THE REACTIONS OF DIMETHYLAMINOTETRAFLUOROPHOSPHORANE WITH ANHYDROUS HYDROGEN HALIDES

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ABSTRACT

THE REACTIONS OF DIMETHYLAMINOTETRAFLUORO-PHOSPHORANE WITH ANHYDROUS HYDROGEN HALIDES

by Ronald Michael Rogowski

The reactions between dimethylaminotetrafluorophosphorane and anhydrous hydrogen halides have been investigated. By means of these reactions, it has been possible to prepare tetrafluorochlorophosphorane and the previously unknown tetrafluorobromophosphorane. These compounds have been characterized by molecular weight, ^{19}F and ^{31}P nmr, mass and infrared spectral measurements. In contrast to the behavior of hydrogen chloride and hydrogen bromide, hydrogen iodide gives only PF_3 and I_2 as volatile products. The stoichiometry of these reactions, structure, and symmetry of the prepared compounds is considered.

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I. INTRODUCTION

While the simplest fluorophosphorane, the parent compound, PF_5, has been known since 1876, well before the discovery of elemental fluorine, a fluorophosphorane (defined as any compound of the variety R_nPF_{5-n}, where R is any alkyl, aryl, amino, or halo derivative) was first referred to in the patent literature ten years ago[1].

Fluorophosphoranes were not actually isolated and characterized completely until 1958 when A. B. Burg and his co-workers[2], and W. C. Smith[3] reported the preparation of some perfluoroalkyl derivatives and phenyl- and isooctenyltetrafluorophosphorane, respectively.

The first known method for the synthesis of fluorophosphoranes was based upon the fluorination of complexes between PCl_3 or alkyldichlorophosphines, alkyl halides, and $AlCl_3$[4, 5].

$$[R_nPCl_{4-n}]AlCl_4 \xrightarrow[SbF_3]{HF} R_nPF_{5-n} \quad (n = 1, 2)$$

Later, methods for the synthesis of fluorophosphoranes were developed using various types of fluorinating agents[3, 6-9]. These were followed by redox methods[10] and a number of synthetic methods involving phosphorous-oxygen compounds[11], as well as the use of organometallics[12, 13].

Most of the known fluorophosphoranes are distillable liquids at room temperature. The lower alkyl or perfluoroalkyl phosphoranes are gases at room temperature[14]. Most fluorophosphoranes exhibit typical covalent properties; ionic forms are seldon observed[15, 16]. This behavior is different than that of the halofluorophosphoranes.

These compounds can be ionic or covalent. They also lack the thermal stability characteristic of most phosphoranes. The halofluorophosphoranes undergo hydrolysis readily.

While all the chlorofluorophosphoranes, and a few bromofluorophosphoranes are known, none of the iodofluorophosphoranes have been isolated[15]. Halofluorophosphoranes are usually prepared by the direct addition of the appropriate halogen to the trihalide, as shown by the following reaction[17].

$$PF_3 + Cl_2 \xrightarrow{25^o} PF_3Cl_2 + PCl_4^+PF_6^- + PCl_4^+F^-$$

Carter and Holmes recently prepared PF_4Cl using a controlled low-temperature fluorination of the molecular form of PCl_2F_3[18].

The mixed halofluorophosphoranes PF_3Cl_2 and PF_3Br_2 were the subject of investigation by Salthouse and Waddington[19]. Their data indicated that these molecules possess C_{2v} symmetry, and that the chloro or bromo groups tend to substitute in equatorial positions on the trigonal bipyramidal structure[19]. The nmr data indicated that both PF_3Cl_2 and PF_3Br_2 have a trigonal bipyramidal structure with one equatorial and two axial fluorine atoms[20, 21].

The ease with which halodifluorophosphines may be formed from dialkylaminodifluorophosphine[22-24] and the ease with which halodifluorophosphoryl and halodifluorothiophosphoryl compounds may be obtained from the corresponding dialkylaminodifluorophosphoryls and dialkylaminodifluorothiophosphoryls[25, 26] has prompted this investigation of the action of anhydrous hydrogen halides upon dimethylaminotetrafluorophosphorane[27-30]. These previous results suggested that the dimethylamino group of $(CH_3)_2NPF_4$ could be replaced by a halide atom to give the compounds PF_4Cl, PF_4Br, and PF_4I.

The last member of the $PF_{5-n}Cl_n$ series, PF_4Cl, was completely characterized by Carter and Holmes[18, 31]. The characterization of PF_4Cl would provide a check on the reaction of $(CH_3)_2NPF_4$ with anhydrous hydrogen chloride.

Neither PF_4Br nor PF_4I had been reported and it was hoped that the interaction of $(CH_3)_2NPF_4$ and hydrogen halides would result in a synthesis of these compounds.

II. EXPERIMENTAL METHODS

Standard high vacuum techniques were employed throughout. The dimethylaminotetrafluorophosphorane was prepared as described by Brown, Fraser, and Sharp[29]. Their original process was modified for vacuum line methods and larger amounts of reactants. A 50 g sample of anhydrous dimethylamine was distilled in vacuo onto 150 ml of freshly distilled dry toluene. Phosphorous pentafluoride was then passed over the stirred mixture which was maintained at -78° for two hours. The pressure was monitored using a monometer. The reaction was assumed to be complete when phosphorous pentafluoride was no longer absorbed by the amine. The toluene was then removed from the white suspension by distillation in vacuo to a -78° trap. The adduct, $(CH_3)_2NH{:}PF_5$ remained behind as a white solid. After the removal of all toluene, the adduct was heated to 130° and the volatile products separated by distillation in vacuo through traps held at -45, -78, and -196°. The -78° fraction was then re-distilled on a spinning band column under an atmosphere of dry nitrogen. The fraction which boiled between 60-63° was collected.

The identity of the phosphorane was established by a comparison of its infrared spectrum with the previously reported spectrum[29]. The proton nmr and glpc suggested that the material was more than 95% pure. The water white liquid was stored at -60° until used.

The anhydrous hydrogen chloride (Matheson) was distilled in vacuo just prior to use. Commercial anhydrous hydrogen bromide (Matheson) contained large amounts of hydrogen chloride. It was therefore necessary to prepare anhydrous HBr and HI via the reaction of bromine and iodine, respectively, with 1,2,3,4 tetrahydronapthalene[32].

The reaction bulb used for all experimental work was patterned after the model used by Treichel to prepare HPF_4[13], and is shown in figure I. The bulb was baked at 150° for two days, evacuated on the vacuum line and flamed before use.

The infrared spectra were obtained on a Perkin-Elmer 237B grating spectrophotometer. For the region below 600 cm^{-1}, a Perkin-Elmer 301 spectrophotometer was employed. For all volatile materials a gas cell with a 7.5 cm path length and CsI windows was used.

Proton nmr spectra were observed on a Varian Model A-60 nuclear magnetic resonance spectrometer operating at the ambient temperature of the instrument. Fluorine nmr spectra were obtained on a Varian Model 56/60 nuclear magnetic spectrometer operating at 56.4 Mc. For the proton spectra tetramethyl silane and methylene chloride were used as external standards. For fluorine magnetic resonances, fluorotrichloromethane was used as an external reference, by the tube interchange technique. Whenever possible, samples were run as neat liquids. Phosphorus nmr absorptions were obtained on a Varian Model HA-100 spectrometer with 85% phosphoric acid used as a reference.

All mass spectra were obtained on a Consolidated Electrodynamics Corporation Model 21-103C Spectrometer operating with an ionizing voltage of 56V.

A F&M Research Chromatograph was used for glpc, with helium as the carrier gas and a flame ionization detector. Glpc of the products was performed on a 0.125 in x 20 ft stainless steel column packed with 20% silicon gum rubber SE-30 on Chromosorb W. The column was operated at 70°.

GAS PHASE REACTION BULB

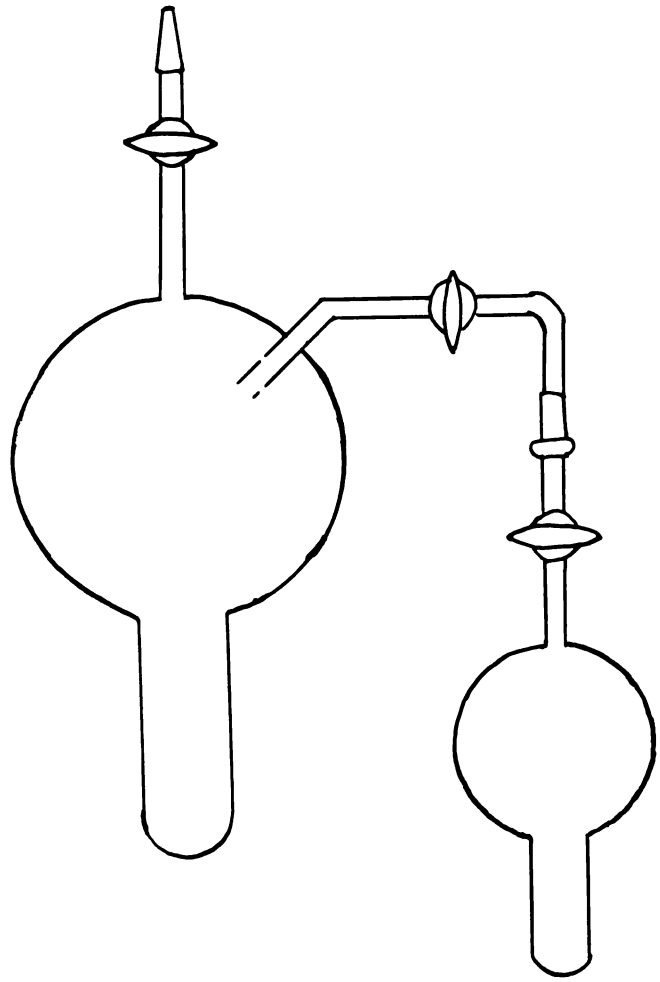

Figure 1

The Reaction of Dimethylaminotetrafluorophosphorane with Anhydrous Hydrogen Chloride.

Because of the difficulties encountered when this reaction was allowed to proceed in a condensed state, the reaction between $(CH_3)_2NPF_4$ and anhydrous HCl was carried out entirely in the gas phase using a system previously described by Treichel, Goodrich, and Pierce[33]. Two reaction bulbs of about 1 liter capacity and about 250 ml capacity were connected together with an intervening stopcock. In a typical reaction, a 6.28 mmol sample of anhydrous HCl was condensed in vacuo at -196° into the smaller bulb. A 3.51 mmol sample of $(CH_3)_2NPF_4$ was then condensed in vacuo into the larger bulb at -196°. Both reactants were allowed to warm to 23° until no liquid $(CH_3)_2NPF_4$ was observed. When the stopcock between the two bulbs was opened, the HCl expanded into the larger bulb. An immediate reaction was observed by the formation of a fine white solid. The volatile products of this reaction were condensed into a -196° trap on the vacuum system and then fractionated through traps held at 0, -78, and -196°. This fractionation was repeated three times to insure complete separation. The -78° fraction contained 0.30 mmol of unreacted $(CH_3)_2NPF_4$, identified by its gas-phase ir spectra. The -196° trap contained 3.12 mmol of PF_4Cl. The PF_4Cl was identified by its gas-phase ir spectrum. This spectrum was identical with the previously reported spectrum of PF_4Cl[31], except those bands which were attributed to POF_3 are of lower intensity. The spectrum obtained in the region from 300 to 1600 cm^{-1} is shown in figure II. The infrared peaks and some band assignments based on the work of R. R. Holmes[31] are listed in table I.

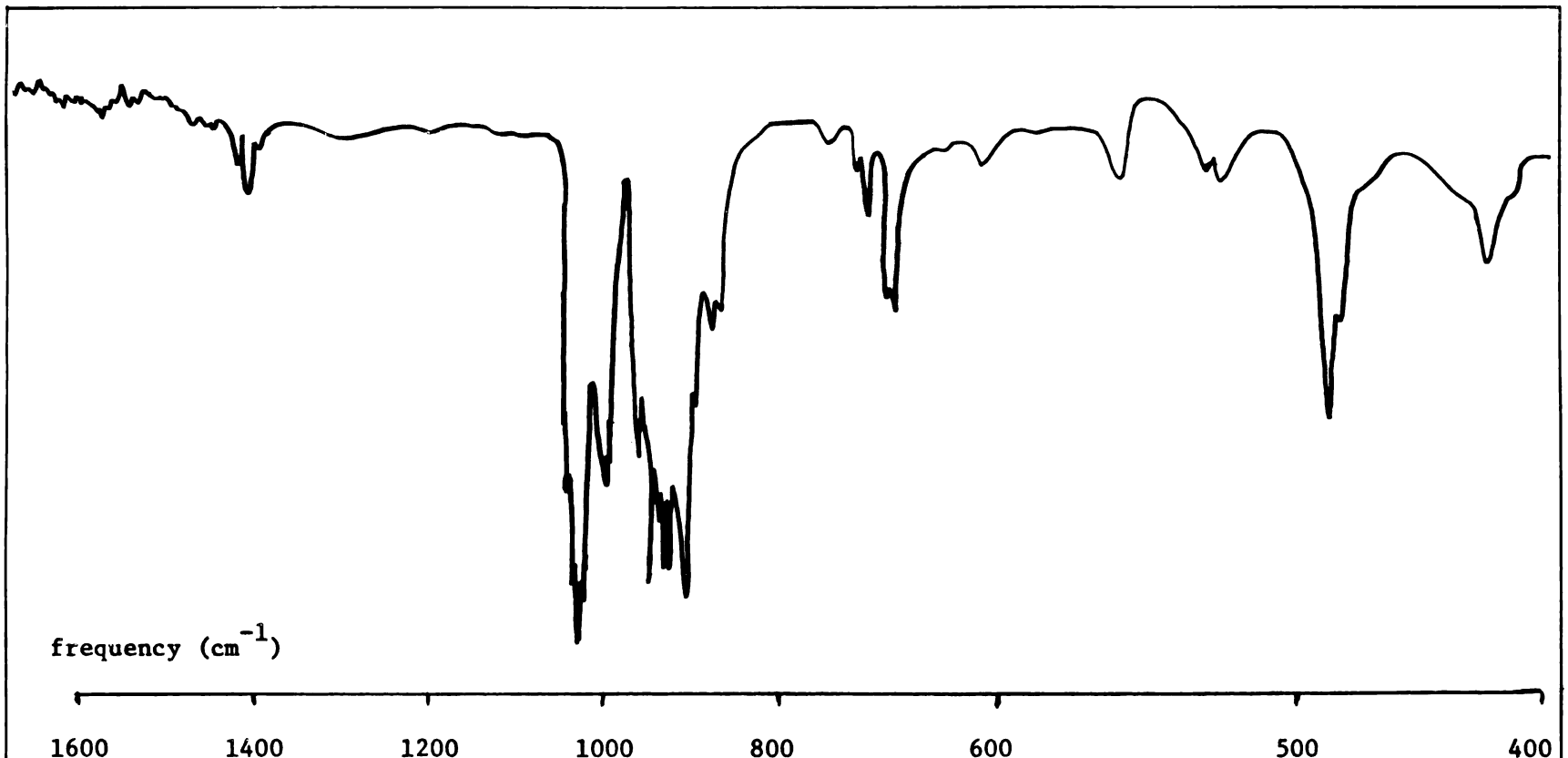

Figure II The Infrared Spectrum of $PF_4Cl(g)$

Table I

Gas-Phase Infrared Data on PF_4Cl

Absorption (cm^{-1})	Assignment (C_{2v})
430(w)	$\nu_4(a_1)$
480(vs)	$\nu_8(b_1)\nu_3(a_1)$
530(m)	PF_5
565(s)	$\nu_{11}(b_2)$
625(m)	?
670(s)	PCl_2F_3
691(m)	$\nu_2(a_1)$
700(m)	?
868(m)	$\nu_2(POF_3)$
895(vs)	$\nu_1(a_1)$
903(vs)	$\nu_{10}(b_2)$
925(vs)	$\nu_1(b_1)$
945(m)	$PF_5 - POF_3$
954(m)	POF_3
995(s)	POF_3
1019(vs)	PF_5
1025(vs)	PF_5
1415(wm)	POF_3

The product was also identified by a gas-phase molecular weight of 141.1 g/mol (theoretical 142.4 g/mol) and by its ^{19}F nmr at -60^{o} which exhibited a doublet pattern at +24.3 ppm (literature[18]; +23.5 ppm) from CCl_3F. The coupling constant (J_{PF}) was 1000 $\pm$ 10 cps (literature[18]; 1000 cps). The nmr spectrum exhibited no peaks which can be attributed to POF_3 or PF_3Cl_2, but did exhibit peaks which can be attributed to minor amounts of PF_5 at +68 ppm with a coupling constant (J_{PF}) of 930 cps (literature: δ +72.5 ppm[34]; J_{PF} = 916 cps[20]). The ^{19}F nmr is shown in figure III.

Mass spectral data obtained at 56V also supported the formulation of PF_4Cl. Peaks attributed to the product with mass number and relative abundance respectively are shown in table II. No parent peak ions were detected at 56V, which is consistent with other phosphorane results[33].

No vapor pressure data is reported because the sample contained traces of HCl which were difficult to separate from PF_4Cl due to the similarity in vapor pressure. Carter and Holmes report vapor pressure data obtained at -123^{o} and -54^{o}[18], however all their spectral data reveal amounts of impurities in their samples.

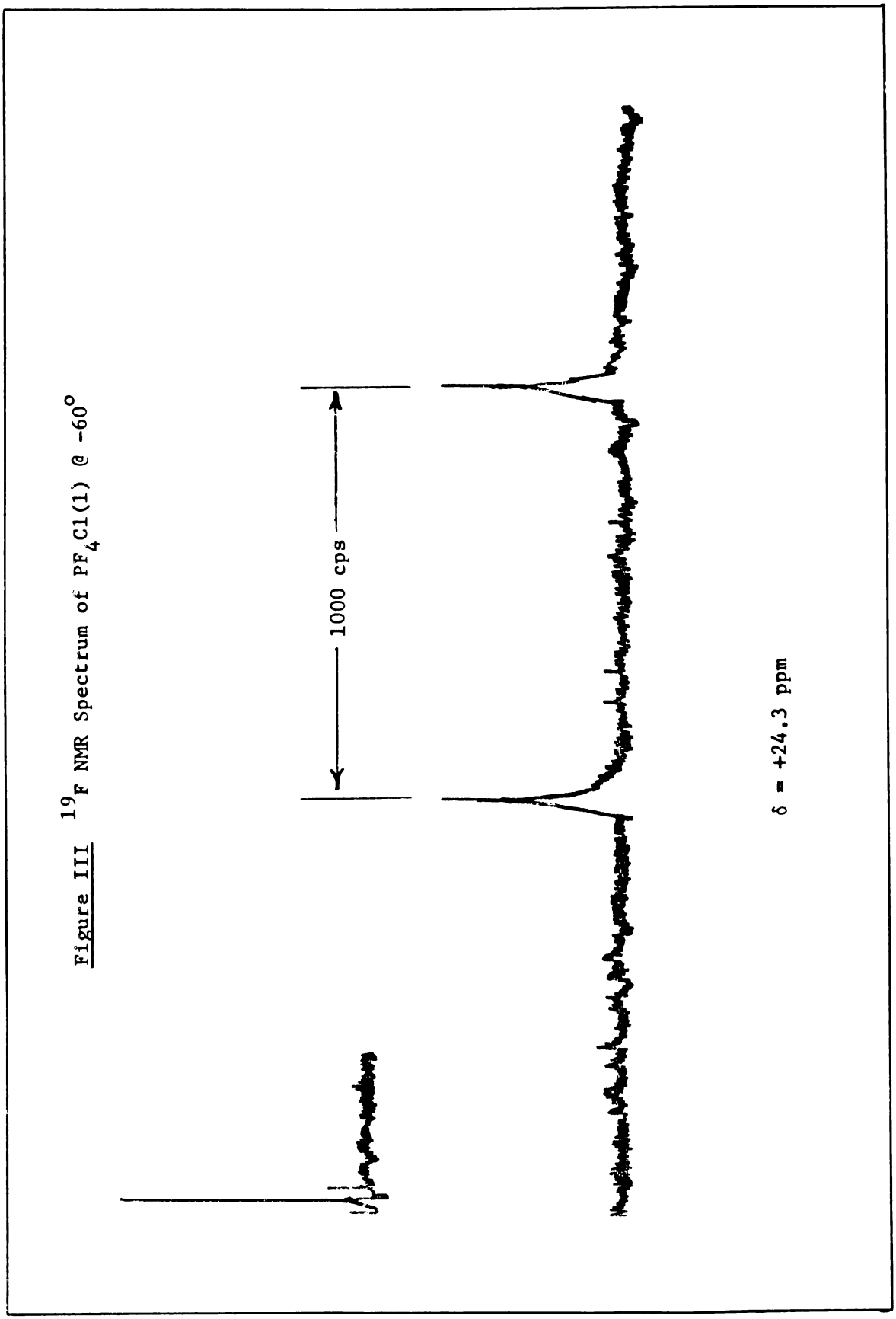

Figure III ^{19}F NMR Spectrum of $PF_4Cl(1)$ @ -60°

Table II

Mass Spectrum of PF_4Cl

m/e	Relative Intensity	Assignment
17.5	42	Cl_{35}^{2+}
18	40	$HCl_{35}^{2+} - H_2O^+$
18.5	14	Cl_{37}^{2+}
19	5	HCl_{37}^{2+}
25	6	PF^{2+}
28	57	N_2^+
31	7	P^+
32	12	O_2^+
33	4	POF^{2+}
35	72	Cl_{35}^+
36	100	HCl_{35}^+
37	24	Cl_{37}^+
38	32	HCl_{37}^+
44	80	PF_3^{2+}
50	10	PF^+
57	1.5	POF_3^{++}
66	1.5	POF^+
69	62	PF_2^+
85	68	$POF_2^+ - PFCl_{35}^+$
87	13	$PFCl_{37}^+$
88	18	PF_3^+
104	22	$POF_3^+ - PF_2Cl_{35}^+$
106	2.0	$PF_2Cl_{37}^+$
107	18	PF_4^+

The Reaction of Dimethylaminotetrafluorophosphorane with Anhydrous Hydrogen Bromide.

This reaction was run in a manner identical with that previously described for the reaction involving HCl. The same precautions were taken with the reaction bulb to ensure anhydrous conditions. A 7.22-mmol sample of freshly distilled anhydrous HBr was condensed *in vacuo* at -196° into the smaller reaction bulb. A 3.35-mmol sample of $(CH_3)_2NPF_4$ was then condensed *in vacuo* at -196° into the larger bulb. After warming the bulbs to ambient temperature (23°) the stopcock between the bulbs was opened to allow the 7.22 mmol sample of HBr to interact with the 3.35 mmol sample of $(CH_3)_2NPF_4$. The reaction proceeded with the formation of a white powder. After allowing the reaction to proceed for two minutes, the volatile products were condensed in a -196° trap and then fractionated three times through traps held at -78, -126, and -196° respectively. Again the -78° trap contained traces of unreacted $(CH_3)_2NPF_4$, identified by its gas-phase ir spectrum. A 3.22 mmol sample of a gas, later identified as a mixture of about 80% PF_4Br and about 20% PF_5, was obtained from the -126° fraction. A 0.35 mmol sample of HBr, identified by its infrared spectrum, was recovered from the -196° trap. Characterization of PF_4Br is presented in subsequent portions of this thesis.

The infrared gas-phase spectrum of the -126° fraction exhibited peaks attributed to PF_4Br, POF_3, and PF_5. Several tentative assignments on PF_4Br were made on the basis of assignments carried out for PF_4Cl[31] assuming that PF_4Br and PF_4Cl are of the some C_{2v} symmetry. Figure IV shows a typical ir spectrum and table III lists the peaks and some tentative band assignments based on PF_4Cl[31].

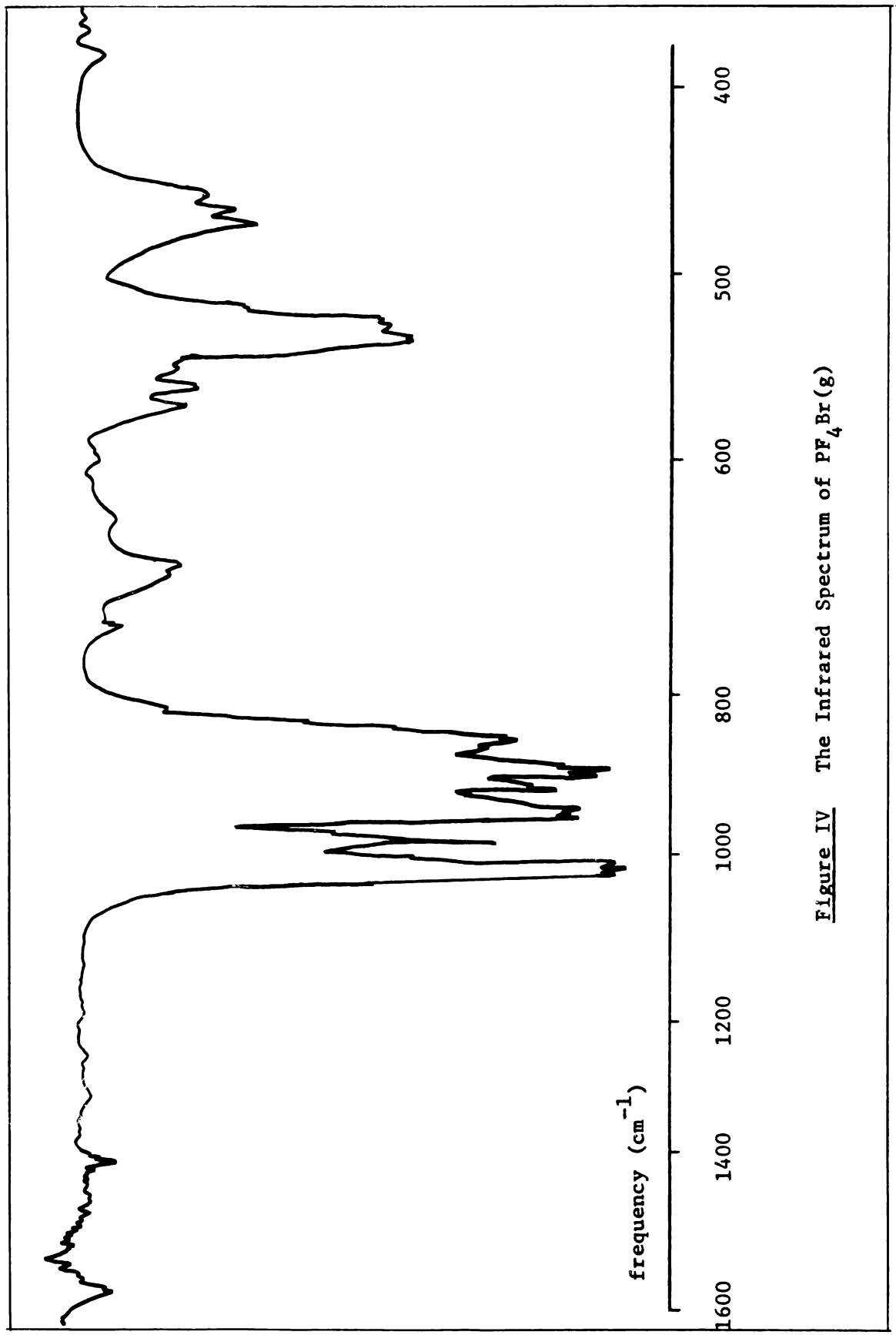

Figure IV The Infrared Spectrum of $PF_4Br(g)$

Table III

Gas-Phase Infrared Data on PF_4Br

Absorption (cm^{-1})	Assignment (C_{2v})
387(w)	ν_4, (PBr stretch)
461, 470, 480(s)	ν_8 and ν_3, (PF_2 and PF_2Br in-plane bend)
522(ms)	PF_5
532, 542(s)	ν_{11}, (PF_2Br out-of-plane bend)
573, 584(ms)	?
617(mw)	?
675, 678(s)	ν_2, (PF_2 stretch)
725(vw)	?
855, 865(m)	POF_3
855(vs)	ν_1 (PF_2 stretch)
899(vs)	ν_{10}, (PF_2 stretch)
906, 915(s)	ν_7, (PF_2 stretch)
945(vs)	POF_3 or PF_5
955(s)	POF_3
985, 990, 1000(s)	POF_3
1020, 1025, 1035(s)	PF_5
1365(w)	($\nu_{10} + \nu_8 = 1370$)
1405, 1415, 1426(mw)	POF_3
1570(mw)	($\nu_1 + \nu_2 = 1560$)
1760(vw)	($2\nu_1 = 1770$)

A mass spectrum obtained at 56V on the -126° fraction demonstrates that parent ions again were not detected. The results of this data with mass numbers and relative abundances are shown in table IV. The large amount of HBr which appears is apparently formed by hydrolysis of PF_4Br at the injection part of the mass spectrometer. No bands which could be attributed to HBr were observed in the infrared spectra of PF_4Br at 80 mm pressure.

The gas-phase molecular weight of the -126° fraction was 178.5 g/mol (theoretical for PF_4Br; 186.9 g/mol).

The Reaction of Dimethylaminotetrafluorophosphorane with Anhydrous Hydrogen Iodide.

The reaction was run as described previously. Into the throughly dried reaction bulb was condensed *in vacuo* at -196° a sample of anhydrous HI which had been freshly distilled. A sample of $(CH_3)_2NPF_4$ was then condensed *in vacuo* into the larger bulb. The contents were then warmed to 23° and the stopcock was opened. The reaction proceeded with the initial formation of a white powder, which turned a deep purple within seconds after forming. This mixture was fractionated through traps held at -78, -126, and -196°. The -78° fraction contained unreacted $(CH_3)_2NPF_4$, while the -196° trap contained PF_3, which was identified by its gas-phase infrared spectra and a gas-phase molecular weight of 88.3 g/mol (theoretical; 88.0 g/mol).

The solids remaining in the reaction bulb were a deep purple. A portion of these solids could be dissolved in CCl_4. The visible spectrum of this solution was identical with that of a solution of

Table IV

Mass Spectrum of PF_4Br

m/e	Relative Intensity	Assignment
25	6.3	PF^{2+}
31	10.7	P^+
39.5	12.5	Br_{79}^{2+}
40	13.8	HBr_{79}^{2+}
40.5	12.5	Br_{81}^{2+}
41	13.8	HBr_{81}^{2+}
44	18.4	PF_3^{++}
50	12.5	PF^+
69	40	PF_2^+
79	86.5	Br_{79}^+
80	100	HBr_{79}^+
81	86	Br_{81}^+
82	100	HBr_{81}^+
85	46	POF_2^+
88	22.6	PF_3^+
104	38.7	POF_3^+
107	58	PF_4^+
129	2.7	$PFBr_{79}^+$
131	2.7	$PFBr_{81}^+$
148	4.0	$PF_2Br_{79}^+$
150	4.0	$PF_2Br_{81}^+$

Table IV (continued)

m/e	Relative Intensity	Assignment
189	2.3	$PBr_{2\ (79)}^{+}$
191	4.7	$PBr_{79}Br_{81}^{+}$
193	2.3	$PBr_{2(81)}^{+}$
208	1.0	$PFBr_{2(79)}^{+}$
210	2.0	$PFBr_{79}Br_{81}^{+}$
212	1.0	$PFBr_{2(81)}^{+}$

elemental iodine dissolved in CCl_4. The amount of I_2 produced in this reaction was determined using standard techniques[35].

These results suggest that the experimental stoichiometry for the overall reaction is

$$1.00(CH_3)_2NPF_4 + 1.99\ HI \rightarrow 0.94PF_3 + 0.92I_2 + \text{Solids}$$

The solid remaining in the reaction flask may be identified, on the basis of this data, as $(CH_3)_2NH_2^+F^-$. Each of these gas-phase reactions was repeated several times with the same qualitative results observed for each trial.

III. DISCUSSION

Anhydrous hydrogen bromide or hydrogen chloride react with dialkylaminotetrafluorophosphorane to yield tetrafluorobromophosphorane and tetrafluorochlorophosphorane according to the equation

$$(CH_3)_2NPF_4 + 2HX \rightarrow PF_4X + [(CH_3)_2NH_2]^+X^-$$

in contrast to this behavior, hydrogen iodide reacts with $(CH_3)_2NPF_4$ according to the equation

$$(CH_3)_2NPF_4 + 2HI \rightarrow PF_3 + I_2 + [(CH_3)_2NH_2]^+F^-$$

Cavell and Charlton[36] have shown that hydrophosphoryl difluoride, OPF_2H, is formed when $(CH_3)_2NPOF_2$ is allowed to interact with HI. The fact that PF_4H is not produced from the interaction of $(CH_3)_2NPF_4$ and HI may be a result of the inability of PF_4H to exist in the presence of reducing agents such as HI.

Of the two tetrafluorohalophosphoranes prepared by this method, PF_4Cl is much more stable and easier to isolate and characterize. It has been previously reported[18] that a sample of PF_4Cl could be stored in the gaseous state for four days before deposition of a white solid on the walls of the storage container could be observed. This observation was also corroborated in these experiments. In contrast to this behavior, when a sample of PF_4Br was stored in the gaseous state (in a sealed glass ampoule), it was observed that a yellow-red solid was deposited on the walls of the ampoule within 15 minutes. A liquid sample of water white PF_4Br deposits a deep red solid on the walls of the container in less than one minute at room temperature. On the other hand, no change was observed when a liquid, water white

sample of PF_4Cl was held at room temperature for 30 minutes. This thermal instability of PF_4Br suggests that the compound decomposes when allowed to strike the warm tubing between the cold traps on the vacuum system. That this is the case is also suggested by the fact that attempts to purify PF_4Br by recycling in vacuo the partially purified material four times through traps held at -78, -126, and -196° did not result in a tensiometrically homogeneous sample. In spite of the fact that PF_4Br could not be obtained in a state of high purity, physical measurements presented below, strongly suggest that PF_4Br in about 80% yield is obtained from the interaction of $(CH_3)_2NPF_4$ and anhydrous HBr.

First, the ^{19}F nmr spectrum (shown in figure V) of a sample presumed to be PF_4Br consisted at -60° of a simple doublet pattern at +9.6 ppm upfield from CCl_3F. The coupling constant was 1085 ± 10 cps. The chemical shift and the (J_{PF}) coupling constant for PF_4Br is intermediate between the values for PF_5 and PF_3Br_2[37]. The ^{19}F nmr spectrum also exhibited absorptions which can be attributed to PF_5 at +66.7 ppm with J_{PF} of 940 ± 10 cps (literature; [34, 20] δ = +72.5 ppm; J_{PF} = 916 cps). On the basis of the area under the peaks, the sample contained about 20% PF_5. No absorptions attributed to PF_3Br_2 were observed. These data are consistent with molecular weight determinations which always yielded values lower then the theoretical values. As mentioned previously, we were unable to remove the PF_5 by fractional distillation in vacuo. At the lowest temperature obtainable on the nmr spectrometer employed, -60°, no line broadening was observed, suggesting that the molecule was exchanging intramolecularly at a rate faster than could be observed by nmr techniques at -60°.

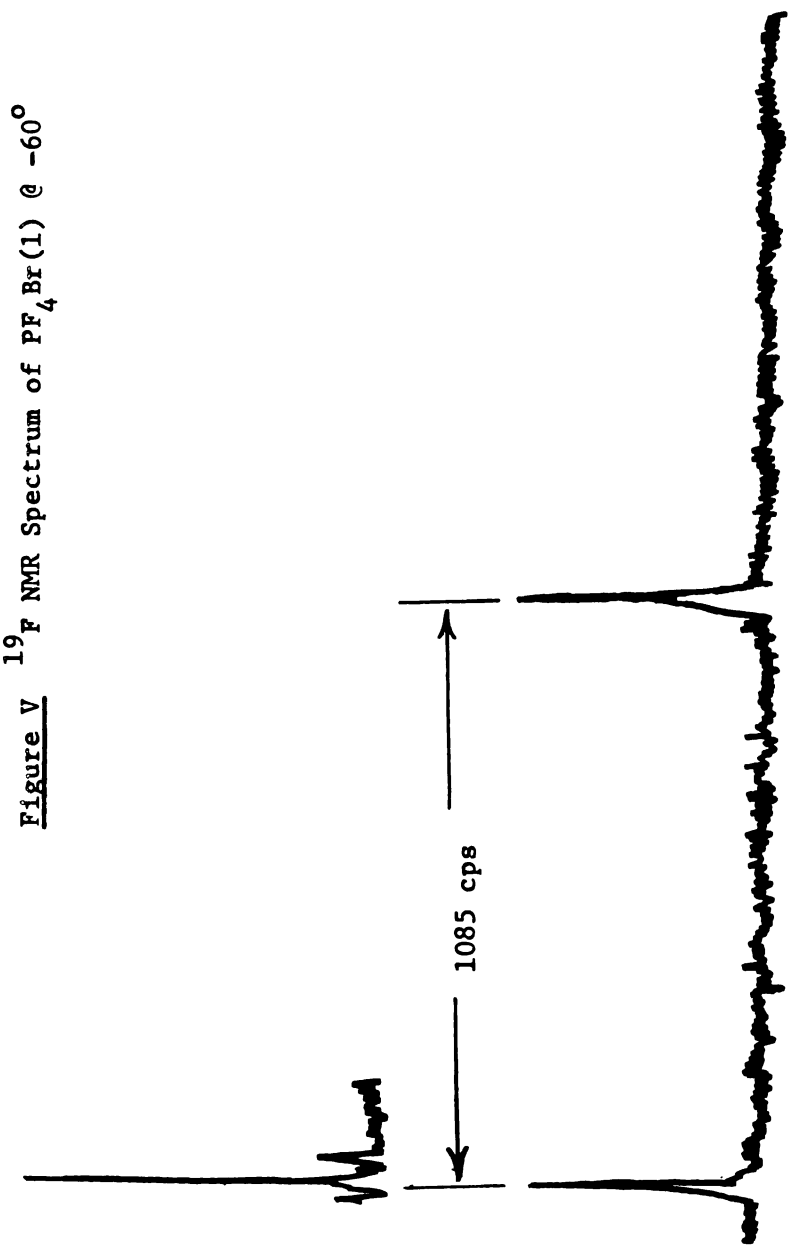

Figure V ^{19}F NMR Spectrum of $PF_4Br(1)$ @ -60°

Second, the ^{31}P nmr spectrum at -70^{o} of this same sample (shown in figure VI) consisted of a simple quintet of 1:4:6:4:1 intensity at +72.6 ppm with a J_{PF} of 1075 $\pm$ 15 cps. No other absorptions were observed probably because of the low magnetogyric ratio of phosphorous; the signal is about an order of magnitude less intense than that of fluorine. The lack of sensitivity accounts for the fact that the expected septet due to the 20% impurity of PF_5 and the outer members of the PF_4Br quintet were not observed; but the ^{31}P spectral data can only be rationalized by the existance of a tetrafluorophosphorus group.

Third, the formula PF_4Br is also supported by the infrared data. Several assignments may be made on the basis of assignments carried for PF_4Cl[31], assuming that PF_4Br and PF_4Cl are of C_{2v} symmetry. In the P-F stretching region of the PF_4Br spectrum, the very intense bands at 885, 899, and 915 cm^{-1} are associated with the P-F stretching modes. In PF_4Cl these are found[31] at 895, 903, and 921 cm^{-1}. The PF_2 symmetric axial stretch has been assigned[31] to bands at 691 cm^{-1} in PF_4Cl, and is probably observed at 675 cm^{-1} in PF_4Br. An out-of-plane bending motion appears at 560 cm^{-1} in PF_4Cl[31], and is probably associated with the intense bands at 532 and 542 cm^{-1} in PF_4Br. An intense band centered at 470 cm^{-1} in PF_4Br and at 490 cm^{-1} in PF_4Cl may be assigned to either PF_2 in-plane bending or a PF_2X in-plane bending motion. Medium weak bands in PF_4Cl which are easily ascribed to P-Cl stretching vibration appear at 427 and 434 cm^{-1} in PF_4Cl. These are absent in the spectrum of PF_4Br. However, a band at 387 cm^{-1} in PF_4Br may be associated with a P-Br stretching motion; other bands in the infrared absorption spectra of PF_4Br may be ascribed to impurities.

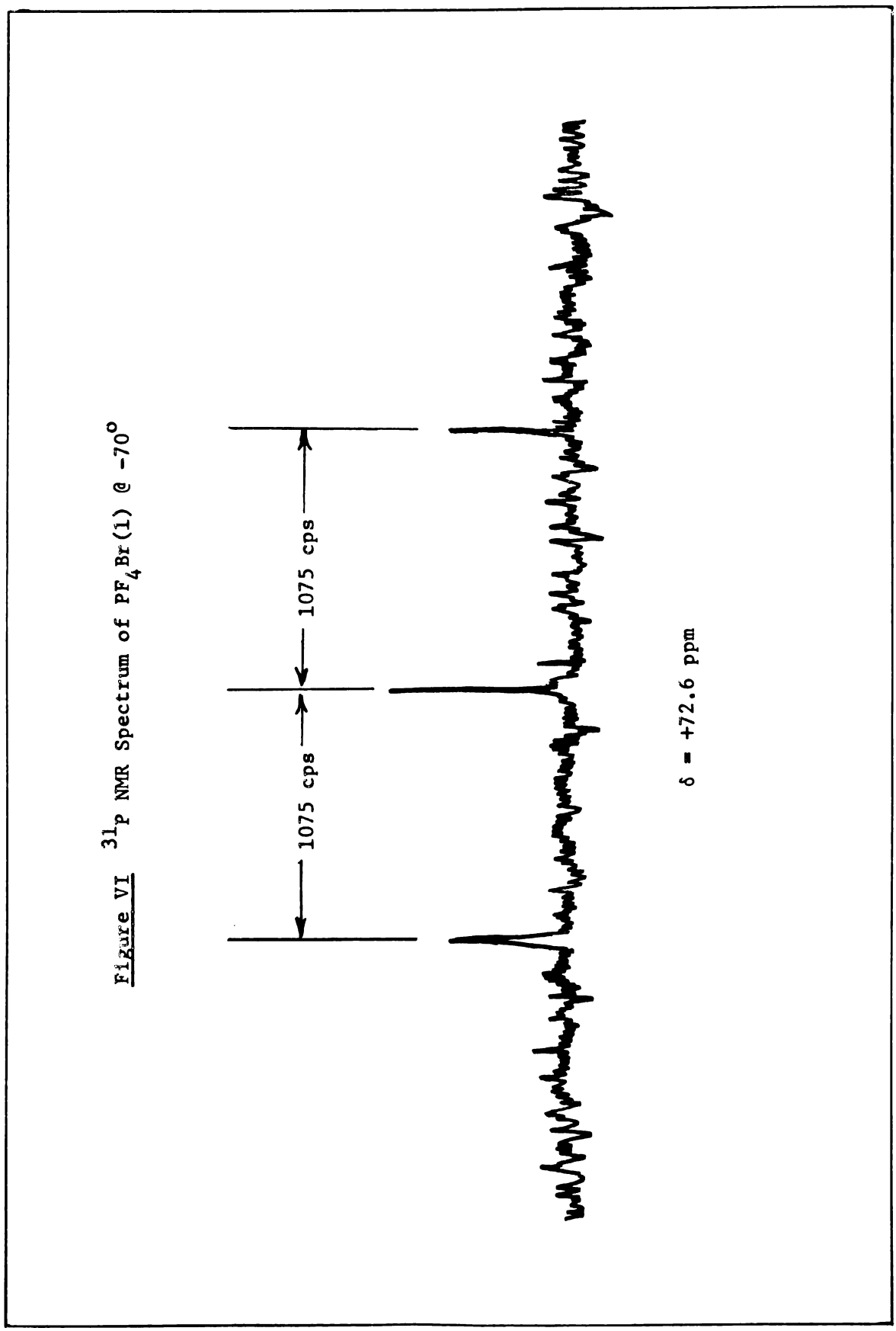

Figure VI ^{31}P NMR Spectrum of $PF_4Br(1)$ @ -70°

Fourth, mass spectral data obtained at 56V of PF_4Cl and PF_4Br are quite similar, as expected. See tables II and III for the mass spectral data of PF_4Cl and PF_4Br respectively. In both cases parent ions were not detected, which is consistent with other fluorophosphorane results[33]. Intense peaks appear at m/e corresponding to PF_4^+, PF_3^+, PF_2^+, and X^+. The similarity of the mass spectra of PF_4Cl and PF_4Br further augment the formulation as PF_4Br. The presence of molecular ions containing two bromine atoms in the spectrum of PF_4Br suggests that small amounts of PF_3Br_2 are formed when PF_4Br decomposes[18], or that some rearrangement of ion particles in the mass spectrometer occurs. If PF_3Br_2 does form, it appears to be, on the basis of the ^{19}F nmr data, substantially removed upon distillation in vacuo.

The symmetry of PF_4X molecules was shown by R. R. Holmes using low temperature Raman studies to be C_{2v}[31]. A comparison of the dipole moment of PF_4Cl with the values of other phosphorous(V) chlorofluorides shows the assignment of C_{2v} symmetry to PF_4Cl is self-consistent. The observed value of 0.78 D for PF_4Cl is close to the gas state value observed for PCl_2F_3 (0.68 D) shown to be a trigonal bipyramid with the two chlorine atoms located in equatorial positions[38]. The fact that the dipole moments are only 0.1 D apart supports the contention that they have the same symmetry. Small changes in electronic distribution and degrees of distortion between the two molecules could easily account for the difference.

The dipole moment of the trigonal bipyramidal structure of PF_4Cl having an axial chlorine atom (C_{3v}) was vectorially considered in terms of an axial P-Cl opposing an axial P-F bond dipole[39].

These calculations led to a theoretical value for the gas-state dipole moment of about 0.2 D[39]. Experimentally, as previously mentioned, the value was determined to be 0.78 D, suggesting that a C_{3v} symmetry for PF_4Cl is incorrect.

For PCl_4F theoretical calculations of the gas-state dipole moment yielded a value of about 0.2 D[39] for a C_{3v} symmetry of this molecule. Experimentally the value observed was 0.21 D[39] suggesting that the molecule does possess C_{3v} symmetry, with the fluorine atom in an axial position.

Holmes also did pure chlorine nuclear quadrupole measurements on PF_4Cl and found further evidence supporting the fact that the chlorine atom is located at an equatorial site in PF_4Cl[31], which is consistent with C_{2v} symmetry. Work done by Bartell and Hansen[40] using electron diffraction techniques concluded the molecule CH_3PF_4 is a distorted trigonal bipyramid with methyl groups occupying equatorial positions. A microwave spectrum of CH_3PF_4 obtained by Cornwell and Cohen revealed that the molecule is an asymmetric top and hence cannot be either a tetragonal pyramid or an axially substituted bipyramid[40].

E. L. Muetterties and co-workers[41] completed a study of five-coordinate phosphorous(V) fluorides. They reported that at 25° the ^{19}F nmr spectrum of $(C_2H_5)_2NPF_4$ comprises two peaks of equal intensity. On cooling the sample, the doublet gradually broadens and eventually is resolved into two doublets[41]. This data establishes a structure in which there are two fluorine atom environments, each of which contains two fluorine atoms. Because geometry closely approximating a trigonal bipyramid prevails in

$(C_2H_5)_2NPF_4$, there are only two possible geometrical isomers[41]. Apical substitution may be ruled out since in no way could a 2:2 fluorine atom environment be generated. Thus we expect that PF_4Br, a RPF_4 type molecule, does possess C_{2v} symmetry like PF_4Cl. The larger size of the bromine atom may suggest more axial distortion than found in PF_4Cl.

The hydrolysis of PF_4X has been observed; a sample was placed in the infrared gas cell and the results of an addition of moisture were observed. The spectrum shows an increase in the bands due to POF_3, and traces of HCl are noted with the PF_4Cl, while peaks due to HBr are observed upon the hydrolysis of PF_4Br. The suggested stoichiometry of the hydrolysis reaction is

$$HOH + PF_4X \rightarrow [PF_4OH + HX] \rightarrow HF + HX$$

Suggestions for Future Research

Much work has been done on the phosphorus(V) chlorofluorides, of which PF_4Cl was the last member to be synthesized. However, much less is known about the phosphorus(V) bromofluorides, and phosphorus(V) iodofluorides. Perhaps dipole moments and low temperature Raman studies could be done on PF_4Br in a manner similar to the work of Holmes with PF_4Cl[31]. The ionic and covalent behavior of these compounds is also of interest. The preparation of PF_4I may be feasible and should be further investigated. The P-Br bond should be studied and perhaps its lability may be utilized in the development of synthetic routes for the preparation of new fluorophosphoranes. It may be possible to synthesize and characterize F_4PPF_4, PF_4CN, and F_4POPF_4 by a series of reactions analogous to the reactions which were developed by Rudolph to prepare F_2PPF_2, PF_2CN, and F_2POPF_2 from PF_2I[42] and the pentavalent phosphorus reactions developed in this thesis.

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