Chem.*, **68**, 2290 (1964).

(28) M. Halmann, *J. Chem. Soc., London*, 3270 (1962).

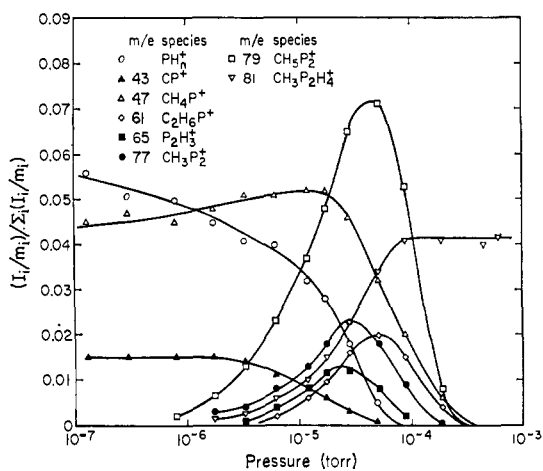


Figure 3. Variation of ion abundance with pressure at 70 eV for the minor ions in methylphosphine. Ion abundances of three minor fragments, PH_n^+ ($n = 0-2$), have been summed. Species amounting to less than 1% of total ionization are omitted.

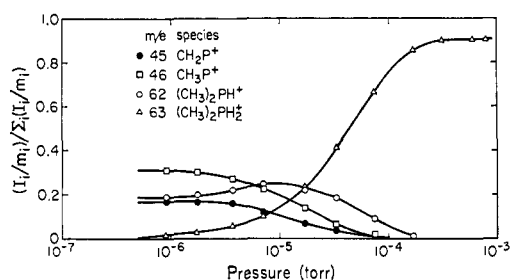
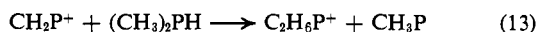


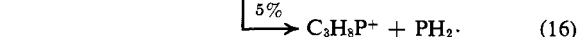
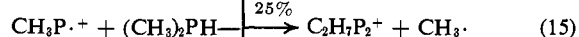
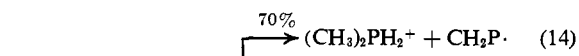
Figure 4. Variation of ion abundance with pressure at 70 eV for the major ions in dimethylphosphine.

agreement with previously reported mass spectra.^{28,29} The substantial increase in $\text{C}_2\text{H}_6\text{P}^+$ (m/e 61) is shown by double resonance to result at least in part from hydride abstraction by the abundant fragment CH_2P^+ (m/e 45), reaction 13. Ion chemistry of the parent and



protonated parent is similar to that of methylphosphine. Parent ion increases slightly with pressure due to charge transfer from fragment ions which were not investigated in detail. It reacts as discussed above to give protonated trimethyldiphosphine $(\text{CH}_3)_3\text{P}_2\text{H}_2^+$ (m/e 109) and protonated parent, $(\text{CH}_3)_2\text{PH}_2^+$ (m/e 63). Double resonance shows that all of the fragment ions appearing in Figures 4 and 5 also contribute to producing protonated parent which amounts to 90% of the ionization at high pressure.

Double resonance experiments allow the identification of a number of condensation reactions by fragment ions. Reactions of the odd electron fragment CH_3P^+ (m/e 46) again include condensation with loss of $\text{CH}_3\cdot$ or $\text{PH}_2\cdot$, reactions 14–16. Reaction 15 corresponds to



(29) J. Fischler and M. Halmann, *J. Chem. Soc., London*, 31 (1964).

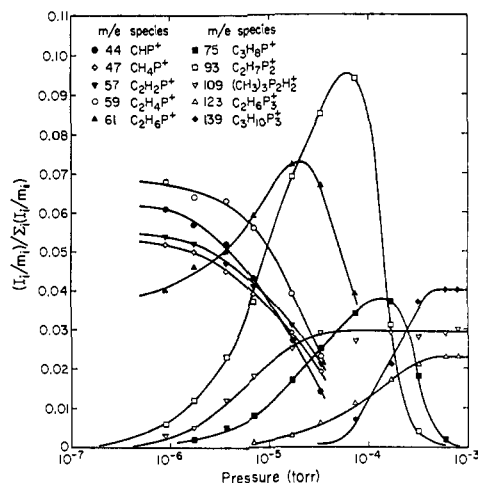


Figure 5. Variation of ion abundance with pressure at 70 eV for the minor ions in dimethylphosphine. Species amounting to less than 2% of total ionization are omitted.

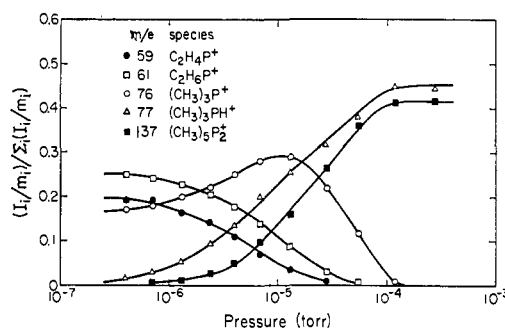


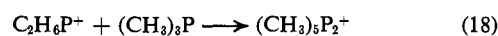
Figure 6. Variation of ion abundance with pressure at 70 eV for the major ions in trimethylphosphine.

P^+ transfer which also occurs from the fragment $\text{C}_2\text{H}_4\text{P}^+$ (m/e 59), reaction 17. The product, $\text{C}_2\text{H}_7\text{P}_2^+$



(m/e 93), reacts further to give $\text{C}_2\text{H}_6\text{P}_3^+$ (m/e 123) and $\text{C}_3\text{H}_{10}\text{P}_3^+$ (m/e 139). The product of reaction 16, $\text{C}_3\text{H}_8\text{P}^+$ (m/e 75), also results from condensation reactions by $\text{C}_2\text{H}_6\text{P}^+$ (m/e 61) with loss of CH_3PH_2 and CH_4P^+ (m/e 47) with loss of PH_3 .

Ion-Molecule Reactions in Trimethylphosphine. Variation of ion abundance with pressure at 70 eV for trimethylphosphine is illustrated in Figures 6 and 7. Relative ion abundances at low pressure are in good agreement with previously reported mass spectra.²⁷⁻³⁰ The parent ion, $(\text{CH}_3)_3\text{P}^+$ (m/e 76), increases significantly with pressure due to charge transfer from minor fragments, which were not investigated in detail. It reacts to give $(\text{CH}_3)_3\text{P}_2^+$ (m/e 137), reaction 6, $n = 3$, which also results from $\text{C}_2\text{H}_6\text{P}^+$ (m/e 61) in a condensation with no neutral product, reaction 18. The penta-



methyldiphosphine product ion becomes a substantial 42% of total ionization at high pressures.

The other major ion at high pressures (45%) is the protonated parent, $(\text{CH}_3)_3\text{PH}^+$ (m/e 77), which results from reaction of all of the fragments, Figures 6 and 7, except $\text{C}_3\text{H}_8\text{P}^+$ (m/e 75) and C_3H_5^+ (m/e 41). The latter,

(30) R. G. Gillis and G. J. Long, *Org. Mass Spectrom.*, 2, 1315 (1969).

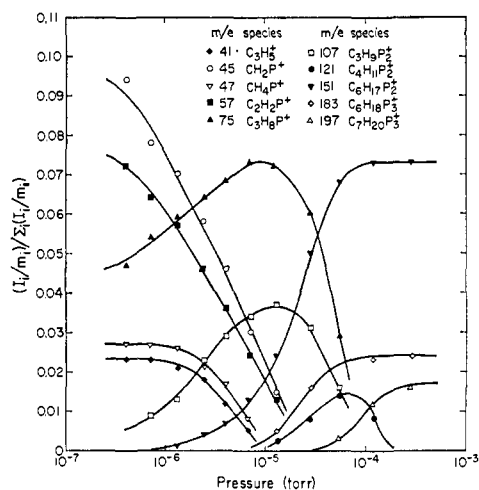
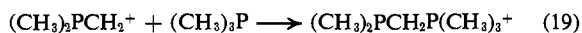


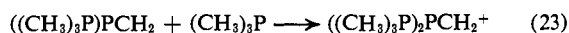
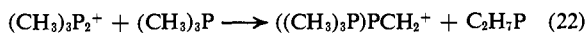
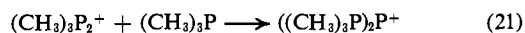
Figure 7. Variation of ion abundance with pressure at 70 eV for the minor ions in trimethylphosphine. Species amounting to less than 2% of total ionization are omitted.

in addition to a contribution from $C_2H_4P^+$ (m/e 59), reacts by hydride abstraction producing the increase in $C_3H_8P^+$ (m/e 75) at intermediate pressures. This in turn condenses to give $C_6H_{17}P_2^+$ (m/e 151), reaction 15. As is the case for reaction 18, there is no neutral product



from the condensation, suggesting a long lifetime for the adduct which either facilitates collisional stabilization or permits direct observation of the adduct.

The fragment ion $C_2H_4P^+$ (m/e 59) also reacts, as in dimethylphosphine, by a process formally involving transfer of P^+ , reaction 20. At higher pressures the



product $(CH_3)_3P_2^+$ (m/e 107) reacts further in two processes, the first involving clustering with the neutral to give $((CH_3)_3P)_2P^+$ (m/e 183), reaction 21. The second process formally involves addition of methylene, reaction 22, and then a neutral to give $((CH_3)_3P)_2PCH_2^+$ (m/e 197), reaction 23. The relative importance of these processes may be assessed by examining the abundances of the participating ions, Figure 7.

Basicities of the Methylphosphines. Of principal interest in the present study is the determination of gas phase basicities of the methylphosphines. Reactions of the protonated parent ions were thus examined in mixtures of each of the methylphosphines with various other molecules using the methodology described in the introduction. The occurrence and direction of the proton transfer reactions were confirmed by examining the variation of ion abundance with pressure and time and by double resonance. Reactions observed and implied limits on proton affinities of the methylphosphines are summarized in Table II.

In several mixtures proton transfer reactions were observed to occur in both directions indicating that the proton affinities of the two neutrals are relatively close (within *ca.* 3 kcal/mol). Further examination of these systems using trapped ion icr techniques allowed the

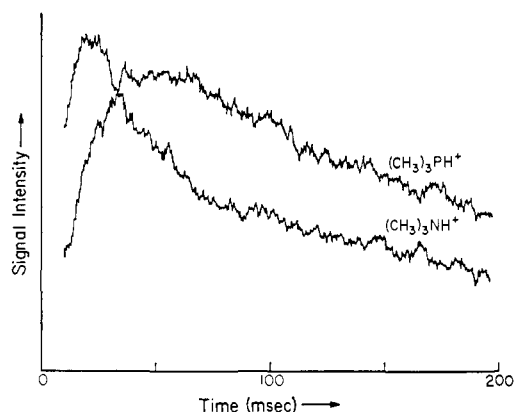


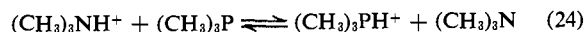
Figure 8. Variation with time of $(CH_3)_3PH^+$ and $(CH_3)_3NH^+$ signal intensities following a 10-msec 12-eV electron beam pulse in an 8.2:1 mixture of $(CH_3)_3N$ and $(CH_3)_3P$ at 1.2×10^{-5} Torr total pressure. Initial buildup of the protonated species results from reaction by $(CH_3)_3N^+$ (decay not shown). Decay of the signals at long times results from diffusion losses due to the relatively high total pressure used for this experiment.

Table II. Proton-Transfer Reactions Observed in Mixtures of Methylphosphines with Various Other Molecules

Reaction	PA ^{a,b}
$NH_4^+ + MePH_2 \rightleftharpoons MePH_3^+ + NH_3$	$\sim 207.0^c$
$MePH_3^+ + MeNH_2 \rightarrow MeNH_3^+ + MePH_2$	$< 216.3^d$
$MePH_3^+ + (2-Pr)_2O \rightarrow (2-Pr)_2OH^+ + MePH_2$	$< 208.1^d, e$
$MePH_3^+ + Me_2N_2 \rightarrow Me_2N_2H^+ + MePH_2$	$< 209.4^f$
$Et_2OH^+ + MePH_2 \rightarrow MePH_3^+ + Et_2O$	$> 202.6^d, e$
$2-PrOEtH^+ + MePH_2 \rightleftharpoons MePH_3^+ + 2-PrOEt$	$\sim 205.8^d, e$
$CF_3CH_2NH_3^+ + MePH_2 \rightleftharpoons MePH_3^+ + CF_3CH_2NH_2$	$\sim 205.4^d, e$
$NH_4^+ + Me_2PH \rightarrow Me_2PH^+ + NH_3$	$> 207.0^c$
$Me_2PH_2^+ + Me_2NH \rightarrow Me_2NH_2^+ + Me_2PH$	$< 222.4^d$
$MeNH_3^+ + Me_2PH \rightarrow Me_2PH_2^+ + MeNH_2$	$> 216.3^d$
$EtNH_3^+ + Me_2PH \rightleftharpoons Me_2PH_2^+ + EtNH_2$	$\sim 218.8^d$
$Me_3NH^+ + Me_3P \rightleftharpoons Me_3PH^+ + Me_3N$	$\sim 226.6^d$
$Me_3PH^+ + Et_3N \rightarrow Et_3NH^+ + Me_3P$	$< 233.3^g$
$Me_3PH^+ + Me_2EtN \rightleftharpoons Me_2EtNH^+ + Me_3P$	$\sim 229.0^d, e$
$Me_3PH^+ + MeEt_2N \rightarrow MeEt_2NH^+ + Me_3P$	$< 231.2^d, e$

^a All values in kcal/mol. ^b Implied limit, as indicated, on the PA of the methylphosphine participant, see text. Where the reaction is observed to proceed in both directions (double arrows), the PA of the methylphosphine participant is inferred to be approximately equal (± 3 kcal/mol) to that of the reference molecule. ^c Reference 18. ^d Reference 3. ^e R. W. Taft, private communication. ^f M. S. Foster and J. L. Beauchamp, *J. Amer. Chem. Soc.*, **94**, 2425 (1972). Measurements of the proton affinity of azomethane have recently been refined: M. S. Foster and J. L. Beauchamp, unpublished results. ^g Reference 4.

determination of equilibrium constants. For example in an 8.2:1 mixture of $(CH_3)_3N$ and $(CH_3)_3P$ at 1.2×10^{-5} Torr total pressure, ion intensities were found to vary with time as shown in Figure 8. Initial buildup of the protonated species results from reaction by $(CH_3)_3N^+$ which is the major ion formed by the 10-msec 12-eV electron beam pulse. Subsequent reaction between protonated species and neutrals, reaction 24, results in a



rapid approach to equilibrium. The ratio of ion abundances at long times yields a value of 10.2 for the equilibrium constant of reaction 24, corresponding to a free energy change $\Delta G^\circ_{298} = -1.4$ kcal/mol. Results from equilibrium studies of all three methylphosphines are summarized in Table III.

Table III. Proton Affinities of Methylphosphines Derived from Equilibrium Constants for Proton Transfer Reactions

Reaction	K^a	PA ^{b,c}
$\text{CF}_3\text{CH}_2\text{NH}_3^+ + \text{MePH}_2 \rightleftharpoons \text{MePH}_3^+ + \text{CF}_3\text{CH}_2\text{NH}_2$	11.8	206.9
$\text{EtNH}_3^+ + \text{Me}_2\text{PH} \rightleftharpoons \text{Me}_2\text{PH}_2^+ + \text{EtNH}_2$	1.5	218.9
$\text{Me}_3\text{NH}^+ + \text{Me}_3\text{P} \rightleftharpoons \text{Me}_3\text{PH}^+ + \text{Me}_3\text{N}$	11.4	228.0
$\text{Me}_3\text{PH}^+ + \text{Me}_2\text{EtN} \rightleftharpoons \text{Me}_2\text{EtNH}^+ + \text{Me}_3\text{P}$	5.5	228.0

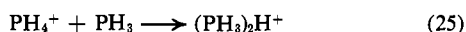
^a Average of at least three independent determinations. ^b All values in kcal/mol. ^c Proton affinity, defined in text. Free energy data derived from K converted to enthalpies as described in ref 3 and 4. Values used for the proton affinities of the reference molecules are given in Table II. All data relative to $\text{PA}(\text{NH}_3) = 207 \pm 3$ kcal/mol (ref 18).

Discussion

Ion Chemistry. The ion chemistry of the methylphosphines continues the tendency toward complexity apparent in the exceedingly rich ion chemistry of phosphine itself.¹⁹⁻²² While the present study has only attempted to characterize the reactions of the parent and more abundant fragment ions, a great variety of products are observed. The majority of these react further with the parent neutral to eventually generate the protonated parent ion. At 70-eV electron energy, this species amounts to 93, 90, and 45% of the total ionization at high pressures in the case of methyl-, dimethyl-, and trimethylphosphine, respectively. The lower abundance of protonated parent in the case of trimethylphosphine may be attributed to the failure of the parent ion to form the protonated parent ion, a process which is the major reaction channel for methyl- and dimethylphosphine parent ions.

The total reaction rate of the parent ions decreases with increasing methyl substitution. A similar variation of reactivity is observed for the congener amines.^{31,32} In the latter case, however, the reaction rate constants are all approximately a factor of 2 higher than the corresponding phosphines.^{31,32}

In contrast to the methylamines where the protonated parent ions react to form proton bound dimers under conditions similar to those under which the methylphosphines were studied;³³ proton bound dimer formation in the methylphosphines is not a facile process. It is noteworthy in this regard that the negative of the enthalpy change for the clustering process 25



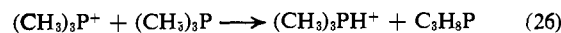
is 11.5 kcal/mol, which is substantially less than the 24.8 kcal/mol enthalpy change for the corresponding process involving ammonia.¹² It is not clear, however, whether the failure to observe facile proton bound dimer formation in the case of the methylphosphines can be attributed to weakening of the hydrogen bond or to more obscure kinetic factors. If the former is the case, then failure to observe dimer formation ($\leq 1\%$ of the protonated monomer) below 10^{-3} Torr at $\sim 298^\circ$ indicates that $-\Delta G \leq 5.4$ kcal/mol. Assuming $\Delta S \cong -25$ eu^{12,22} for clustering of the methylphosphines gives $-\Delta H \leq 13$ kcal/mol which is reasonable in view of the value observed for phosphine itself.

(31) L. Hellner and L. W. Sieck, *Int. J. Chem. Kinet.*, **5**, 177 (1973).

(32) M. S. B. Munson, *J. Phys. Chem.*, **70**, 2034 (1966).

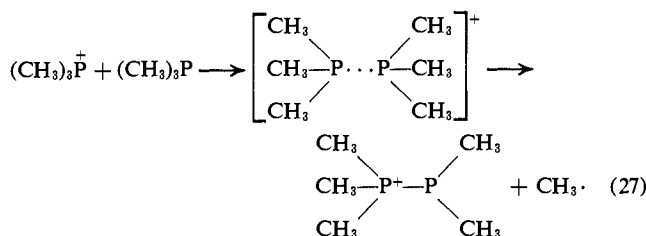
(33) D. Holtz, W. G. Henderson, and J. L. Beauchamp, unpublished results.

The ion chemistry of trimethylphosphine differs from that of methyl- and dimethylphosphine in that the parent ion does not react readily to produce the protonated parent ion. This process is observed in the case of trimethylamine. If it is assumed, then, that reaction 26 is



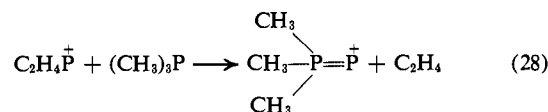
endothermic, we may write $D(\text{C}-\text{H}) > D(\text{P}^+-\text{H})$. The value of $D(\text{P}^+-\text{H}) = 99.2$ kcal/mol obtained below for trimethylphosphine may thus be taken as a lower limit for $D(\text{C}-\text{H})$ in trimethylphosphine. This limit is only suggested and not rigorously established by the observed ion chemistry.

Condensation reactions are relatively more important in the methylphosphines than in the methylamines. This contrasting behavior is apparent in the parent ions themselves, with the generalized process 6 involving loss of CH_3 being observed in each system. It appears logical to formulate this process (indicated in reaction 27 for trimethylphosphine) as involving phos-



phorus-phosphorus bond formation in the product ion. Significantly it is observed in each case that the condensation product in reaction 6 does not react further with the parent neutral. This suggests that either these species do not possess a labile proton or that the labile protons in the products are bound to species with somewhat higher proton affinities than the parent neutrals.

A second interesting process which appears to involve phosphorus-phosphorus bond formation formally involves transfer of P^+ from $\text{C}_2\text{H}_4\text{P}^+$ to dimethylphosphine (reaction 17) and trimethylphosphine (reaction 20). The structure of the product ion in the latter process is suggested in reaction 28. Although there are



obvious uncertainties in the structures involved in these and other condensation reactions, it is likely that phosphorus-phosphorus bond formation in condensation reactions of the phosphines is an important consideration. Cowley³⁴ has recently reviewed the chemistry of compounds with phosphorus-phosphorus bonds and discusses participation of $d\pi-p\pi$ orbitals in multiple bond formation in these species. A more extensive investigation of the chemistry of substituted diphosphines might provide further insights into the energetics of P-P bond formation.

Gas Phase Basicities of the Methylphosphines. The evaluation of the proton affinity of trimethylphosphine by McDaniel and coworkers²³ has been corroborated by the more quantitative results presented above, thus settling the question raised by Arnett¹⁷ regarding the validity of the earlier results.

(34) A. H. Cowley, *Chem. Rev.*, **65**, 617 (1965).

In accordance with eq 4, the proton affinities measured in equilibrium studies can be utilized in conjunction with adiabatic ionization potentials measured by photoelectron spectroscopy to calculate BH^+ homolytic bond dissociation energies for the conjugate acids of the methylphosphines. These data are summarized in Table IV along with similar data for the methylamines, which are included for the purpose of comparison.

Table IV. Gas Phase Basicities, Adiabatic Ionization Potentials, and $D(B^+-H)$ Homolytic Bond Dissociation Energies for Methylphosphines and Methylamines^a

Molecule	PA ^b	IP ^b	$D(B^+-H)^{b,c}$
PH ₃	187.9 ^d	229.6 (9.96) ^f	104.0
MePH ₂	206.9 ^e	210.2 (9.12) ^g	103.6
Me ₂ PH	218.9 ^e	195.3 (8.47) ^g	100.7
Me ₃ P	228.0 ^e	184.7 (8.01) ^g	99.2
NH ₃	207.0	235.0 (10.19)	128.4
MeNH ₂	216.3	206.8 (8.97)	109.5
Me ₂ NH	222.4	190.0 (8.24)	98.8
Me ₃ N	226.6	180.3 (7.82)	93.3

^a Data for amines taken from ref 3. ^b All data in kcal/mol except values quoted in parentheses for ionization potentials are in electron volts. ^c Calculated using eq 4 in the text. ^d Proton affinity determined in equilibrium studies relative to $PA(CH_3CHO) = 186.0$ kcal/mol: K. M. A. Refaey and W. A. Chupka, *J. Chem. Phys.*, **48**, 5205 (1968). ^e Data from Table III. ^f J. P. Maier and D. W. Turner, *J. Chem. Soc.*, **68**, 711 (1972); A. W. Potts and W. C. Price, *Proc. Roy. Soc., Ser. A*, **326**, 181 (1972). ^g Adiabatic ionization potentials determined using photoelectron spectroscopy. Estimated uncertainties ± 0.07 eV due to difficulties in identifying ionization thresholds. The adiabatic ionization potential of trimethylphosphine has been determined to be 8.04 eV by J. C. Green and D. W. Turner (unpublished results). See also S. Craddock, E. A. V. Ebsworth, W. J. Savage, and R. A. Whiteford, *J. Chem. Soc.*, **68**, 934 (1972), and I. H. Hillier and V. R. Saunders, *J. Chem. Soc. D*, **316** (1970).

In analyzing the thermochemical parameters relating to the intrinsic basicities of the methylphosphines and amines, there are certain obvious trends in the data worth summarizing for the purpose of discussion. (1) In both series increased methyl substitution leads to an increase in basicity, with an increase for the first, second, and third methyl substitution of 9.3, 6.1, and 4.2 kcal/mol in the case of the amines and 19.0, 12.0, and 9.1 kcal/mol in the case of the phosphines. Methyl substituent effects in the phosphine series are observed to be twice as large as in the amine series. The effects of successive substitution are nonadditive, decreasing in both series. (2) Increased methyl substitution leads to a marked decrease in the BH^+ homolytic bond dissociation energy in the amine series, decreasing from 128.4 kcal/mol in NH_4^+ to 93.3 kcal/mol in $(CH_3)_3NH^+$. In comparison the decrease observed in the phosphine series is significantly less, ranging only from 104.0 kcal/mol in PH_4^+ to 99.2 kcal/mol in $(CH_3)_3PH^+$.

Even though proton affinities and BH^+ homolytic bond dissociation energies are directly connected by the adiabatic ionization potential of the base in accordance with eq 4, it appears that fundamentally different factors are responsible for the observations summarized above regarding these quantities.

For example, the ionization potentials of ammonia and phosphine are approximately the same. The difference in proton affinities thus appears to be a consequence of the weakening of the PH_3^+-H bond relative to the

NH_3^+-H bond.² A similar reduction occurs in the bond dissociation energies of the isoelectronic neutrals, from 104 kcal/mol for CH_4 to 85 kcal/mol for SiH_4 .³⁵ To the extent that the latter result is reasonable³⁶ (and explicable), then so is the former. A more useful approach, perhaps, in explaining the difference in the basicity of ammonia and phosphine involves a consideration of the character of the lone pair to which the proton binds in these species. Recent *ab initio* localized orbital calculations suggest that the lone pair in PH_3 has substantially more s character ($sp^{0.8}$ according to Guest, Hillier, and Saunders³⁷) than appropriate for sp^3 hybridization. This contrasts with ammonia, where sp^3 hybridization in the neutral provides a reasonable description on the bonding.³⁸ Thus a significant rehybridization energy is expected in forming the conjugate acid of PH_3 , which should not be observed in the case of NH_3 .³⁹ Increased s character is also related to the fact that the ionization potential of PH_3 is higher (relative to NH_3) than might be expected based on periodic correlations of hydride ionization potentials.

This line of reasoning can be continued to explain the effects of methyl substitution on the basicity of ammonia and phosphine. In proceeding from ammonia to trimethylamine, the dipole moment decreases from 1.47 to 0.61 D.³⁸ This is *opposite* to the trend in the methylphosphines, where the dipole moment increases from 0.58 D for PH_3 to 1.19 D for $(CH_3)_3P$.³⁸ Weaver and Parry³⁸ summarize evidence which suggests that the largest contribution to the dipole moment of amines can be assigned to the lone pair and that this changes significantly with increasing methyl substitution. This suggests that there is a pronounced shift of the center of the lone pair charge distribution toward the nitrogen nucleus.⁴⁰ In terms of hybridization concepts this implies that methyl substitution introduces more s character into the lone pair orbital. The dipole moments of the phosphines, on the other hand, can be rationalized in terms of a negligible contribution from the lone pair throughout the methylphosphine series. This conjecture of Weaver and Parry is substantiated by the calculations of Guest, Hillier, and Saunders which suggest that the lone pair of both PH_3 and $(CH_3)_3P$ can be described as $sp^{0.8}$ and that no rehybridization accompanies methyl substitution.³⁷

Protonation of the methylamines is thus accompanied by a rehybridization energy which is small in the case of NH_3 but increases with increasing methyl substitution. This acts in opposition to the stabilization afforded the conjugate acid by interaction of the charge with the polarizable methyl groups. In the phosphine series the rehybridization energy is significant but does not change

(35) J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966). The bond dissociation energy for SiH_4 is calculated from $D(SiH_3^+-H^+) = 366$ kcal/mol (R. T. McIver, Jr., unpublished results) and $EA(SiH_3) = 1.4$ eV (J. I. Brauman, unpublished results).

(36) Viewed in this fashion BH^+ homolytic bond energies follow periodic trends in all hydrides which have thus far been examined (see ref 2 for discussion).

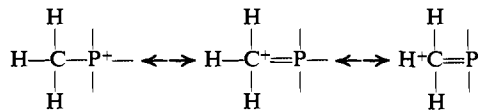
(37) M. F. Guest, I. H. Hillier, and V. R. Saunders, *J. Chem. Soc., London*, **68**, 867 (1972); I. H. Hillier and V. R. Saunders, *J. Chem. Soc. D*, **316** (1970).

(38) J. R. Weaver and R. W. Parry, *J. Inorg. Chem.*, **5**, 718 (1966).

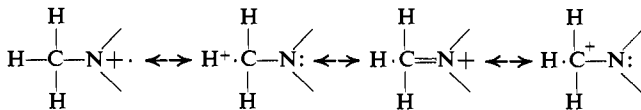
(39) For an early discussion of rehybridization effects, see J. H. Gibbs, *J. Chem. Phys.*, **22**, 1460 (1954).

(40) For a discussion of the effect of methyl groups on the electron density of nitrogen, see W. J. Hehre and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 2191 (1970). Calculations suggest that for the methylamine series, increasing base strength is *not* associated with increasing electron density on the nitrogen atom.

with methyl substitution, which thus appears to lend greater stabilization to the conjugate acids than is observed in the amine series. Another possible origin of the larger methyl substituent effects in the phosphines as compared to the amines could be increased importance of structure of the type



which involve donation from π type orbitals of the CH_3 group into empty phosphorus $d\pi$ orbitals. Since these structures stabilize the conjugate acids, they lead to increased bond dissociation energies and proton affinities with methyl substitution in the phosphine series relative to the amine series. With this possible exception, the effects of methyl substitution on the BH^+ homolytic bond dissociation energies can be considered apart from the effects on the proton affinities. As previously suggested³ the lowering of the BH^+ homolytic bond dissociation energies with increasing methyl substitution in the amine series can be attributed to delocalization of charge and spin to the alkyl substituents in the radical cations.



Structures of this type are less important due to poor orbital overlap in the case of the methylphosphines, where BH^+ homolytic bond dissociation energies are relatively constant.

Comparison to Solution Basicities. The $\text{p}K_a$ of PH_3 has been estimated to be -14 , compared to values of 3.91 and 8.65 for $(\text{CH}_3)_2\text{PH}$ and $(\text{CH}_3)_3\text{P}$, respectively, in aqueous solution.⁴¹ The difference in free energy of protonation in the case of PH_3 and $(\text{CH}_3)_3\text{P}$ is thus ~ 30 kcal/mol. This is comparable to the difference of 30.6 kcal/mol for the enthalpy of protonation in the strongly acidic HSO_3F medium.¹⁶

The more quantitative data of Arnett and Wolf¹⁶ for heats of protonation of PH_3 and $(\text{CH}_3)_3\text{P}$ in HSO_3F can

(41) W. A. Henderson and C. A. Streuli, *J. Amer. Chem. Soc.*, **82**, 5791 (1960).

be used in conjunction with the gas phase proton affinity data derived in this study to calculate differences in enthalpies of solvation for the conjugate acids of these species. Using the same thermochemical cycle described for the methylamines,⁴ the species $(\text{CH}_3)_3\text{PH}^+$ is less favorably solvated than PH_4^+ by 5.7 kcal/mol, Table V. For comparison, the conjugate acids of the

Table V. Relative Heats of Solvation in HSO_3F

Ion	$\delta_R \Delta H_s^{a,b}$
NH_4^+	0
MeNH_3^+	5.3
Me_2NH_2^+	8.9
PH_4^+	11.3
Me_3NH^+	13.4
Me_3PH^+	17.0

^a Heat of solvation in HSO_3F relative to NH_4^+ obtained as described in ref 4. Solution data from ref 16. ^b All data in kcal/mol.

alkylamines CH_3NH_2 , $(\text{CH}_3)_2\text{NH}$, and $(\text{CH}_3)_3\text{N}$ are less favorably solvated than NH_3 by 5.3 , 8.9 , and 13.4 kcal/mol, respectively, in HSO_3F .¹⁶ It has been argued for the amine series that the unfavorable effects of methyl substitution result primarily from loss of strong specific hydrogen bonds in aqueous solution. Arnett and Wolf report a close linear correlation between heats of solvation of ammonium ions in H_2O and HSO_3F , suggesting similar effects of alkyl groups in both media. If loss of hydrogen bonding to acidic sites is responsible for the effects of methyl substitution in HSO_3F , then our data suggest that hydrogen bonding to the conjugate acids of phosphines is substantially weaker than in the amine series. This conclusion is corroborated by the weaker hydrogen bonds in phosphine as compared to amine dimers.

Acknowledgment. The authors acknowledge useful collaborative interactions with Professors R. W. Taft and E. M. Arnett during the course of these studies. This research was supported in part by the United States Atomic Energy Commission under Grant No. AT(04-3)767-8. The ion cyclotron resonance spectrometer used in these studies was financed by the National Science Foundation under Grant No. NSF-GP-18393.