

MASS SPECTRAL STUDIES OF
SOME SUBSTITUTED PHOSPHINES

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THESIS



ABSTRACT

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The mass spectra of a selected group of substituted halophosphines and aminohalophosphines are reported. The main features of the spectra of analogous series of compounds are compared and contrasted. Fragmentation, rearrangement, recombination, and metastable transitions are discussed. Correlations are drawn between relative molecular stabilities under electron-impact. When possible, conclusions are compared to those drawn from other physical data for the compounds under investigation. Suggestions for future work are made.

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By

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INTRODUCTION

As a result of the developments in the field of synthetic inorganic chemistry during the past two decades, a number of new substituted phosphines have been prepared¹⁻⁶. Refinements in physical methods and theoretical approaches have made possible studies of the bonding and molecular structure of these new compounds⁷⁻⁹.

This work is concerned with the investigation of the positive-ion mass spectra of a selected group of substituted halophosphines and amino-halophosphines. The study was undertaken to compare the mass spectral data of analogous series of compounds, to draw correlations between molecular stabilities under electron-impact, and to compare relative bond strengths. The results obtained are then compared to existing physical data which has been reported for some of these compounds.

HISTORICAL

Until recently the development of mass spectrometry has been oriented toward the design and improvement of methods for the investigation of organic compounds, particularly those of interest to the petroleum industry. Only within the last fifteen years has the utility of mass spectrometry received renewed attention by the inorganic chemist. Several relatively simple inorganic species have been subjected to electron-impact studies. Recently, work in the field of mass spectrometry has begun to include larger, more complex inorganic molecules¹⁰⁻¹⁴.

Extensive electron-impact studies have been conducted on the phosphorus hydrides¹⁵⁻¹⁹. The appearance potentials¹⁹⁻²³ and heats of formation^{19,23} of the most abundant ion fragments from phosphine have been reported by several authors. The ion-molecule reactions of phosphine in a mass spectrometer have been investigated²⁴.

Somewhat fewer studies have been carried out on the phosphorus trihalides, however the mass spectra of phosphorus trichloride^{25,26} and phosphorus tribromide²⁷ have been reported, and the appearance potentials and heats of formation of the most abundant ions have been calculated. The surprisingly low appearance potential of the PCl_2^+ ion prompted Halmann and Klein²⁶ to investigate the negative-ion spectrum of phosphorus trichloride. They showed that Cl^- was produced in high abundance, and that the formation of PCl_2^+ could be explained by its production, together with Cl^- , in an ion pair. This study is relatively unique because most work in mass spectrometry is concerned with the observations of positive ions formed by processes such as $\text{M} + \text{e}^- \longrightarrow \text{M}^+ + 2\text{e}^-$ where M^+ is the molecular ion, or if fragmentation occurs,

$M + e^- \longrightarrow m^+ + n + 2e^-$ where m^+ is an ion-fragment and n is a neutral fragment.

Work carried out on the alkyl-substituted phosphines^{17,22,28} includes mass spectral cracking patterns and appearance potentials for the methyl and ethyl substituted compounds. Williams, Ward, and Cooks²⁹ have undertaken a somewhat more sophisticated study of some organo-phosphorus compounds. They have used deuterium labeling to study reactions induced by electron-impact in triphenylphosphine, triphenylphosphine oxide and methylenetriphenylphosphorane.

Other authors³⁰⁻³² have carried out mass spectral investigations of the fluoroalkyl and fluoroaryl derivatives of phosphorus in order to gain more information about molecular rearrangements and mechanisms for the transfer of fluorine from carbon to phosphorus. Miller³⁰ has examined the mass spectra of a series of pentafluorophenyl derivatives of phosphorus. Bond-forming rearrangements were observed such as the elimination of PF_2 from the $(C_6F_5)_2P^+$ species giving $(C_6F_4)_2^+$. Cavell and Dobbie^{31,32} have observed extensive rearrangement and transfer of fluorine during the fragmentation of the trifluoromethylphosphines.

The mass spectra of the dimethylaminohalophosphines are of particular interest because of recent investigations which have demonstrated the ability of the phosphorus atom to act as a Lewis base in the presence of various electron acceptors. Difluorochlorophosphine¹ has been prepared by allowing hydrogen chloride to react with dimethylaminodifluorophosphine, $(CH_3)_2NPF_2$. Difluorobromophosphine¹ has been prepared in a similar manner.

The coordination chemistry of dimethylaminodifluorophosphine has been studied by several authors. Ter Haar and Sr. Fleming³³ have shown that this ligand will displace carbon monoxide from B_4H_8CO to form $B_4H_8[(CH_3)_2NPF_2]$. Schmutzler³⁴ has prepared $Ni[(CH_3)_2NPF_2]_4$ and $Mo(CO)_3[(CH_3)_2NPF_2]_3$ by a similar displacement of CO from metal carbonyls. Both Cavell and Sr. Fleming³⁶ have independently reported the addition of BF_3 to $(CH_3)_2NPF_2$ in a 1:1 ratio.

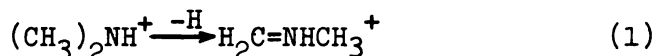
Cohn and Parry³⁷ have prepared two new coordination compounds, $CuCl[(CH_3)_2NPF_2]$ and $CuCl[(CH_3)_2NPF_2]_2$ by allowing the ligand to react with anhydrous copper (I) chloride. The infrared and nmr spectra of these compounds suggest that bonding occurs through the phosphorus atom rather than the nitrogen atom³⁷. A single crystal X-ray diffraction study by Douglas and Nordman⁹ has established that the coordinate bond is formed through phosphorus in $B_4H_8[(CH_3)_2NPF_2]$.

Cohn and Parry³⁷ have postulated that the Lewis basicity of the phosphorus atom in the ligand is enhanced by donation of the nitrogen electron pair to the empty phosphorus d orbitals. A recent nmr study of chloro(dimethylamino)phenylphosphine³⁸ has shown restricted rotation around the phosphorus-nitrogen bond. Rotational barriers in the order of 12 kcal/mol for P-N bonds³⁸ are too large to be attributed to conformational effects of the kind operating in ethane or methylamine. For this reason Cowley, Dewar, and Jackson³⁸ suggest that the barrier might be attributed to a lone-pair — lone-pair interaction.

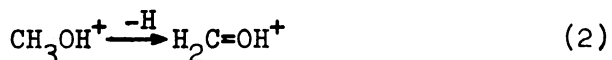
RESULTS AND DISCUSSION

GENERAL

A brief discussion of the mass spectral fragmentation patterns of alkyl amines is advantageous at this point because 1) several of the phosphines discussed herein contain dimethylamino substituents and 2) phosphorus and nitrogen possess chemical similarities, both being Group V elements. Gohlke and McLafferty³⁹ have shown that the mass spectra of a number of aliphatic amines may be correlated with certain structural features. Amines which contain alkyl groups larger than methyl undergo cleavage of the carbon-carbon bond adjacent to nitrogen. This cleavage, in which the largest possible group is lost preferentially, provides the base peak (or most abundant ion) in the spectrum. The intensity of the molecular ion decreases regularly with increasing molecular weight. The hydrogen radical is eliminated only when no other alternative exists. The base peak in the mass spectrum of dimethylamine³⁹ (Table IV) has a mass-to-charge (m/e) ratio of $M-1$ where M is the mass of the molecular ion. The positive charge is stabilized on the nitrogen via the formation of an immonium ion (eqn 1).



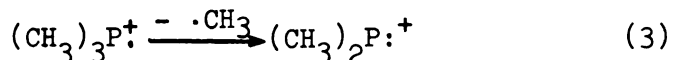
This stabilization of the positive charge by the heteroatom is not unique to the amines. Aliphatic alcohols eliminate a hydrogen radical to form the stable oxonium ion⁴⁰. The base peak in the mass spectrum of methanol (eqn 2) corresponds to the $M-1$ ion. McLafferty⁴¹ points



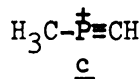
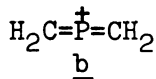
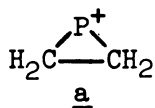
out that the even electron fragment, whether ion or neutral generally has the greater stability and therefore exerts the greater influence on the

the course of the degradation reaction. In the aliphatic thioethers there is an increased tendency toward cleavage of the carbon-sulfur bond with charge retention on sulfur. According to Budzikiewicz, Djerassi, and Williams⁴² this is because sulfur has a greater ability than oxygen to stabilize the electron deficiency by participation of inner shell electrons.

Examination of the mass spectra of the alkyl-substituted phosphines shows a more pronounced cleavage of the carbon-heteroatom bond (as compared to the amines) because of the greater ability of phosphorus to accommodate an electron sextet⁴³. Loss of a methyl group provides the base peak in the spectrum of trimethylphosphine²⁸ (eqn 3).



The second strongest peak in the spectrum of trimethylphosphine is an ion of mass 59. This ion, which is also present in the spectra of other alkylphosphines, may be represented as a cyclic phosphiran structure a, or as a linear phosphonium ion b or c¹⁷. It is analogous to the immonium ion observed at m/e 42 in the spectrum of trimethylamine⁴⁴.



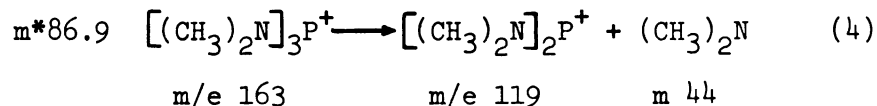
The main process in the fragmentation of the ethylphosphines is not the loss of a methyl radical as is the case with the analogous amines. Instead, the main cleavage involves the elimination of ethylene via a rearrangement in which a phosphorus-hydrogen bond is formed²⁸. Budzikiewicz, Djerassi, and Williams⁴⁵ suggest that the formation of a phosphonium ion is not as favored as the formation of the analogous immonium species, probably because of better stabilization of the electron deficiency by phosphorus through participation of the d-shell. This

hypothesis is supported by the abundance of ions of the type H_3CP^+ , H_2CP^+ and HCP^+ in the mass spectra of the methyl phosphines¹⁷ and their higher homologs²⁸.

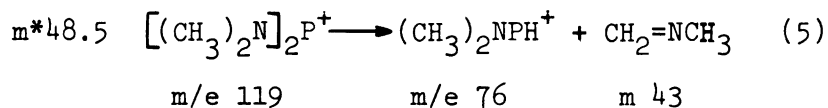
TRIS(DIMETHYLAMINO)PHOSPHINE

Upon examination of the mass spectrum of tris(dimethylamino)phosphine (Table V) a high abundance of two types of positive ions is apparent. The first type is the group of immonium ions with the positive charge stabilized by nitrogen, and the second is the group of disubstituted phosphorus ions of the general formula $:\text{PXY}^+$ where X may or may not be identical to Y. The predominance of these two types of ions supports the hypothesis⁴⁵ that the stabilization of the electron deficiency by phosphorus is through participation of the d-shell rather than the formation of a phosphonium ion.

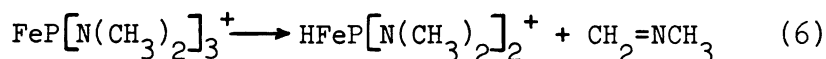
Strong evidence for two metastable transitions* in the mass spectrum of tris(dimethylamino)phosphine was observed. The first of these transitions (eqn 4) results in the formation of the ion at m/e 119. The metastable peak occurs at m/e 86.9 and was calculated to be at m/e 86.9. The process which results in the formation of the ion at m/e 76 (eqn 5) involves a 1-3 hydrogen shift to phosphorus. The metastable peak was observed at m/e 48.6 and was calculated to be at m/e 48.5. This data is in agreement with the observations of others⁴⁷.



* A metastable peak occurs when an ion of mass m_0 dissociates into a daughter ion of lower mass m and a neutral fragment n between the ion repeller plate and the magnetic field⁴⁶. The mass-to-charge ratio of the metastable peak m^* is given by $m^* = m^2/m_0$.



Braterman¹⁰ in a study of transition metal carbonyl derivatives of tris(dimethylamino)phosphine, has observed a similar rearrangement with a 1-4 hydrogen transfer to the metal (eqn 6).



The peak at m/e 60 in the spectrum of $[(\text{CH}_3)_2\text{N}]_3\text{P}$ is of interest because of its relatively high intensity. This ion can best be represented as $\text{CH}_2=\text{NPH}^+$. The process which gives rise to this fragment is unknown. One possibility is the elimination of a neutral CH_4 group from the ion at m/e 76, however there is no metastable evidence for such a transition.

It is difficult to pinpoint the center of positive charge in the phosphorus containing ion; it seems likely that there is a sharing of the electron deficiency between the phosphorus and nitrogen atoms. The relatively high abundance of the immonium ion species suggests that during fragmentation, the amine nitrogen can accommodate the electron deficiency nearly as well as phosphorus.

THE BIS(DIMETHYLAMINO)HALOPHOSPHINES

The mass spectral data for this series of compounds has been summarized in Tables I and II. The most important ions have been tabulated according to relative intensity and percent total ionization. Comparison of the data in this way shows trends which are indicative of the relative stabilities of each of the molecules to electron-impact.

The mass spectrum of $[(\text{CH}_3)_2\text{N}]_2\text{PF}$ exhibits features which make it unique among the spectra of the bis(dimethylamino)halophosphines. The number of different ion fragments is small compared to the number in the

spectra of the chloro and bromo compounds. Occuring in the spectrum of the fluorophosphine are two fragments of the type $(\text{CH}_3)_2\text{NPX}_2^+$ and PX_2^+ , which could not have arisen from simple fragmentation of the parent molecule. These ions, which do not occur in the spectra of the other two compounds, could have been formed by an ion-radical reaction involving atomic fluorine or they could have occurred by disproportionation of the original compound in the heated ion source. The PF_2^+ ion has been shown to be an extremely stable species formed by rearrangement in the spectra of the fluoroalkyl^{31,32} and fluorophenylphosphines³⁰.

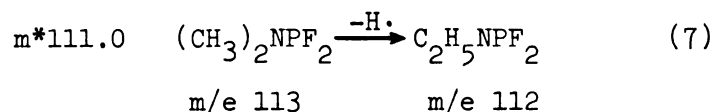
The most abundant ion in the spectrum of each of the bis(dimethylamino)phosphines is a disubstituted phosphorus fragment of the type $:\text{PXY}^+$, where $\text{X}=\text{Y}=(\text{CH}_3)_2\text{N}$ for the bromo compound. There is a higher abundance of immonium type ions in the spectra of the fluoro and chloro compounds than in the spectrum of the bromo compound (see Table II). Conversely there is a higher percentage of phosphorus containing ions in the spectrum of the bromophosphine.

The ion represented by the general formula $(\text{CH}_3)_2\text{NPX}^+$ is of interest because it occurs in the spectrum of the fluorophosphine in a very high abundance. The percentage of this ion decreases sharply in the chloro compound and reaches a minimum in the bromo compound. This evidence suggests that there is a decrease in stability to electron-impact of the bis(dimethylamino)halophosphines as the atomic weight of the substituted halogen increases.

THE DIMETHYLAMINODIHALOPHOSPHINES

As would be expected, this series of compounds shows a higher abundance of fragments which contain phosphorus and halogen only (see Table II). In contrast to the bis(dimethylamino)halophosphines,

there are few fragments without a halogen which contain an amino group attached to phosphorus. Again the fluorine containing compound shows a considerably lower number of different positive ion fragments than the analogous dichloro and dibromophosphines. In contrast to the series of bis(dimethylamino)halophosphines, $(\text{CH}_3)_2\text{NPF}_2$ is the only member of the dihalophosphine series which shows a metastable transition (eqn 7).



The metastable peak was observed at $m/e \ 111.0$ and was calculated to be at $m/e \ 111.0$. This evidence suggests that the difluoro compound is the most stable to electron-impact of any of the other aminohalophosphines considered. It should be noted that the peak at $m/e \ 112$ arising from the metastable transition (eqn 7) is equally as intense as the molecular ion, M , at $m/e \ 113$. This suggests that when the molecule is subjected to electron-impact, the preferred method of accommodating the electron deficiency involves the elimination of a hydrogen radical with charge stabilization by an immonium nitrogen. This results in considerably less fragmentation of the M and $M-1$ ions.

There are other trends in the series of dimethylaminodihalophosphines which are important. The PX_3^+ type fragment is absent in the spectrum of the difluorophosphine, however this ion is present in low abundance in the spectra of the other two compounds. This suggests that the possibility of recombination (or disproportionation) is greater for the dichloro and dibromophosphines than for the difluoro compound. (Again the heated ion source may be responsible for this.) The abundance of the ion with the general formula $(\text{CH}_3)_2\text{NPX}^+$ increases with increasing atomic weight of the halogen substituent (Table II). This is in direct contrast to the

behavior of the bis(dimethylamino)halophosphines. The decreasing abundance of the molecular ion with increasing molecular weight further suggests that the dichloro and dibromo compounds are considerably less stable to electron-impact than is the difluoro compound. This conclusion is in agreement with the data calculated by Farran⁷ (Table III) for the phosphorus-halogen force constants in compounds of the general formula $(\text{CH}_3)_2\text{NPX}_2$. Mass spectral data for the phosphorus trihalides are included in Tables I and II for purposes of comparison.

The mass spectrum of dimethylaminotetrafluorophosphorane is reported in Table XV. This compound is of interest because of its similarity to dimethylaminodifluorophosphine and because of its unusual stability to electron-impact. Miller³⁰ has observed no molecular ions in the mass spectra of such compounds as $(\text{C}_6\text{F}_5)_3\text{PCl}_2$ and $(\text{C}_6\text{F}_5)_2\text{PCl}_3$ even after reduction of the ionizing voltage from 70 to 40 eV. Kennedy and Payne⁴⁸ detected a very weak molecular ion peak in the spectrum of PF_3Cl_2 at an ionizing voltage of 15 eV. Rogowski and Cohn⁴⁹ observed no molecular ions in the spectra of PF_4Cl and PF_4Br at 56 eV. Demitras and MacDiarmid⁵⁰, however have reported a molecular ion peak at m/e 151 with a relative intensity of 19% in the mass spectrum of $(\text{CH}_3)_2\text{NPF}_4$. This compares well with the results of this work in which the molecular ion in the spectrum of $(\text{CH}_3)_2\text{NPF}_4$ had a intensity of 19.5% relative to the PF_4^+ base peak.

THE METHYLDIHALOPHOSPHINES

The mass spectra of CH_3PF_2 and CH_3PCl_2 are reported in Tables XVI and XVII respectively. As might be expected, the base peak in both of these spectra is the PX_2^+ ion. The molecular ion in each spectrum has a relative intensity of 42 - 43% of the base peak. The majority of the

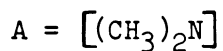
TABLE I
RELATIVE INTENSITIES OF PRINCIPAL IONS*

$$A = [(\text{CH}_3)_2\text{N}]$$

ION	A ₃ P	A ₂ PF	A ₂ PCl	A ₂ PBr	APF ₂	APCl ₂	APBr ₂	PF ₃	PCl ₃	PBr ₃
$[(\text{CH}_3)_2\text{N}]_3\text{P}^+$	27.5									
$[(\text{CH}_3)_2\text{N}]_2\text{P}^+$	100.0		34.4	100.0						
$(\text{CH}_3)_2\text{NHP}^+$	97.7	2.6	44.7	84.3						
CH_3NP^+	41.8	5.1	36.0	44.2		11.9	17.3			
$(\text{CH}_3)_2\text{N}^+$	85.5	31.7	39.6	21.3	4.0	17.0	18.8			
$(\text{CH}_2)_2\text{N}^+$	33.7	42.7	45.5	41.6	100.0	78.1	43.4			
CH_3^+	47.4	34.3	41.2	38.8	32.4	54.8	25.7			
$[(\text{CH}_3)_2\text{N}]_2\text{PX}^+$		19.7	36.9	6.0						
$(\text{CH}_3)_2\text{NPX}^+$		100.0	100.0	26.8	12.2	100.0	100.0			
$(\text{CH}_3)_2\text{NPX}_2^+$		6.5			54.1	37.9	7.8			
P^+			2.7	5.6	2.0	19.2	8.8	7.1	13.3	33.9
PX^+		3.5		9.9	6.4	19.5	14.5	9.3	14.9	29.7
PX_2^+		4.7			29.1	67.7	10.3	100.0	100.0	100.0
PX_3^+						22.1	3.3	46.7	41.6	65.0
X^+						20.0	9.4		22.3	71.6

* Peaks representing ions which differ only in isotopic composition are summed for the purposes of this table. If the intensity of the base peak is affected, the intensities of the other peaks are normalized accordingly.

TABLE II

PERCENT TOTAL IONIZATION^o OF PRINCIPAL IONS*

ION	A ₃ P	A ₂ PF	A ₂ PCl	A ₂ PBr	APF ₂	APCl ₂	APBr ₂	PF ₃	PCl ₃	PBr ₃
$[(\text{CH}_3)_2\text{N}]_3\text{P}^+$	6.3									
$[(\text{CH}_3)_2\text{N}]_2\text{P}^+$	<u>23.1</u>		9.0	<u>26.4</u>						
$(\text{CH}_3)_2\text{NHP}^+$	22.5	1.0	11.7	22.1						
CH_3NP^+	9.6	2.0	9.4	11.7		2.7	6.7			
$(\text{CH}_3)_2\text{N}^+$	19.7	12.6	10.4	5.6	1.7	3.8	7.3			
$(\text{CH}_2)_2\text{N}^+$	7.8	17.0	11.9	11.0	<u>41.6</u>	17.4	16.7			
CH_3	10.9	13.7	10.8	10.2	13.5	12.2	9.9			
$[(\text{CH}_3)_2\text{N}]_2\text{PX}^+$		7.9	9.7	1.6						
$(\text{CH}_3)_2\text{NPX}^+$		<u>39.8</u>	<u>26.3</u>	7.1	5.1	<u>22.3</u>	<u>38.6</u>			
$(\text{CH}_3)_2\text{NPX}_2^+$		2.6			22.5	8.4	3.0			
P^+			0.7	1.5	0.8	4.3	3.4	4.6	6.9	11.3
PX^+		1.4		2.6	2.7	4.4	5.6	5.7	7.8	9.9
PX_2^+		1.9			12.1	15.1	4.0	<u>61.3</u>	<u>52.1</u>	<u>33.3</u>
PX_3^+						4.9	1.3	28.7	21.7	21.6
X^+						4.5	3.6		11.6	23.9

^o Defined as $\sum(\text{Int})_n$ where n includes only those ions appearing in the table.

* Base peak is underlined.

remaining fragments are of the PXY^+ type mentioned previously. There is a low abundance of phosphonium type ions in both spectra.

TABLE III

Stretching Force Constants from Normal
Coordinate Calculations for Molecules
of the Type $(CH_3)_2NPX_2$ ⁷

Bond	Force Constant - mdynes/A
P-N	6.5 ± 0.8
P-F	4.0 ± 0.4
P-Cl	1.7 ± 0.2
P-Br	0.85 ± 0.09

THE SUBSTITUTED DIFLUOROPHOSPHINES

The mass spectra of PF_2Cl and PF_2Br are reported in Tables XVIII and XIX respectively. The base peak in both of these spectra corresponds to the PF_2^+ ion. Both compounds showed recombination (or disproportionation) to give a relatively high abundance of PF_3^+ . The presence in low abundance of ions containing both oxygen and hydrogen indicate that a small amount of hydrolysis occurred. This probably took place in the inlet system of the mass spectrometer, since vapor pressure measurements showed less than 1% impurity in the compounds.

The mass spectrum of PF_2I has been reported by Rudolph⁵¹ (Table XX). The molecular ion provides the base peak in the spectrum of this compound. Because this spectrum was obtained with the same type of instrument and at the same ionizing voltage as the other compounds in this series, a comparison of the spectra of the three substituted difluorohalophosphines can be made.

The molecular ion in the spectrum of PF_2Br has a higher relative intensity than the molecular ion in the spectrum of PF_2Cl . The PF_2^+ ion in the spectrum of PF_2I has a relative intensity of 60% of the PF_2I^+

base peak. The PF_3^+ recombination peak in the spectra of the three phosphines shows a decrease in relative intensity as the molecular weight of the compound increases. This data suggests that there is an increase in stability to electron-impact of the difluorohalophosphines with increasing molecular weight. This represents a reversal of the trend shown in the series of dimethylaminohalophosphines.

The mass spectra of difluorophosphine and cyanodifluorophosphine have also been reported by Rudolph⁵¹. These are included in Tables XXI and XXII respectively. The base peak in the spectrum of PHF_2 corresponds to the molecular ion, however PF_2^+ provides the base peak in the spectrum of PF_2CN .

SUGGESTIONS FOR FUTURE WORK

Other investigations which would enlarge the scope of this work can be recommended. Determination of the appearance potentials of key positive ions in the spectra of the compounds discussed would provide a quantitative basis for calculation of the ionization potentials and heats of formation of the ions. In this way the stabilities of the molecules to electron-impact could be more rigorously compared. Studies of the negative-ion spectra of these compounds would provide information concerning ion pair production. Investigations of ion-molecule reactions in a mass spectrometer could lead to the proposal of mechanisms for the formation of ions by recombination. Because thermal effects in the heated ion source of a mass spectrometer can cause errors in data interpretation⁵², studies could be conducted which would determine the nature and extent of thermal reactions in the substituted phosphines.

DATA AND EXPERIMENTAL

INSTRUMENTATION AND PURITY OF COMPOUNDS

All mass spectra were determined with a Consolidated Electrodynamics Corporation Model 21-103C mass spectrometer using the gas inlet system and a nominal source pressure of 4×10^{-5} torr. The ion-source temperature was 250° C. The ionizing voltage used was 70 eV.

The purity of all compounds with boiling points above 25° C was determined to be greater than 99% by vapor-phase chromatography. The instrument used was an Aerograph Model A90-P3 with Sargent Recorder SR. The column was 5' x $\frac{1}{4}$ " packed with 20% SE-30 on Chromosorb W.

The purity of all compounds with boiling points below 25° C was determined to be greater than 99% on the basis of vapor pressure data.

PREPARATION OF COMPOUNDS

The compounds discussed were prepared, purified, and characterized by the most convenient literature methods, some with slight modifications which are noted herein. The tris(dimethylamino)phosphine was prepared by the method of Burg and Slota². A minor modification of the method involved the addition of the dimethylamine through a dry ice condenser into the reaction flask containing phosphorus trichloride dissolved in ether.

The bis(dimethylamino)chlorophosphine was prepared by the method of Nöth and Vetter⁴. The bis(dimethylamino)fluorophosphine was prepared by fluorinating $[(CH_3)_2N]_2PCl$ using zinc difluoride. The method was adapted from a description of the preparation of $(CH_3)NPF_2$ by Nöth and Vetter⁵. The bis(dimethylamino)bromophosphine and dimethylaminodibromophosphine were prepared as described by Nöth and Vetter⁴.

Dimethylaminodichlorophosphine, dimethylaminodifluorophosphine, difluorochlorophosphine and difluorobromophosphine were all prepared by the methods of Morse, Cohn, Rudolph and Parry¹.

The methylchlorophosphine was obtained from The Department of the Army, U.S. Army Edgewood Arsenal, Edgewood Arsenal, Maryland. This compound was redistilled before use to assure maximum purity. The methyltrifluorophosphine was prepared by the method of Seel, Rudolph, and Budenz⁶.

DATA

The mass spectra are tabulated according to the relative intensities of the ions based on the most abundant ion in the spectrum. All the ions with greater than 2% relative intensity are reported. In some cases ions of special interest with relative intensities below 2% are reported.

TABLE IV

MASS SPECTRUM OF DIMETHYLAMINE

m/e	Relative Intensity			Assignment
	This Work	Others ^a	Others ^b	
15	17.5	20	0	CH ₃ ⁺
18	17.2	16	14	NH ₄ ⁺
27	6.0	8	3	
28	47.3	68	26	N ₂ ⁺
29	3.0		2	
30	7.5	13	4	CH ₂ NH ₂ ⁺
39	2.3			
40	4.7			
41	4.2		3	
42	15.3	19	15	C ₂ H ₄ N ⁺
43	12.3	14	13	C ₂ H ₅ N ⁺
44	100.0	100	100	C ₂ H ₆ N ⁺
45	53.9	51	56	C ₂ H ₇ N ⁺

^a See reference 53.

^b See reference 39.

TABLE V

MASS SPECTRUM OF TRIS(DIMETHYLAMINO)PHOSPHINE

m/e	Relative Intensity	Assignment
15	47.4	CH_3^+
17	3.3	
18	21.2	$\text{NH}_4^+, \text{H}_2\text{O}^+$
27	7.2	
28	54.3	N_2^+
29	3.6	
30	15.0	$\text{CH}_2\text{NH}_2^+, \text{CH}_2\text{NPH}^{++}$
32	3.3	
33	3.9	
39	2.2	
40	5.0	
41	5.8	
42	33.7	$\text{C}_2\text{H}_4\text{N}^+$
43	13.6	$\text{C}_2\text{H}_5\text{N}^+$
44	85.5	$\text{C}_2\text{H}_6\text{N}^+$
45	37.9	$\text{C}_2\text{H}_7\text{N}^+$
46	3.6	
47	4.7	
59	3.8	
60	41.8	CH_2NPH^+
61	2.4	

TABLE V (Continued)

MASS SPECTRUM OF TRIS(DIMETHYLAMINO)PHOSPHINE

m/e	Relative Intensity	Assignment
74	2.2	$\text{C}_2\text{H}_5\text{NP}^+$
75	11.1	$(\text{CH}_3)_2\text{NP}^+$
76	97.7	$(\text{CH}_3)_2\text{NPH}^+$
77	2.9	$(\text{CH}_3)_2\text{NPH}_2^+$
81.5	3.6	$[(\text{CH}_3)_2\text{N}]_3\text{P}^{++}$
94	3.7	
110	4.4	
119	100.0	$[(\text{CH}_3)_2\text{N}]_2\text{P}^+$
120	5.5	$[(\text{CH}_3)_2\text{N}]_2\text{PH}^+$
163	27.5	$[(\text{CH}_3)_2\text{N}]_3\text{P}^+$
164	2.2	$[(\text{CH}_3)_2\text{N}]_2\text{PH}^+$

Metastable peaks

m* 48.5 (see eqn 5 page 8)

m* 86.9 (see eqn 4 page 7)

TABLE VI

MASS SPECTRUM OF BIS(DIMETHYLAMINO)FLUOROPHOSPHINE

m/e	Relative Intensity	Assignment
15	34.3	CH_3^+
16	2.1	
17	19.5	
18	77.8	$\text{NH}_4^+, \text{H}_2\text{O}^+$
27	2.6	
28	13.4	N_2^+
29	2.0	
30	16.2	$\text{CH}_2\text{NH}_2^+, \text{CH}_2\text{NPH}^{++}$
40	2.6	
41	4.0	
42	42.7	$\text{C}_2\text{H}_4\text{N}^+$
43	5.9	$\text{C}_2\text{H}_5\text{N}^+$
44	31.7	$\text{C}_2\text{H}_6\text{N}^+$
45	2.6	$\text{C}_2\text{H}_7\text{N}^+$
50	3.5	PF^+
51	6.1	PHF^+
60	5.1	CH_2NPH^+
65	5.2	$(\text{CH}_3)_2\text{NH} \cdot \text{HF}^+ ?$
69	4.7	PF_2^+
76	2.6	$(\text{CH}_3)_2\text{NPH}^+$

TABLE VI (Continued)

MASS SPECTRUM OF BIS(DIMETHYLAMINO)FLUOROPHOSPHINE

m/e	Relative Intensity	Assignment
78	7.6	CH_2NPF^+
80	1.7	
93	7.0	$\text{C}_2\text{H}_5\text{NPF}^+$
94	100.0	$(\text{CH}_3)_2\text{NPF}^+$
95	5.2	$(\text{CH}_3)_2\text{NPHF}^+$
112	6.3	$\text{C}_2\text{H}_5\text{NPF}_2^+$
113	6.5	$(\text{CH}_3)_2\text{NPF}_2^+$
138	19.7	$[(\text{CH}_3)_2\text{N}]_2\text{PF}^+$

TABLE VII

MASS SPECTRUM OF BIS(DIMETHYLAMINO)CHLOROPHOSPHINE

m/e	Relative Intensity	Assignment
15	54.2	CH_3^+
18	6.6	$\text{NH}_4^+, \text{H}_2\text{O}^+$
27	3.5	
28	25.8	N_2^+
30	12.6	$\text{CH}_2\text{NH}_2^+, \text{CH}_2\text{NPH}^{++}$
31	3.5	P^+
32	5.4	
33	6.6	
36	2.8	
40	3.5	
41	6.0	
42	59.8	$\text{C}_2\text{H}_4\text{N}^+$
43	9.4	$\text{C}_2\text{H}_5\text{N}^+$
44	52.0	$\text{C}_2\text{H}_6\text{N}^+$
45	8.2	$\text{C}_2\text{H}_7\text{N}^+$
46	4.4	
47	6.3	
58	2.3	
59	7.8	CH_2NP^+
60	47.3	CH_2NPH^+
67	4.1	

TABLE VII (Continued)

MASS SPECTRUM OF BIS(DIMETHYLAMINO)CHLOROPHOSPHINE

m/e	Relative Intensity	Assignment
69	2.2	
74	2.6	$C_2H_5NP^+$
75	13.5	$(CH_3)_2NP^+$
76	58.8	$(CH_3)_2NPH^+$
77	2.6	$(CH_3)_2NPH_2^+$
81	3.1	$(CH_3)_2NH \cdot H^{35}Cl^+ ?$
94	6.1	$CH_2NP^{35}Cl^+$
96	2.4	$CH_2NP^{37}Cl^+$
109	5.4	$C_2H_5NP^{35}Cl^+$
110	100.0	$(CH_3)_2NP^{35}Cl^+$
111	2.4	$C_2H_5NP^{37}Cl^+$
112	31.4	$(CH_3)_2NP^{37}Cl^+$
119	45.5	$[(CH_3)_2N]_2P^+$
120	2.6	$[(CH_3)_2N]_2PH^+$
154	36.5	$[(CH_3)_2N]_2P^{35}Cl^+$
156	12.0	$[(CH_3)_2N]_2P^{37}Cl^+$

Metastable peak

m* 48.5 (see eqn 5 page 8)

TABLE VIII

MASS SPECTRUM OF BIS(DIMETHYLAMINO)BROMOPHOSPHINE

m/e	Relative Intensity	Assignment
15	38.8	CH_3^+
18	4.5	$\text{NH}_4^+, \text{H}_2\text{O}^+$
27	2.9	
28	17.5	
30	8.0	$\text{CH}_2\text{NH}_2^+, \text{CH}_2\text{NPH}^{++}$
31	5.6	P^+
32	4.3	
33	5.9	
40	2.7	
41	5.1	
42	41.6	$\text{C}_2\text{H}_4\text{N}^+$
43	6.2	$\text{C}_2\text{H}_5\text{N}^+$
44	21.3	$\text{C}_2\text{H}_6\text{N}^+$
45	5.9	$\text{C}_2\text{H}_7\text{N}^+$
46	3.8	
47	6.2	
59	7.3	CH_2NP^+
60	44.2	CH_2NPH^+
74	2.9	$\text{C}_2\text{H}_5\text{NP}^+$
75	15.9	$(\text{CH}_3)_2\text{NP}^+$

TABLE VIII (Continued)

MASS SPECTRUM OF BIS(DIMETHYLAMINO)BROMOPHOSPHINE

m/e	Relative Intensity	Assignment
76	84.3	$(\text{CH}_3)_2\text{NPH}^+$
77	2.4	$(\text{CH}_3)_2\text{NPH}_2^+$
85	2.9	
94	2.9	
110	7.2	P^{79}Br^+
112	2.7	P^{81}Br^+
119	100.0	$[(\text{CH}_3)_2\text{N}]_2\text{P}^+$
120	5.3	$[(\text{CH}_3)_2\text{N}]_2\text{PH}^+$
124	7.7	
154	13.4	$(\text{CH}_3)_2\text{NP}^{79}\text{Br}^+$
156	13.4	$(\text{CH}_3)_2\text{NP}^{81}\text{Br}^+$
198	3.0	$[(\text{CH}_3)_2\text{N}]_2\text{P}^{79}\text{Br}^+$
200	3.0	$[(\text{CH}_3)_2\text{N}]_2\text{P}^{81}\text{Br}^+$

Metastable peak

$m^* 48.5$ (see eqn 5 page 8)

TABLE IX

MASS SPECTRUM OF DIMETHYLAMINODIFLUOROPHOSPHINE

m/e	Relative Intensity	Assignment
15	32.4	CH_3^+
18	4.4	$\text{NH}_4^+, \text{H}_2\text{O}^+$
27	2.5	
28	31.1	N_2^+
30	3.8	CH_2NH_2^+
31	2.0	P^+
32	7.1	
40	4.5	
41	5.6	
42	100.0	$\text{C}_2\text{H}_4\text{N}^+$
43	10.2	$\text{C}_2\text{H}_5\text{N}^+$
44	4.0	$\text{C}_2\text{H}_6\text{N}^+$
50	6.4	PF^+
51	3.5	$\text{CH}_3\text{NH}_2 \cdot \text{HF}^+ ?$
65	2.0	$(\text{CH}_3)_2\text{NH} \cdot \text{HF}^+ ?$
69	29.1	PF_2^+
78	3.2	CH_2NPF^+
94	12.2	$(\text{CH}_3)_2\text{NPF}^+$
112	54.1	$\text{C}_2\text{H}_5\text{NPF}_2^+$
113	54.1	$(\text{CH}_3)_2\text{NPF}_2^+$

Metastable peak

m* 111 (see eqn 7 page 10)

TABLE X

MASS SPECTRUM OF DIMETHYLAMINODICHLOROPHOSPHINE

m/e	Relative Intensity	Assignment
15	70.2	CH_3^+
18	9.1	$\text{NH}_4^+, \text{H}_2\text{O}^+$
26	2.5	
27	6.3	
28	25.6	N_2^+
29	3.2	
30	17.2	$\text{CH}_2\text{NH}_2^+, \text{CH}_2\text{NPH}^{++}$
31	24.6	P^+
32	7.7	
33	6.0	
35	19.3	$^{35}\text{Cl}^+$
36	15.1	H^{35}Cl^+
37	6.3	$^{37}\text{Cl}^+$
38	5.3	H^{37}Cl^+
39	3.2	
40	6.0	
41	9.1	
42	100.0	$\text{C}_2\text{H}_4\text{N}^+$
43	29.1	$\text{C}_2\text{H}_5\text{N}^+$
44	21.8	$\text{C}_2\text{H}_6\text{N}^+$
45	8.1	$\text{C}_2\text{H}_7\text{N}^+$
46	3.2	$\text{C}_2\text{H}_8\text{N}^+$
47	4.6	
50	2.5	
58	3.8	CHNP^+
59	4.5	CH_2NP^+
60	15.3	CH_2NPH^+
61	2.0	CH_3NPH^+
66	18.5	P^{35}Cl^+

TABLE X (Continued)
 MASS SPECTRUM OF DIMETHYLAMINODICHLOROPHOSPHINE

m/e	Relative Intensity	Assignment
67	5.9	$\text{HP}^{35}\text{Cl}^+$
68	6.5	P^{37}Cl^+
69	3.1	$\text{HP}^{37}\text{Cl}^+$
81	4.8	
85	5.2	
94	10.5	
101	49.0	$\text{P}^{35}\text{Cl}_2^+$
103	32.2	$\text{P}^{35}\text{Cl}^{37}\text{Cl}^+$
105	5.4	$\text{P}^{37}\text{Cl}_2^+$
109	2.5	
110	96.9	$(\text{CH}_3)_2\text{NP}^{35}\text{Cl}^+$
111	3.4	$(\text{CH}_3)_2\text{NPH}^{35}\text{Cl}^+$
112	31.2	$(\text{CH}_3)_2\text{NP}^{37}\text{Cl}^+$
113	0.9	$(\text{CH}_3)_2\text{NPH}^{37}\text{Cl}^+$
129	3.2	
136	12.4	$\text{P}^{35}\text{Cl}_3^+$
138	11.7	$\text{P}^{35}\text{Cl}_2^{37}\text{Cl}^+$
140	3.8	$\text{P}^{35}\text{Cl}^{37}\text{Cl}_2^+$
142	0.4	$\text{P}^{37}\text{Cl}_3^+$
144	3.3	$\text{C}_2\text{H}_5\text{NP}^{35}\text{Cl}_2^+$
145	27.7	$(\text{CH}_3)_2\text{NP}^{35}\text{Cl}_2^+$
146	2.9	$\text{C}_2\text{H}_5\text{NP}^{35}\text{Cl}^{37}\text{Cl}^+$
147	17.8	$(\text{CH}_3)_2\text{NP}^{35}\text{Cl}^{37}\text{Cl}^+$
148	0.9	$\text{C}_2\text{H}_5\text{NP}^{37}\text{Cl}_2^+$
149	3.1	$(\text{CH}_3)_2\text{NP}^{37}\text{Cl}_2^+$

TABLE XI

MASS SPECTRUM OF DIMETHYLAMINODIBROMOPHOSPHINE

m/e	Relative Intensity	Assignment
15	50.2	CH_3^+
18	4.7	$\text{NH}_4^+, \text{H}_2\text{O}^+$
27	3.8	
28	21.3	N_2^+
29	2.2	
30	9.7	$\text{CH}_2\text{NH}_2^+, \text{CH}_2\text{NPH}^{++}$
31	17.2	P^+
32	7.8	
33	6.0	
36	2.5	
40	4.7	
41	8.2	
42	84.6	$\text{C}_2\text{H}_4\text{N}^+$
43	10.3	$\text{C}_2\text{H}_5\text{N}^+$
44	36.7	$\text{C}_2\text{H}_6\text{N}^+$
45	8.2	$\text{C}_2\text{H}_7\text{N}^+$
46	3.4	
47	5.0	
58	3.1	CHNP^+
59	7.9	CH_2NP^+
60	33.8	CH_2NPH^+
74	2.6	$\text{C}_2\text{H}_5\text{NP}^+$
75	11.0	$(\text{CH}_3)_2\text{NP}^+$
79	9.1	$^{79}\text{Br}^+$
81	9.3	$^{81}\text{Br}^+$
110	17.7	P^{79}Br^+
111	3.3	$\text{HP}^{79}\text{Br}^+$
112	10.6	P^{81}Br^+
113	3.2	$\text{HP}^{81}\text{Br}^+$

TABLE XI (Continued)
 MASS SPECTRUM OF DIMETHYLAMINODIBROMOPHOSPHINE

m/e	Relative Intensity	Assignment
125	2.5	
127	2.5	
154	100.0	$(\text{CH}_3)_2\text{NP}^{79}\text{Br}^+$
155	3.3	$(\text{CH}_3)_2\text{NPH}^{79}\text{Br}^+$
156	95.1	$(\text{CH}_3)_2\text{NP}^{81}\text{Br}^+$
157	2.8	$(\text{CH}_3)_2\text{NPH}^{81}\text{Br}^+$
189	5.3	$\text{P}^{79}\text{Br}_2^+$
191	9.9	$\text{P}^{79}\text{Br}^{81}\text{Br}^+$
193	4.8	$\text{P}^{81}\text{Br}_2^+$
233	4.0	$(\text{CH}_3)_2\text{NP}^{79}\text{Br}_2^+$
235	7.5	$(\text{CH}_3)_2\text{NP}^{79}\text{Br}^{81}\text{Br}^+$
237	3.7	$(\text{CH}_3)_2\text{NP}^{81}\text{Br}_2^+$
268	0.9	$\text{P}^{79}\text{Br}_3^+$
270	2.5	$\text{P}^{79}\text{Br}_2^{81}\text{Br}^+$
272	2.3	$\text{P}^{79}\text{Br}^{81}\text{Br}_2^+$
274	0.7	$\text{P}^{81}\text{Br}_3^+$

TABLE XII

MASS SPECTRUM OF PHOSPHORUS TRIFLUORIDE

m/e	Relative Intensity	Assignment
31	7.1	P^+
50	9.3	PF^+
69	100.0	PF_2^+
88	46.7	PF_3^+

TABLE XIII

MASS SPECTRUM OF PHOSPHORUS TRICHLORIDE

m/e	Relative Intensity	Assignment
31	23.4	P^+
35	29.8	$^{35}Cl^+$
37	9.3	$^{37}Cl^+$
66	19.3	$P^{35}Cl^+$
68	6.9	$P^{37}Cl^+$
101	100.0	$P^{35}Cl_2^+$
103	64.9	$P^{35}Cl^{37}Cl^+$
105	10.7	$P^{37}Cl_2^+$
136	32.0	$P^{35}Cl_3^+$
138	29.8	$P^{35}Cl_2^{37}Cl^+$
140	10.1	$P^{35}Cl^{37}Cl_2^+$
142	1.2	$P^{37}Cl_3^+$

TABLE XIV
MASS SPECTRUM OF PHOSPHORUS TRIBROMIDE

m/e	Relative Intensity	Assignment
31	67.8	P ⁺
79	72.2	⁷⁹ Br ⁺
81	71.1	⁸¹ Br ⁺
110	30.0	P ⁷⁹ Br ⁺
112	29.4	P ⁸¹ Br ⁺
189	51.1	P ⁷⁹ Br ₂ ⁺
191	100.0	P ⁷⁹ Br ⁸¹ Br ⁺
193	48.9	P ⁸¹ Br ₂ ⁺
268	17.2	P ⁷⁹ Br ₃ ⁺
270	48.9	P ⁷⁹ Br ₂ ⁸¹ Br ⁺
272	47.8	P ⁷⁹ Br ⁸¹ Br ₂ ⁺
274	16.1	P ⁸¹ Br ₃ ⁺

TABLE XV

MASS SPECTRUM OF DIMETHYLAMINOTETRAFLUOROPHOSPHORANE

m/e	Relative Intensity	Assignment
15	26.9	CH_3^+
17	3.0	
18	11.7	$\text{NH}_4^+, \text{H}_2\text{O}^+$
28	16.1	N_2^+
40	3.6	
41	4.2	
42	39.2	$\text{C}_2\text{H}_4\text{N}^+$
43	29.4	$\text{C}_2\text{H}_5\text{N}^+$
69	5.3	PF_2^+
88	4.1	PF_3^+
91	2.0	
107	100.0	PF_4^+
116	3.4	$\text{CH}_2\text{NPF}_3^+$
132	15.0	$(\text{CH}_3)_2\text{NPF}_3^+$
150	2.4	$(\text{C}_2\text{H}_5)\text{NPF}_4^+$
151	19.5	$(\text{CH}_3)_2\text{NPF}_4^+$

TABLE XVI

MASS SPECTRUM OF METHYLDIFLUOROPHOSPHINE

m/e	Relative Intensity		Assignment
	This Work	Others ^c	
15	8.7		CH_3^+
17	4.0		
18	14.0		$\text{NH}_4^+, \text{H}_2\text{O}^+$
28	2.3		N_2^+
31	4.8	0.8	P^+
44	5.6	17.6	HCP^+
45	11.5	5.2	H_2CP^+
50	6.3	1.9	PF^+
63	2.0	1.4	HCPF^+
65	10.2		H_3CPF^+
69	100.0	100.0	PF_2^+
83	5.0	4.9	H_2CPF_2^+
84	42.3	37.7	H_3CPF_2^+

^c See reference 6.

TABLE XVII

MASS SPECTRUM OF METHYLDICHLOROPHOSPHINE

m/e	Relative Intensity	Assignment
15	9.8	CH_3^+
18	3.1	$\text{NH}_4^+, \text{H}_2\text{O}^+$
28	4.0	N_2^+
31	10.7	P^+
35	15.0	$^{35}\text{Cl}^+$
36	43.8	H^{35}Cl^+
37	4.8	$^{37}\text{Cl}^+$
38	14.3	H^{37}Cl^+
43	5.5	CP^+
44	28.3	HCP^+
45	61.9	H_2CP^+
46	6.2	H_3CP^+
47	2.1	H_3CPH^+
66	13.0	P^{35}Cl^+
67	2.2	$\text{PH}^{35}\text{Cl}^+$
68	4.3	P^{37}Cl^+
79	5.5	$\text{CHP}^{35}\text{Cl}^+$
80	8.4	$\text{CH}_2\text{P}^{35}\text{Cl}^+$
81	29.8	$\text{CH}_3\text{P}^{35}\text{Cl}^+, \text{CHP}^{37}\text{Cl}^+$
82	3.6	$\text{CH}_2\text{P}^{37}\text{Cl}^+$
83	9.1	$\text{CH}_3\text{P}^{37}\text{Cl}$
101	100.0	$\text{P}^{35}\text{Cl}_2^+$
103	65.9	$\text{P}^{35}\text{Cl}^{37}\text{Cl}^+$
105	11.0	$\text{P}^{37}\text{Cl}_2^+$
116	43.4	$\text{CH}_3\text{P}^{35}\text{Cl}_2^+$
118	28.1	$\text{CH}_3\text{P}^{35}\text{Cl}^{37}\text{Cl}^+$
120	4.6	$\text{CH}_3\text{P}^{37}\text{Cl}_2^+$

TABLE XVIII

MASS SPECTRUM OF DIFLUOROCHLOROPHOSPHINE

m/e	Relative Intensity	Assignment
18	3.7	H_2O^+
19	5.7	F^+
25	10.1	PF^{++}
28	29.2	N_2^+
31	7.7	P^+
32	9.1	$\text{O}_2^+ ?$
34.5	3.0	PF_2^{++}
35	6.7	$^{35}\text{Cl}^+$
36	14.4	H^{35}Cl^+
37	2.3	$^{37}\text{Cl}^+$
38	4.7	H^{37}Cl^+
44	6.4	PF_3^{++}
47	3.7	PO^+
50	11.1	PF^+
66	2.4	POF^+
67	2.4	HPOF^+
69	100.0	PF_2^+
85	7.9	$\text{PF}^{35}\text{Cl}, \text{POF}_2^+$
86	5.1	HPOF_2^+
87	2.2	$\text{PF}^{37}\text{Cl}^+$
88	30.6	PF_3^+
104	11.5	$\text{PF}_2^{35}\text{Cl}^+$
106	3.9	$\text{PF}_2^{37}\text{Cl}^+$

TABLE XIX

MASS SPECTRUM OF DIFLUOROBROMOPHOSPHINE

m/e	Relative Intensity	Assignment
15	2.2	CH_3^+
19	4.4	F^+
25	5.8	PF^{++}
28	15.0	N_2^+
31	7.8	P^+
32	2.8	$\text{O}_2^+ ?$
34.5	2.2	PF_2^{++}
44	4.7	PF_3^{++}
47	6.9	PO^+
50	13.0	PF^+
66	3.0	POF^+
67	5.1	HPOF^+
69	100.0	PF_2^+
79	6.1	$^{79}\text{Br}^+$
81	6.0	$^{81}\text{Br}^+$
85	9.0	POF_2^+
86	9.2	HPOF_2^+
88	23.0	PF_3^+
110	1.0	P^{79}Br^+
112	1.0	P^{81}Br^+
129	3.2	$\text{PF}^{79}\text{Br}^+$
131	3.2	$\text{PF}^{81}\text{Br}^+$
148	14.0	$\text{PF}_2^{79}\text{Br}^+$
150	14.0	$\text{PF}_2^{81}\text{Br}^+$

TABLE XX

MASS SPECTRUM OF DIFLUOROIODOPHOSPHINE⁵¹

m/e	Relative Intensity	Assignment
196	100	PF ₂ I ⁺
177	15	PF ₂ I ⁺
158	6	PI ⁺
127	71	I ⁺
88	1	PF ₃ ⁺
69	60	PF ₂ ⁺
63.5	4	I ²⁺
50	29	PF ⁺
31	11	P ⁺
19	3	F ⁺

TABLE XXI

MASS SPECTRUM OF DIFLUOROPHOSPHINE ⁵¹

m/e	Relative Intensity	Assignment
70	100.0	PHF ₂ ⁺
69	52.4	PF ₂ ⁺
51	84.3	PHF ⁺
50	27.5	PF ⁺
34.5	0.8	PF ₂ ²⁺
32	3.9	PH ⁺
31	16.0	P ⁺
25.5	1.0	PHF ²⁺
25	3.0	PF ²⁺
20	0.6	HF ⁺
19	4.6	F ⁺
16	1.2	PH ²⁺
16.5	2.3	P ²⁺

TABLE XXII

MASS SPECTRUM OF CYANODIFLUOROPHOSPHINE ⁵¹

m/e	Relative Intensity	Assignment
95	27.1	PF ₂ CN ⁺
88	2.0	PF ₃ ⁺
76	14.2	PFCN ⁺
69	100.0	PF ₂ ⁺
57	1.9	PCN ⁺
50	17.6	PF ⁺
43	1.8	PC ⁺
38	1.4	PFCN ²⁺
31	13.3	P ⁺
27	12.6	HCN ⁺
26	9.6	CN ⁺
19	1.6	F ⁺
14	2.5	N ⁺

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