O^{17} showed that the radical observed in this system probably contains two nonequivalent oxygen atoms.

The OOF radical was also reported by Arkell,[8] who produced this radical during photolysis of OF_2–O_2 or F_2–O_2 mixtures in oxygen, nitrogen, and argon matrices at 40°K. Spratley, Turner, and Pimentel[9] also observed the OOF radical.

If the F^{19} nmr data are considered independently, there is a possibility that the two incompletely resolved lines observed are due to two slightly different fluorine atoms in O_3F_2. If however, it is assumed that the two F^{19} signals are due to $(OOF)_n$ and O_2F_2 (which substantiates the O^{17} nmr results), it can be concluded that the $(OOF)_n$ species observed probably does not contain a free electron. The presence of a free electron in the molecule should substantially shift the F^{19} signal, and it would not be in approximately the same position as the F^{19} signal of O_2F_2. The fact that the chemical shift and the line width of the F^{19} signal change with temperature also helps to explain the system.

The paramagnetic species in solution could produce a distribution of local magnetic fields. Changing the lifetime of the spin states in turn changes both the chemical shift and the line width. From the fact that the chemical shift increases and the line width decreases as the temperature increases, it can be concluded that the concentration of free radicals decreases with increasing temperature; that is, the OOF radicals are decomposing as the temperature is increased.

As pointed out, the O^{17} nmr spectrum of O_3F_2 consists of a large line (due to O_2F_2) and two equivalent smaller signals. It is concluded that the two equivalent lines are due to $(O_2F)_n$. It is most likely that the $(O_2F)_n$ species is O_4F_2, although there is a remote possibility that the observed spectrum is due to OOF bonded in some way to O_2F_2. If, as reported by Kasai and Kirshenbaum,[6] the OOF species is present in the range of 5% compared to the O_3F_2 species, it probably would not be observed in the O^{17} nmr spectrum. Under the best of circumstances it is difficult to observe an nmr signal of such a small amount of material. Also, the free electron in the same molecule as the observed nucleus would be expected to broaden and shift the signals.

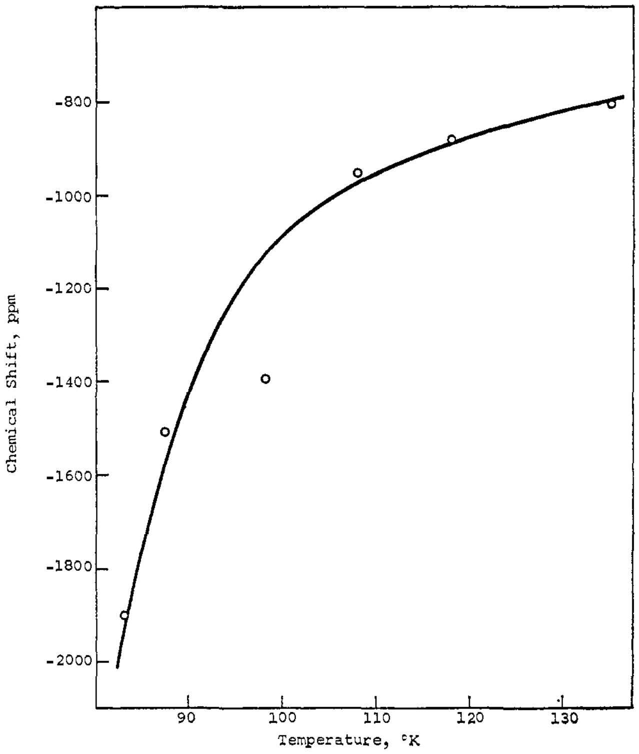

Figure 5. F^{19} chemical shift *vs.* temperature for O_3F_2(?).

The F^{19} nmr data, although not independently conclusive, substantiates the conclusions drawn from the O^{17} nmr results; that is, one F^{19} signal is due to O_2F_2 and the other to $(O_2F)_n$.

Thus considering all of the data, the system is best explained as

$$\begin{tikzcd}[O_2F_2, O_4F_2] \arrow[d, shift left] \\ 2OOF \arrow[u, shift left] \arrow[r] & O_2F_2 + O_2\end{tikzcd}$$

that is, what has been called O_3F_2 does not exist as a molecular species and is actually a mixture of O_2F_2 and probably O_4F_2 in equilibrium with O_2F, which decomposes irreversibly as the temperature is increased.

Acknowledgment.—Technical direction was provided by the Director of Engineering Sciences, SREP, Air Force Office of Scientific Research, Contract No. AF 4-9(638)-1175.

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[8] A. Arkell, *J. Am. Chem. Soc.*, **87**, 4057 (1965).

[9] R. D. Spratley, J. J. Turner, and G. C. Pimentel *J. Chem. Phys.*, **44**, 2063 (1966).

Synthesis and Characterization of HPF_4 and H_2PF_3[1]

P. M. Treichel, Ruth A. Goodrich, and S. B. Pierce

Contribution from the Department of Chemistry, The University of Wisconsin, Madison, Wisconsin. *Received October 29, 1966*

Abstract: The gas-phase reaction of $(CH_3)_3SnH$ and PF_5 results in formation of the gaseous fluorophosphoranes HPF_4 and H_2PF_3. The deuterium derivatives DPF_4 and D_2PF_3 were prepared in an analogous reaction with $(CH_3)_3SnD$. These compounds were characterized by vapor pressure data, mass spectrographic studies, infrared spectra, and ^{19}F, ^{1}H, and ^{31}P nmr spectra. A decomposition product of HPF_4, $HPOF_2$, was isolated and characterized also.

While the field of alkylfluorophosphorane chemistry has been extensively studied in recent years,[2a,b] only brief and indirect mention has been made of the simple related molecules H_xPF_{5-x}.[3] In

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[1] Presented at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, Abstract O-83.

[2] (a) R. Schmutzler, *Angew. Chem., Intern. Ed. Engl.*, 4 496 (1965); (b) R. Schmutzler, "Fluorophosphoranes," International Review on Halogen Chemistry, Academic Press Inc., New York, N. Y., in press. We are indebted to R. Schmutzler for a prepublication copy of this review.

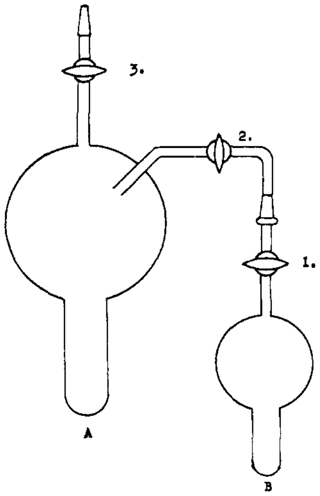

Figure 1. Gas-phase reaction bulbs.

this paper we wish to report a convenient synthesis and complete characterization of the two compounds HPF_4 and H_2PF_3 and their deuterium analogs.

Experimental Section

Synthesis. This work was carried out in Pyrex systems using standard vacuum techniques. Stopcocks were greased with Apiezon N grease. Although the desired amount of $(CH_3)_3SnH$ could be weighed out in small ampoules fitted with vacuum stopcocks, it was found to be just as convenient for small-scale runs to measure out aliquots of the vapor in a calibrated volume on the line. All other gaseous reactants and products were measured by means of the calibrated volume and are reported here in millimoles. Phosphorus pentafluoride from the Matheson Co. was fractionated to tensimetric purity as described in the literature.[4]

Trimethyltin hydride was prepared in a nitrogen atmosphere by the slow addition of $(CH_3)_3SnCl$ in butyl ether to a butyl ether slurry of $LiAlH_4$.[5,6] The trimethyltin hydride was initially purified by distillation (bp 59–62°). Final purification of this material was carried out on the vacuum line; the product was collected in a −64° trap. The product used had a vapor pressure of 71 mm at 0° (lit.[7] 71 mm at 0°).

Trimethyltin deuteride was prepared using $LiAlD_4$ (98% purity) from Metal Hydrides Inc. Purification was accomplished by direct vacuum system fractionation because of the small quantities of product involved.[6] In this preparation and purification, a small amount of tetramethyltin collected with the trimethyltin deuteride. It was difficult to separate the tetramethyltin from D_2PF_3,

The Reaction of Trimethyltin Hydride and Phosphorus Pentafluoride. Several runs were made by condensing approximately equimolar amounts of the two reactants from the vacuum line into a reaction bulb at −196°. Reaction occurred as the reactants slowly warmed to room temperature. This type of reaction, primarily involving the reactants in a condensed state, led to a considerable amount of noncondensable gas and a yellow solid along with the desired products. As a consequence, the reaction of $(CH_3)_3SnH$ and PF_5 was carried out entirely in the gas phase by the use of the system shown in Figure 1.

Bulb A (~1-l. capacity) was constructed with a stopcock and ground-glass joint for entry to the line, a freeze-off tube, and a gas inlet of 10-mm tubing which extended approximately 2 in. toward the center of the bulb. The inlet tubing was connected to a stopcock and a ground-glass joint. Fitted into this joint was a second bulb (B, 250 ml) with a stopcock and freeze-off tube. The whole system was evacuated and then flamed several times to remove traces of water. First a measured amount of PF_5 was condensed into the smaller bulb. Then $(CH_3)_3SnH$ was condensed into the larger bulb. Since the vapor pressure of $(CH_3)_3SnH$ at room temperature is only about 160–170 mm, the amount of sample used in the 1-l. bulb must be limited to about 12 mmoles if this compound is to be present as a gas only. Both reactants were allowed to warm to room temperature, with special care being taken to note the absence of any liquid $(CH_3)_3SnH$. When the stopcocks between the two bulbs were opened, the PF_5, being at higher pressure, expanded into the 1-l. bulb. An immediate reaction was observed by formation of a very fine, white solid. Within minutes the solid started to settle; the apparatus was opened to the line, and all volatile components transferred to the vacuum system. Under these conditions noncondensable gas and yellow solid were absent.

A typical run involved the reaction of 13.0 mmoles of PF_5 with 12.5 mmoles of $(CH_3)_3SnH$. The volatile products of this reaction were condensed in a −196° trap on the vacuum system and then fractionated through traps held at −112, −126, and −196°. The −112° fraction contained 4.5 mmoles of gaseous products. Gas-phase infrared spectra run at several pressures showed that this fraction contained about 10% PF_5; the major component of this fraction was H_2PF_3. The sample was refractionated through a −96° trap which retained only the product (4.05 mmoles). The molecular weight of this substance, determined at 25° by gas density measurements at pressures of 112.6 and 123.0 mm, was found to be 90.1 (calculated for H_2PF_3, 90.0). The −126° fraction contained HPF_4 (3.8 mmoles). After refractionation a center cut of this fraction was shown to have a molecular weight, by gas density measurements at pressures of 47.2 and 138.8 mm, of 108.8 (calculated for HPF_4, 108.). The −196° fraction contained 2.4 mmoles of PF_5 and a trace of PF_3, as determined by its infrared spectrum.

All the hydrogen available from the $(CH_3)_3SnH$ can be accounted for as either H_2PF_3 (8.1 mmoles) or HPF_4 (3.8 mmoles). The 2.4 mmoles of residual PF_5 along with the P in the products leaves 2.7 mmoles of P unaccounted for. The missing P was identified in the solid, by use of the method described previously,[8] involving addition of anhydrous NH_3 (25.0 mmoles) to the solid residue. After 4 hr 19.5 mmoles of unreacted NH_3 was collected. Thus the 5.4 mmoles of NH_3 used in formation of the complex $(CH_3)_3Sn(NH_3)_2^+\ PF_6^-$ verifies the presence of 2.7 mmoles of PF_5, which had been retained in the residue as $(CH_3)_3SnPF_6$.[8]

When allowed to react in a 1:1 ratio, $(CH_3)_3SnH$ and PF_5 yield predominantly HPF_4, while excess $(CH_3)_3SnH$ produces more H_2PF_3. These latter reactions, however, are very dissatisfying even when a complete gas-phase reaction is carried out, since the presence of excess hydride leads to the formation of yellow solids.

It should be noted that complete separation and purification of the product mixtures from this reaction is quite tedious and further complicated by the reactivity of HPF_4 and H_2PF_3 in a glass system. The most successful purification scheme appears to be to trap the less volatile decomposition products at −64°, H_2PF_3 at −96°, POF_3 at −112°, HPF_4 at −126°, PF_5 at −145°, and PF_3, PH_3, SiF_4 at −196°. Several fractionations, and utilization of center cuts, are necessary to ensure complete purity.

The Reaction of Trimethyltin Deuteride and Phosphorus Pentafluoride. Before preparing the deuterated species, the entire reaction system was cleaned, baked at 500°, assembled, and evacuated for several days. The reaction of $(CH_3)_2SnD$ with PF_5 was carried out in an entirely analogous fashion to the hydride reaction. Pure fractions of DPF_4 had a vapor pressure of 1.3 mm at −111.6° and 16.4 mm at −96°. The vapor pressure of D_2PF_3 was 7.6 mm at −64.3° and 52.6 mm at −45.5°. The sample was not tensimetrically pure, however; the limited sample size made it very difficult to remove the last traces of the contaminating tetramethyltin which had been present in the original $(CH_3)_2SnD$ sample.

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(3) The first mention of the compounds HPF_4 and H_2PF_3 may be found in a conference report in 1961: B. Blaser and K. W. Worms, *Angew. Chem.*, 73, 76 (1961). Subsequently this work, describing the preparation of these compounds from HF and H_3PO_2 or H_3PO_3, appeared in several patents: German Patent 1,106,736 (1961); *Chem. Abstr.*, **56**, 11215*g* (1962); U. S. Patent 3,061, 406 (1962). No further literature report has appeared on this work; however, Schmutzler[2b] cites a private communication from J. Goubeau on infrared and Raman spectral studies on H_2PF_3. More recently R. R. Holmes (Abstracts of the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, Abstract O-64; R. R. Holmes and R. N. Storey, *Inorg. Chem.*, **5**, 2146 (1966)) reports the synthesis of H_2PF_3 by the method of Blaser and Worms,[3] and spectral studies of this compound.

(4) R. A. Goodrich and P. M. Treichel, *J. Am. Chem. Soc.*, **88**, 3509 (1966).

(5) A. E. Finholt, A. C. Bond, K. E. Wilzbach, and H. Schlessinger, *ibid.*, **69**, 2692 (1947).

(6) M. L. Mattox, N. Flitcroft, and H. D. Kaesz, *J. Organometal. Chem.* (Amsterdam), **4**, 50 (1965).

(7) R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y.,1948, p 148.

(8) P. M. Treichel and R. A. Goodrich, *Inorg. Chem.*, **4**, 1424 (1965).

Table I. Decomposition of Gaseous HPF_4[a]

Hours at room temp	% decomposed
3	12
4	16
4.5	31
5.2	62
80	90
130	93

[a] In a Kel-F sample tube with 4 atm of SiF_4. Original HPF_4 gas pressure was also 4 atm.

Table II. Data for HPF_4 and H_2PF_3

HPF_4			H_2PF_3		
Temp, °C	P_{obsd}, mm	P_{calcd}, mm	Temp, °C	P_{obsd}, mm	P_{calcd}, mm
		A. Vapor Pressure Data (Solid[a])			
−98.6	12.8	12.7	−49.8	37.9	39.5
−99.5	11.1	11.2	−52.8	28.8	29.0
−100.7	9.9	9.6	−57.2	18.1	18.1
−103.4	6.8	6.7	−59.7	13.3	13.7
−104.3	5.6	5.9	−64.6	7.7	7.8
−106.7	4.5	4.2	−67.8	5.1	5.3
−106.9	4.1	4.1			
−111.6	2.0	2.0			
		(Liquid[b])			
−64.2	164.2	167	−22.9	221	219
−74.2	88.1	88.1	−23.6	204	210
−84.7	42.8	41.9	−24.3	206	202
−86.1	37.5	37.8	−25.7	190	186
−95.1	17.8	18.4	−31.7	128.6	129.7
−95.2	18.4	18.2	−32.6	120.3	122.5
			−36.0	97.7	98.9
			−37.4	87.6	90.4
			−40.2	74.3	75.3
			−45.2	53.0	53.6
			−45.3	54.4	53.3
			−45.5	53.5	52.5

B. Physical Constants

	HPF_4	H_2PF_3
Mp, °C	−98 ± 2 (lit. −89[3])	−47 ± 2 (lit. −51[3])
Bp (extrap.), °C	−35.9 (lit. −37[3])	+0.9 (lit. +2[3])
ΔH_{subl}, kcal/mole	7.9	10.1
ΔH_{vap}, kcal/mole	5.3	7.1
Trouton const, cal/mole deg	22.2	26.1

[a] Solid: log P (mm) = $-(1729/T) + 11.011$ for HPF_4; $-(2216/T) + 11.521$ for H_2PF_3. [b] Liquid: log P (mm) = $-(1152/T) + 7.737$ for HPF_4; $-(1561/T) + 8.579$ for H_2PF_3.

Infrared spectra of samples of DPF_4 and D_2PF_3 stored for long times at −196° showed that very little H-D exchange occurs between these compounds and the glass surface.

Stabilities of HPF_4 and H_2PF_3. Both HPF_4 and H_2PF_3 decomposed slowly when manipulated in Pyrex apparatus. During fractionations, reaction product mixtures left a white or yellow solid which turned orange and evolved PH_3 when heated. The properties of this solid seem to be most consistent with those ascribed to polymeric phosphorus subhydrides.[9]

Decomposition of H_2PF_3 in a sealed Pyrex bulb proceeded rapidly; complete degradation of the sample occurred in 1 hr at room temperature. In addition to the solid residue, gaseous PF_3 and SiF_4 were observed as volatile products of this decomposition. Gaseous HPF_4 was substantially more stable under the same conditions. Samples left in Pyrex infrared gas cells would be seen changing after 3 hr; the original bands due to HPF_4 diminished and new bands appeared in the P-H, P-F, and P═O regions. A sample of HPF_4, stored overnight in a 250-ml reaction bulb which had been dried by evacuation for several hours accompanied by flaming, produced SiF_4, PF_3, a small amount of $HPOF_2$, and a nonvolatile, oily liquid which did not transfer upon prolonged pumping. Other samples which had undergone decomposition gave a less volatile, unstable compound with a vapor pressure >25 mm at room temperature in addition to the above products. The compound was never isolated in large enough quantities for complete characterization. Samples of HPF_4 and H_2PF_3 stored in Pyrex at −196° showed no decomposition.

Apparently the decompositions observed in glass systems are primarily the result of a reaction with the glass. When HPF_4 was stored at room temperature in Kel-F nmr tubing a different, slower decomposition was observed. The ^{19}F nmr spectra of such samples showed a diminishing in the HPF_4 resonance intensity and resonances of increasing intensity due to PF_3 and HF suggesting thermal decomposition according to

$$HPF_4 \longrightarrow HF + PF_3$$

These data are summarized in Table I.

Isolation of $HPOF_2$. Fractionation of partially decomposed samples of HPF_4 through traps held at −112, −126, and −196° yielded a small amount of a volatile P═O containing compound in the warmer trap along with the HPF_4. This product could be obtained pure from the HPF_4 which collected with it by allowing the mixture to expand from a −96° trap, in which the desired product, $HPOF_2$, remained.

A 0.26-mmole gaseous sample of this compound was transferred to a small preweighed ampoule. The sample weighed 0.0231 g; from these data a molecular weight of 88.8 ± 3 can be calculated (calculated for $HPOF_2$, 86).

Characterization

Vapor Pressure Studies. The vapor pressure data for both the solid and liquid phases of HPF_4 and H_2PF_3 were obtained in a calibrated U-tube connected to a mercury manometer. Temperatures were determined to ±0.1° using vapor tension thermometers; pressures were read to within ±0.05 mm using a cathetometer. The initial purity of the samples was verified by constancy of pressure at a given temperature in two different volumes for several different fractions of the sample. However, decomposition of the samples at higher temperatures, especially H_2PF_3, made it necessary to return frequently to a convenient low temperature and check for a pressure increase. Sometimes flashing off the volatile impurities was sufficient, but usually a complete refractionation or the use of new samples was necessary. The linear equations found were obtained by least-squares treatment of the data. Table II shows the observed and calculated pressures.

Vapor pressure measurements were obtained for liquid $HPOF_2$ from −45 to 0° [temp, °C, P_{obsd}, mm (P_{calcd}, mm): 0, 39.1 (38.8); −22.4, 10.5 (10.2); −33, 4.7 (5.0); −45, 2.1 (2.0)]. Although limited in number, these readings best fit the equation log P (mm) = $-(1775/T) + 8.089$. The calculated boiling point is 67.7°, the heat of vaporization is 8.1 kcal/mole and the Trouton constant is 23.8 cal/mole deg.

Mass Spectra. Mass spectra run to 70 ev for samples of HPF_4 and H_2PF_3 (Table III) show traces of impurities, some of which are believed to arise through the decomposition of the gases within the spectrometer. The parent ions HPF_4^+ (*m/e* 108) and $H_2PF_3^+$ (*m/e* 90) could not be detected even at 17 ev for HPF_4 or 12 ev for the H_2PF_3. This is consistent with other phosphorane results.[10] The ions PF_4^+ and HPF_3^+ for the sample of HPF_4, and HPF_3^+ and $H_2PF_2^+$ for H_2PF_3, were found in relatively high abundance in the fragmentation pattern suggesting considerable stability of such species. This is not unexpected in view of the stability of phosphonium ions.

It is interesting that there are approximately equal

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(9) J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1958, p 228; E. C. Evers and Z. H. Street, *J. Am. Chem. Soc.*, **78**, 5726 (1956); T. P. Fehlner, *ibid.*, **88**, 2613 (1966).

(10) R. Schmutzler, private communication.

Table III. Mass Spectra of HPF_4, H_2PF_3, and $HPOF_2$[a,b]

		Relative intensities		
	m/e	HPF_4	H_2PF_3	$HPOF_2$[c]
HPF_4^+	108	...	...	...
PF_4^+	107	29	...	...
SiF_4^+, POF_3^+	104	9	1	7
HPF_3^+	89	39	75	3
PF_3^+	88	60	8	5
$H_2POF_2^+$	87	...	...	3
$HPOF_2^+$	86	11	1	47
SiF_3^+, POF_2^+	85	14	5	100
$H_2PF_2^+$	71	2	100	5
HPF_2^+	70	2	68	3
PF_2^+	69	100	68	44
H_2POF^+	68	...	2	...
$HPOF^+$	67	4	5	20
SiF_2^+, POF^+	66	4	1	21
HPF^+	51	3	82	5
PF^+	50	16	91	9
H_2PO^+	49	3		
HPO^+	48	1	4	...
SiF^+, PO^+	47	7	1	33
PF_3^{2+}	44	4	4	...
SiF_3^{2+}, POF_2^{2+}	42.5	...	2	1
HOF^+	36	2	...	...
HPF_2^{2+}, OF^+	35	2	1	...
PF_2^{2+}	34.5	3	1	...
H_2POF^{2+}	34	...	1	1
$HPOF^{2+}$	33.5	...	...	...
SiF_2^{2+}, POF^{2+}	33	...	1	3
HP^+	32	3	10	3
P^+	31	12	32	9
N_2^+	28	2	2	5
H_2PF^{2+}	26	...	5	
HPF^{2+}	25.5	...	1	
PF^{2+}	25	7	4	

[a] 70 ev. [b] Low-intensity ions containing oxygen found with HPF_4 and H_2PF_3 are believed to arise through a decomposition of the sample within the spectrometer. [c] The $HPOF_2$ sample contained a small amount of POF_3 and SiF_4 as shown by its infrared spectrum.

relative abundances of PF_4^+ and HPF_3^+ in the spectrum of HPF_4, and of HPF_3^+ and $H_2PF_2^+$ in the spectrum of H_2PF_3. This suggests that the thermodynamic stabilities of these ions are not greatly dissimilar. While there are obvious limitations to conclusions which can be drawn from this, it nonetheless suggests a possible chemical stability of such species. The fully hydrogenated ion PH_4^+ is a well-known chemical entity; some halogenated phosphonium ions are known also but there is a notable lack of fluorophosphonium ions (including the ion PF_4^+) which bear more than a single fluorine atom. It may well be possible that such species as PF_4^+ can be made and would be stable chemical entities in the solid state. Also supporting this is the recent synthesis of the NF_4^+ ion.[11] Certainly chemical investigations should be directed toward this end.

Nmr Spectra. Fluorine-19 nmr spectra of these compounds were run on a Varian HR-60 at 56.4 Mcps, and proton nmr spectra were run on this instrument at 60 Mcps. Phosphorus-31 spectra were kindly provided by Dr. G. S. Reddy and Dr. R. Schmutzler at DuPont using a Varian HR-100 at 40.5 Mcps. We are grateful to these workers for their assistance. All data obtained from these studies are assembled in Table IV.

Fluorine and proton spectra were run on both gaseous and liquid samples; solid sodium fluoride was generally added to liquid samples to minimize exchange processes which broaden the signals.[12] The gaseous spectra, run at room temperature in 12-mm Kel-F tubes, provided the most definitive information. In these runs relatively sharp signals (line widths ~30–40 cps) were obtained. This line width was due primarily to variations in field strength through the sample rather than to the nature of the sample itself. The spectra obtained using liquid samples were run at several low temperatures, limited usually by the sample melting temperature on one extreme and rapid decomposition on the other. They often consisted of signals so broad that some primary splittings visible in the gaseous spectra could not be observed.[13] Generally, if a sample which did give spectra as detailed as those reported in Table IV was allowed to warm even to $-20°$ for a few minutes, then this sample would not reproduce the original data when recorded but rather would only give an extremely broad signal. In such cases repurification was necessary before any further data could be obtained. We attribute this result to the presence of impurities arising through decomposition of the sample which occurs on warming. Impurities such as HF in the sample apparently promote intermolecular exchange processes which lead to broad signals. The sodium fluoride probably served to remove these materials.[12]

The expected structure for HPF_4 is an equatorially substituted trigonal bipyramid. This structure would be consistent with known RPF_4 structures except CF_3PF_4; infrared and microwave data[14] on HPF_4 support this structure. The nmr data on HPF_4 and DPF_4 (Table IV) can be interpreted in terms of this structure, if one assumes that the axial and equatorial fluorine atoms are rendered equivalent through a rapid intramolecular process in the temperature range (liquid, -90 to $-50°$; gas, 30°) in which spectra were taken. Spectra of other RPF_4 compounds, *e.g.*, CH_3PF_4, known to be an equatorially substituted trigonal bipyramid,[15] also show an equivalence of fluorine atoms, and for such systems a similar assumption is made.[2,16,17]

The proposed trigonal bipyramid structure for H_2PF_3 with two hydrogen atoms in equatorial positions is consistent with the known structures for R_2PF_3 compounds[15-17] and is supported by the infrared spectrum of this compound. The ^{19}F nmr spectrum of H_2PF_3 shows at a low temperature ($-46°$) the nonequivalence of axial and equatorial fluorine atoms, similar to observations for other R_2PF_3 compounds.[2b] This spectrum consists of two broad peaks in an intensity ratio of approximately 2:1: the downfield doublet arising from the two axial fluorine atoms and the upfield doublet arising from the single equatorial fluorine atom. The doublet splittings observed are due to the P–F coupling. As the sample is warmed to $-15°$, however, the peaks are observed to broaden and coalesce to a doublet at -23 ppm, suggesting that by intramolecular exchange the fluorine atoms experience a similar averaged environment. Note that the P–F coupling is still retained, suggesting intermolecular

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[11] W. E. Tolberg, R. T. Rewick, R. S. Stringham, and M. E. Hill, *Inorg. Nucl. Letters*, 2, 79 (1966); K. O. Christe, J. P. Geurtin, and A. E. Parlath, *ibid.*, 2, 83 (1966).

[12] E. L. Muetterties and W. D. Phillips, *J. Am. Chem. Soc.*, **81**, 1084 (1959).

[13] R. R. Holmes[3] has reported similar results.

[14] C. D. Cornwell and S. B. Pierce, private communication.

[15] L. S. Bartell and K. W. Hansen, *Inorg. Chem.*, **4**, 1777 (1965).

[16] E. L. Muetterties, W. Mahler, and R. Schmutzler, *ibid.*, **2**, 613 (1963).

[17] E. L. Muetterties, W. Mahler, K. J. Paker, and R. Schmutzler, *ibid.*, **3**, 1298 (1964).

Table IV. Nmr Spectra of the Fluorophosphoranes

	δ, ppm			J, cps			
	F	H	P	P–F	P–H	H–F	Remarks
HPF_4							
Gas (32°)	−24.7[a]	−7.4[b]	...	980	1030	92	^{19}F, 2 doublets ^{1}H, 2 quintets, 1:4:6:4:1
Liquid (−50 to −90°)	−28[c]	−6.8[d]	+53.6[e]	986	1115	92	^{19}F, 2 doublets ^{1}H, 1 doublet[f] ^{31}P, 2 quintets, 1:4:6:4:1
DPF_4							
Liquid (−45°)	−28[c]	...	...	986	...	13	^{19}F, 2 triplets, 1:1:1
H_2PF_3							
Gas (32°)	−27.5[a]	−7.0[b]	...	877	825	80	^{19}F, 2 triplets, 1:2:1 ^{1}H, 2 quartets, 1:3:3:1
Liquid (−15 to −46°)	−23[c,g] −47, +29[c,g]	−6.5[d]	+24.1[e]	866[h]	865	80	^{19}F[g] ^{1}H, 2 quartets, 1:3:3:1 ^{19}P, sextet, 1:5:10:10:5:1
D_2PF_3							
Liquid (20°)	−23[c,i]	...	+24.1[e]	600[j]	J_{P-D} 134	..	^{19}F, broad doublet[i] ^{31}P, 1:3:3:1, quartet of 1:4:6:4:1 quintets

[a] Corrected to CF_3COOH (TFA) from internal standard SiF_4. [b] Corrected to $(CH_3)_4Si$ (TMS) from external standard CH_4. [c] External standard TFA. [d] External standard TMS. [e] External standard H_3PO_4. [f] This doublet was fairly broad with some residual structure that could not be resolved. [g] The observed signals as well as the details of the fine structure are a very sensitive function of temperature and sample condition. At −46° two broad resonances are observed, a doublet, $\delta(F_{ax}) = -47$ ppm (P–F coupling observed), and a broad doublet, $\delta(F_{eq}) = +29$ ppm. These coalesce at −15° to a singlet broad doublet, $\delta = -23$ ppm. [h] Average value from higher temperature F and P spectra. [i] The chemical shift was observed to be a function of temperature, as in H_2PF_3. [j] Large uncertainty in this value due to broadness of doublet.

Table V. Gas-Phase Infrared Data on the Fluorophosphoranes

HPF_4[a]		DPF_4[b]		H_2PF_3[a]		D_2PF_3[b]	
Absorption,[c] cm⁻¹	Assignment	Absorption,[c] cm⁻¹	Assignment	Absorption,[c] cm⁻¹	Assignment	Absorption,[c] cm⁻¹	Assignment
2590 (mw)				2545 (ms)	P–H str		
2485 (ms)	P–H str			2465 (ms)	P–H str		
2155 (w)							
1917 (mw)		2000 (w)				1860–1800 (br, ms)	P–D str
1800 (w)		1905 (w,				1780–1730 (br, m)	P–D str
		1840 (ms)					
		1800 (ms)	P–D str				
1525 (m)		1735 (w)					
		1645 (vw)					
1375	$HPOF_2$	1600 (vw)		1440 (m)		1430 (m)	
1295 (w)		1510 (m)		1288 (m)			
1104 (w)		1430	POF_3	1118 (w)		952 (s)	PD_2 in-plane bend
1077 (w)		1065 (vs)		1084 (w)			
1024 (s)	PF_2 eq str	1005 (s)	PF_2 eq str	1019 (s)	PH_2 in-plane bend		
1016 (s)	PF_2 eq str	999 (s)	PF_2 eq str	992 (s)	PH_2 in-plane bend	925 (s)	PD_2 in-plane bend
955 (w)		950 (ms)		930 (w)			
				900 (w)		875 (w)	
880 (vs)	PF_2 axial str	860 (vs)	PF_2 axial str	886 (m)		808 (vs)	PF_2 axial str
				860 (w)			
840–760 (br, m)		810 (m)		820 (vs)	PF_2 axial str	710 (m)	(PF eq str)
		760 (mw)		761 (s)	(PF eq str ?)		
640 (ms)	PF_2 axial str	635 (ms)	PF_2 axial str			695 (w)	
615 (ms)		585 (m)		662 (w)			
				625 (w)	PF_2 axial str	635 (vs)	PF_2 axial str
532 (s)	PF_2 in-plane bend	530 (s)	PF_2 in-plane bend				
				470 (ms)		470 (ms)	

[a] Range reported 400–3000 cm⁻¹; $P = 150$ and 4 mm. [b] Range reported 400–2000 cm⁻¹; $P = 70$ and 4 mm. [c] Relative intensities given in parentheses.

exchange is not important. Equivalence of axial and equatorial fluorine atoms in the gas at 32° is also observed.

Infrared Spectra. Gas-phase infrared spectra of the hydrogen- and deuterium-substituted phosphoranes were recorded on a Beckman IR-10 spectrometer, utilizing a 10-cm gas cell with KBr windows to obtain the spectra in the range 4000–400 cm⁻¹. Higher resolution spectra were obtained with a Perkin-Elmer 421 spectrometer in the range 4000–700 cm⁻¹. Band positions and a partial assignment are given in Table V.

The similarities of these infrared spectra with spectra of CH_3PF_4[18] and $(CH_3)_2PF_3$[19] suggest that HPF_4 and H_2PF_3 have equatorially substituted trigonal bipyramidal structures similar to these alkylfluorophosphoranes. Several assignments of bands are made here on the basis of these similarities.

In the P–F stretching region of the HPF_4 spectrum, the bands at 880 and 640 cm^{-1} (860 and 635 cm^{-1} for DPF_4) were assigned to asymmetric and symmetric axial P–F stretching modes, respectively. These bands are of much higher intensity than those for CH_3PF_4 which could indicate a larger deviation from rigorous trigonal bipyramidal geometry than seen in CH_3PF_4. Two bands at 1024 and 1016 cm^{-1} (1005 and 999 cm^{-1} for DPF_4) were assigned to the equatorial PF_2 stretching modes. In CH_3PF_4 these are found at 1009 and 932 cm^{-1}. The small deviation between the two compounds might well be expected because these frequencies would depend considerably on the nature of the substituent group in molecules of this given geometry.

An equatorial PF_2 *in-plane* bending mode appears at 530 cm^{-1} in HPF_4 and DPF_4. The medium intensity band at 1525 cm^{-1} for HPF_4 (1510 cm^{-1} in DPF_4) is probably an overtone due to the combination of the 880- and 640-cm^{-1} bands (860- and 635-cm^{-1} bands in DPF_4).

The P–H stretching frequency in HPF_4 is seen as a complex pattern at 2485 cm^{-1}. This value is close to that quoted for $CH_3PF_2H[N(C_2H_5)_2]$ and $C_2H_5PF_2H[N(C_2H_5)_2]$[20] but is at substantially higher wavenumbers than the P–H stretching modes observed for P(III) compounds such as PH_3 (2421 and 2327 cm^{-1}) and PF_2H (2241 cm^{-1}).[21] The D–P stretching frequency in DPF_4 is seen near 1800 cm^{-1}, the position expected on the basis of the relative atomic masses. This is to be compared to PD_3 with a stretching frequency at 1694 cm^{-1}. The difference in position in P–H and P–D stretching frequencies in P(III) and P(V) compounds is no doubt related to the different hybridizations associated with different coordination geometries.

A second band found in both P–H and P–D regions of the spectra of HPF_4 and DPF_4 was of considerably lower intensity. We are uncertain of the assignment of this band but suspect that it may be an overtone.

In the spectra of H_2PF_3, one observes strong peaks at 820 and 625 cm^{-1} (808 and 635 cm^{-1} in D_2PF_3) which are assignable to an asymmetric and symmetric axial P–F stretching modes. These frequencies in $(CH_3)_2PF_3$[19] are seen at 780 and 540 cm^{-1}. As is observed in the series of alkylfluorophosphoranes, the substitution of additional groups causes a shift downfield in these absorptions. We have tentatively assigned the band at 761 cm^{-1} (710 cm^{-1} in D_2PF_3) to the equatorial P–F stretching frequency, seen in $(CH_3)_2PF_3$ at 836 cm^{-1}.[19]

The P–H stretching frequencies are observed at 2545 and 2465 cm^{-1} in H_2PF_3; these bands are relatively strong and structured. In D_2PF_3, the expected shift based on the relative masses is observed, giving broad P–D stretching frequencies between 1900 and 1700 cm^{-1}. In-plane bending modes for the PH_2 (PD_2) group are observed to fall in these spectra at 1019 and 992 cm^{-1} (952 and 925 cm^{-1} for D_2PF_3). The remaining predominant peaks in H_2PF_3 at 1440 and 1288 cm^{-1} are overtones of 820 plus 625 and 662 plus 625, respectively. A similar overtone although more highly structured is seen in D_2PF_3 at 1430 cm^{-1}, possibly a combination of 710 plus 695 or 808 plus 635 cm^{-1}.

The gas-phase infrared spectrum of $HPOF_2$ run at 75 and 8 mm in a 10-cm cell showed bands in the P–H stretching region at (cm^{-1}) 2505 (w), 2490 (w), 2470 (w, sh), the P=O stretching region at 1375 (s, highly structured) and the P–F regions of 1000 (s, broad), 935 (m, sh), 920 (s, broad), 885 (s), 518 (m), 500 (m), 480 (m). The position of the P=O stretching frequency differs markedly from the value predicted by the empirical formula of Bell.[22] The latter calculated value would be at 1338 cm^{-1}, not unlike the values calculated and observed for analogous alkyl derivatives, $RPOF_2$. In fact, calculating in the reverse direction, one comes up with an electronegativity of hydrogen between the values for chlorine and fluorine. Since this is clearly an unrealistic value one must assume that the formula itself is at fault here. It seems very likely that the basic assumption underlying this calculation, the assumption of inductive transfer of electrons, is violated. One possible reason, which could give the observed results, is the inclusion of a relatively important ionic contribution to the bonding in the molecule.

$$HPOF_2 \rightleftharpoons H^+POF_2^-$$

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