correction of data obtained with $ZnCl_2$ present was probably determined mainly by the rate of diffusion. However, over the majority of the range ($\geq 315°$), the *equilibrium* pressure of $ZnCl_2$[21] exceeds 0.02 torr so that zinc would now be transported as well by $ZnCl_2(g)$ if anywhere near this $ZnCl_2$ pressure was attained. In actual fact, since a chloride pressure lower than equilibrium has already been anticipated, the sublimation results probably involved some combination of both a transport process and kinetic effects in the rates of evaporation. The evolution of gaseous impurities by the salt could also aid the metal removal.

Explanation of the results obtained at higher temperatures and pressures[3] is more difficult as numerical data for the control experiments with the pure components were not reported. The 5-torr background pressure exceeds the vapor pressure of the metal but not the salt over the majority of the range studied, but this does not apply at 0.05 torr.

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The Preparation and Characterization of Hydrothiophosphoryl Difluoride, SPF_2H, and Hydrophosphoryl Difluoride, OPF_2H

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Anhydrous hydrogen iodide reacts with dimethylaminophosphoryl difluoride and dimethylaminothiophosphoryl difluoride to form hydrophosphoryl difluoride and hydrothiophosphoryl difluoride in good yield. The compounds were characterized by nmr, infrared, and mass spectra and by vapor-pressure studies. Both are volatile liquids: the thiophosphoryl compound boils at 0.2° and is considerably more stable than the phosphoryl compound which boils at 55°. The results of hydrolytic and thermal decomposition studies are discussed.

Introduction

There have been few reports of halogenated phosphines or phosphoranes in which a hydrogen atom and a halogen atom are bound to the same phosphorus atom. The recent synthesis of difluorophosphine, PF_2H, by Rudolph and Parry[1] provides the only substantiated example of a halophosphine although inconclusive reports of the synthesis of chlorophosphines have appeared.[2] The fluorophosphoranes PF_4H and PF_3H_2, first reported by Blaser and Worms,[3] have recently been studied in greater detail[4,5] and an organofluorophosphorane, $C_6H_5PF_3H$, has also been reported.[6] We now report in detail[7] the direct synthesis and characterization of the pentavalent phosphoryl and thiophosphoryl hydrofluorides. One of these, hydrophosphoryl difluoride, has just recently been reported as a product of the reaction of HPF_4 with glass.[5]

Experimental Section

Standard vacuum techniques using Pyrex-glass apparatus were employed throughout. Stopcocks were lubricated with Apiezon "N" grease. Infrared spectra were measured with Perkin-Elmer 421 (4000–200 cm^{-1}) or 337 (4000–400 cm^{-1}) instruments, mass spectra with an AEI MS-9 double-focusing mass spectrometer, and nuclear magnetic resonance spectra with Varian HA 100 (hydrogen) or HA 60 (fluorine and phosphorus) instruments. Fluorine spectra were measured at 56.4 Mcps (relative to CCl_3F standard) and phosphorus spectra at 24.1 Mcps. Hydrogen spectra were measured relative to tetramethylsilane (τ 10.0). Nmr spectra of the solid residues encountered in the study were obtained on dry acetonitrile or deuterioacetonitrile solutions.

Materials.—Commercial hydrogen iodide (Matheson) was purified by fractional distillation before use. The dialkylamino phosphoryl or thiophosphoryl difluorides were prepared from the corresponding dichloro compounds by fluorination with antimony trifluoride (catalyzed by antimony pentachloride when necessary) as described previously[8] followed by fractional distillation under vacuum before use.

Preparation of Hydrothiophosphoryl Difluoride.—In a typical reaction, dimethylaminothiophosphoryl difluoride (13.5 mmoles) was condensed with slightly more than a threefold molar ratio of anhydrous hydrogen iodide (41 mmoles) into a 1-l. glass reaction vessel fitted with a stopcock. The reaction vessel was allowed to warm to room temperatures whereupon reaction began and proceeded at a moderate rate for 1–2 hr. During the reaction the liquid dimethylaminothiophosphoryl difluoride slowly changed from a clear, colorless liquid to yellow then to dark red and finally to a dark red, crystalline mass. The volatile products were removed from the reaction vessel and fractionated; the SPF_2H passed a trap cooled to −81° and collected in a trap cooled to −131° giving yields up to 95% of theoretical (eq 1).

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[2] P. Royen and K. Hill, *Z. Anorg. Allgem. Chem.*, **229**, 112 (1936).

[3] B. Blaser and K. Worms, *Angew. Chem.*, **73**, 76 (1961).

[4] R. R. Holmes and R. N. Storey, *Inorg. Chem.*, **5**, 2146 (1966).

[5] P. M. Treichel, R. A. Goodrich, and S. B. Pierce, *J. Am. Chem. Soc.*, **89**, 2017 (1967).

[6] Zh. M. Ivanova and A. V. Kirsanov, *Zh. Obshch. Khim.*, **31**, 3991 (1961).

[7] See T. L. Charlton and R. G. Cavell, *Chem. Commun.*, 763 (1966), for a preliminary account of the preparation of SPF_2H.

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Hydrogen iodide and other volatile products such as traces of SPF_3 and SiF_4 passed −131° and were collected at −196°. The residual solids were identified as a mixture of molecular iodine and dimethylammonium iodide. Using less than the threefold molar ratio of hydrogen iodide led to the same products plus a quantity of unreacted dimethylaminothiophosphoryl difluoride (which was easily removed from the SPF_2H by condensation in the trap cooled to −81°) in agrement with the stoichiometry expressed by eq 1. Most of the reactions were performed with excess hydrogen iodide since this is the easiest of the two starting materials to remove from the product.

Hydrothiophosphoryl difluoride was characterized by molecular weight (Calcd for SPF_2H: 102. Found: 102), mass spectroscopy including accurate mass measurement of the parent ion (Calcd for $^{32}SPF_2H$: *m/e* 101.9505. Found: *m/e* 101.9503), and analyses (Calcd for SPF_2H: S, 31.45; P, 30.38; F, 37.27. Found: S, 33.31; P, 29.19, 30.33; F, 37.52). The deuterium analog was synthesized as above using deuterium iodide (>99% isotopic purity, Merck Sharp and Dohme) in place of hydrogen iodide and characterized by mass and nmr spectroscopy.

The rate of the reaction depends on the pressure of gases in the reaction vessel. At hydrogen iodide pressures of 2–3 atm (calculated from gas laws assuming no dissolution in the liquid reagent) the reaction was complete in less than 1 hr, but at lower pressures (*i.e.*, 1 atm or less) 24–48 hr was required for complete reaction. Decomposition of SPF_2H did not appear to be significant even in preparations which extended over several days.

The Preparation of Hydrophosphoryl Difluoride.—Hydrophosphoryl difluoride was prepared as described above with modifications necessitated by the lower stability of the phosphoryl compound. Dimethylaminophosphoryl difluoride was combined with slightly more than a threefold molar ratio of hydrogen iodide in a reaction vessel chosen so that the pressure of reactants was at least 2–3 atm at room temperature in order to ensure rapid conversion of the dimethylamino compound. The reaction was allowed to proceed at room temperature for no longer than 15–20 min whereupon the reaction vessel was opened and the contents fractionated in the vacuum system through −23, −81, and −196° traps. Hydrophosphoryl difluoride was collected at −81° and usually no excess dimethylaminophosphoryl difluoride was obtained indicating complete reaction. The yield of hydrophosphoryl difluoride was generally good (60–80%) although some decomposition to POF_3 and PF_3 occurred during the synthesis and separation. The decomposition products were collected at −196° along with unreacted hydrogen iodide. Hydrophosphoryl difluoride was characterized by molecular weight (Calcd for OPF_2H: 86.0. Found: 86.9) and by mass spectroscopy including accurate mass measurement of the parent ion (Calcd for OPF_2H: *m/e* 85.9733. Found: *m/e* 85.9733). No masses greater than the molecular ion were observed in the mass spectrum.

If the reaction did not go to completion in the allotted time, unreacted dimethylaminophosphoryl difluoride was collected at −81° along with OPF_2H. Purification was best effected by vacuum distillation in a LeRoy still.[9]

Pure OPF_2H could be stored for long periods of time at liquid nitrogen temperature without decomposition. The impure compound decomposed quickly at room temperature. The decomposition appears to be catalyzed by the reagents or products involved in the synthesis since reactions which were allowed to proceed at room temperature for 6–8 hr or longer gave only phosphorus trifluoride, phosphoryl fluoride, and difluorophosphoric acid and none of the desired OPF_2H. The products obtained from several room-temperature reactions of different duration are summarized in Table I. All products were identified by infrared spectroscopy,[10-12] and in addition fluorine nmr was used to identify difluorophosphoric acid.[13]

TABLE I

EFFECT OF TIME ON PRODUCTS OBTAINED DURING PREPARATION OF OPF_2H

Time	Volatile products	Method of identification	Approx ratio, POF_3:PF_3
4 days	OPF_3, PF_3, OPF_2OH	Infrared, nmr	1:2
2 hr	OPF_3, PF_3, OPF_2OH, OPF_2H	Infrared, nmr	1:1
5 min	OPF_3, OPF_2H	Infrared, nmr	No PF_3

Vapor Pressures.—The vapor pressures of OPF_2H and SPF_2H were measured in an all-glass spiral gauge microtensimeter using a null-point technique. Several samples of each compound were used and the vapor pressures were measured with both ascending and descending temperatures to check reproducibility and to detect decomposition during the measurements. The results are given in Table II. The vapor pressure of hydrophosphoryl difluoride proved to be reproducible provided that the maximum temperature of measurement did not exceed −25°.

TABLE II

VAPOR PRESSURES OF HYDROTHIOPHOSPHORYL DIFLUORIDE AND HYDROPHOSPHORYL DIFLUORIDE

SPF_2H			OPF_2H		
Temp, °C	Pressure, mm		Temp, °C	Pressure, mm	
	Obsd	Calcd		Obsd	Calcd
−85.2	2.0	2.4	−53.3	1.2	1.1
−76.3	5.9	5.4	−47.6[b]	2.0	1.9
−71.0[a]	9.1	8.6	−45.5	2.3	2.4
−65.5[a]	15.5	13.5	−45.3[c]	5.9	2.4
−60.0	20.9	20.9	−38.0	3.8	4.1
−54.8	32.2	30.9	−34.8[b]	4.4	5.25
−49.0	46.2	46.8	−32.5	6.6	6.2
−41.8	75.7	76.0	−29.5[b]	7.7	7.8
−39.5	91.4	88.1	−29.6[c]	11.20	7.8
−29.0	162.7	167.5	−25.5	10.8	10.5
−25.2[a]	204.9	208.9	−19.1	16.4	16.6
−15.5	343.2	354.8	−17.1	22.4	18.6
			−10.8	28.2	27.5
			− 2.6	47.2	45.7

[a] Measured with descending temperature. All other measurements made with ascending temperature. [b] Measured with descending temperature; maximum temperature of sample −25°. [c] Measured with descending temperature; maximum temperature of sample 0°.

Thermal Decomposition of OPF_2H.—A sample of pure OPF_2H (0.0255 g, 0.272 mmole) was sealed in a 200-cc bulb and kept at room temperature for 14 days. The volatile products obtained by fractionation were PF_3 (0.0133 g, 0.151 mmole) and unreacted OPF_2H (0.0021 g, 0.025 mmole). Thus 92% of the OPF_2H had decomposed. The solid product was identified as phosphorous acid, $OPH(OH)_2$, by infrared and hydrogen nmr spectra.

Attempted Thermal Decomposition of SPF_2H.—A sample of SPF_2H stored for several months at room temperature in a sealed glass ampoule was almost quantitatively recovered. Very small amounts of PF_3 and SPF_3 were obtained and identified by infrared spectroscopy[10,14] and a trace of a yellow, involatile solid remained in the ampoule. In a quantitative experiment 0.5137 g of SPF_2H was sealed in a glass ampoule and kept at 110° for 4 weeks. Recovery of SPF_2H was almost quantitative (0.5100 g, 99%) but a trace of PF_3, identified by its infrared spectrum,[10] was found in the volatile products and the ampoule was again coated with a yellow involatile solid.

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Hydrolysis of Hydrophosphoryl Difluoride.—A sample of OPF_2H (0.324 g, 3.65 mmoles) was sealed with 0.2 g water and allowed to react for several days at room temperature. Fractionation of the volatile products yielded SiF_4 and a small amount of PF_3. No noncondensable gases were found. Removal of the water left a white crystalline material identified by infrared and nmr spectra as phosphorous acid, $OP(OH)_2H$.

Hydrolysis of Hydrothiophosphoryl Difluoride.—A sample of SPF_2H (0.244 g, 2.40 mmoles) was sealed in a glass ampoule with approximately 0.2 ml of water and allowed to react at room temperature. The SPF_2H was immiscible with water but reacted vigorously with evolution of heat when mixed. The mixture was kept at room temperature overnight to ensure complete reaction. The volatile products were an inseparable mixture of SiF_4 and H_2S; the former was identified by infrared and ^{19}F nmr spectroscopy and the latter by ^1H nmr spectroscopy. The pale yellow involatile solid residue was identified as phosphorous acid by infrared and nmr (hydrogen and phosphorus) spectroscopy. Fluorine nmr spectra of the solid also showed the presence of broad singlet absorptions at +140 and +145 ppm *vs.* CCl_3F which can be assigned to fluoride and bifluoride ions. Estimation of the relative proportions of SiF_4 and H_2S in the total mass (0.115 g) of the volatile fraction from the average molecular weight (43.2) indicated that most of the sulfur in the original compound was evolved as H_2S but only a small fraction (10%) of the fluorine as SiF_4.

Results and Discussion

Hydrogen iodide reacts readily with dimethylamino phosphoryl or thiophosphoryl difluorides to yield molecular iodine, dimethylammonium iodide, and the volatile hydrido derivatives hydrophosphoryl difluoride, OPF_2H, or hydrothiophosphoryl difluoride, SPF_2H. Essentially complete conversion of the amino compound to the hydride was obtained using the stoichiometry expressed by

$$EPF_2N(CH_3)_2 + 3HI \longrightarrow EPF_2H + (CH_3)_2\overset{+}{N}H_2I^- + I_2 \quad (1)$$

where E represents O or S. In contrast, the reactions of tervalent dialkylaminophosphorus fluorides with anhydrous hydrogen halides yield the mixed halogenophosphorus fluorides[15-17]

$$PF_2 \cdot NR_2 + 2HX \longrightarrow PF_2X + R_2\overset{+}{N}H_2X^- \quad (2)$$

where X is Cl, Br, or I and similarly the alkylamino phosphoryl and thiophosphoryl difluorides yield the mixed chloro- or bromofluorides[8,17,18]

$$EPF_2 \cdot NR_2 + 2HX \longrightarrow EPF_2X + R_2\overset{+}{N}H_2X^- \quad (3)$$

when allowed to react with hydrogen chloride or bromide.

The difference in the course of the hydrogen iodide reaction probably reflects the greater strength of the P–H bond relative to that of the P–I bond (76 *vs.* 51 kcal).[19]

The use of hydrogen iodide and mercury to reduce PF_2I to PF_2H[1] and the perfluoroalkyliodophosphines and -arsines to the hydrides[20] suggests that the present synthesis of hydrofluorides may proceed through the formation of the iodide EPF_2I in a reaction analogous to eq 3 followed by rapid reduction by hydrogen iodide

$$EPF_2I + HI \longrightarrow EPF_2H + I_2 \quad (4)$$

or the reaction may proceed through an intermediate with a P–P bond.[20,21] Further studies are in progress which will hopefully delineate the scope of the reduction and provide a greater understanding of the mechanism.

Hydrothiophosphoryl difluoride, the most stable of the two compounds, was the easier to isolate and characterize. It is a volatile liquid and the vapor pressure obeys the equation

$$\log P_{mm} = 8.44 - \frac{1518}{T}$$

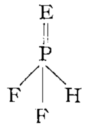
which gives an *extrapolated* boiling point of 0.2°, a heat of vaporization of 6951 cal/mole, and a Trouton constant of 25.5.

The oxygen analog, hydrophosphoryl difluoride, is considerably more difficult to prepare because of its instability and the apparent catalysis of the decomposition by the products or reagents involved in the synthesis. Once isolated and purified, however, the rate of decomposition was slow enough to permit convenient characterization of the compound. The vapor pressure obeyed the equation

$$\log P_{mm} = 8.63 - \frac{1886}{T}$$

corresponding to an extrapolated boiling point of 55.0°, a heat of vaporization of 8632 cal/mole, and a Trouton constant of 26.3. The vapor pressures were not reproducible if the sample had been warmed above −25°, indicating that decomposition occurs at the higher temperatures. The above equation was calculated from the reproducible vapor pressure data obtained on several samples in the range −53 to −25° in order to minimize the effect of decomposition on the vapor pressure equation. The disagreement between our boiling point and the previously reported value[5] can be attributed to decomposition of OPF_2H during measurement since the temperature was allowed to reach 0° in the previous study.[5]

The nuclear magnetic resonance spectra of both compounds are very similar and are consistent with a structure in which two equivalent fluorine atoms interact with single phosphorus and hydrogen atoms. The parameters, which are given in Table III, strongly support the formulation of the compounds as derivatives of pentavalent phosphorus with hydrogen directly attached to phosphorus rather than the trivalent isomers F_2PEH.



E = O, S

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TABLE III

NUCLEAR MAGNETIC RESONANCE DATA FOR HYDROTHIOPHOSPHORYL AND HYDROPHOSPHORYL DIFLUORIDES

	SPF_2H	SPF_2D	OPF_2H		OPF_2D
			+33°	−30°	
		Chemical Shift, ppm			
$\phi^{19}F$ (*vs.* CCl_3F)	+46.1	...	+61.9	+62.8	+63.8
τ^1H (*vs.* tetramethylsilane[a])	1.93	...	2.5 ± 0.2	...	...
		Coupling Constants, cps			
J_{P-H}	725.4[b]	...	844 ± 7[b]	...	...
	728.4[d]				
J_{P-F}	1153[c]	1148[c]	1121.6[c]	1122[c]	1120[c]
	1131[d]	...		...	...
J_{H-F}	98.9[b]	...	116[b]	...	...
	99.0[c]	...	116.5[c]	115[c]	...
J_{D-F}	...	15.1[e]	...	...	18[e]

[a] τ 10.0 for tetramethylsilane. [b] Parameters obtained from the hydrogen spectrum which consists of a doublet of 1:2:1 triplets. [c] Parameters obtained from the fluorine spectrum which consists of a doublet of doublets in the case of the hydrogen compounds and a doublet of 1:1:1 triplets in the case of the deuterium compounds. [d] Parameters obtained from the phosphorus spectrum of a neat liquid sample. The spectrum consists of a doublet of triplets. [e] These values, obtained from the fluorine spectrum, are in good agreement with values calculated from the observed H–F coupling and the ratio of the magnetogyric ratios of deuterium and hydrogen: J. W. Emsley, J. Feeny, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press Ltd., London, 1966, Chapter 5.

The large P–H and F–H coupling constants in particular support the pentavalent structure since the values are considerably larger than those typically observed for trivalent P–H compounds but close to those observed for pentavalent P–H compounds.[1,4,5,13] The observed P–F coupling constants also suggest pentavalent rather than trivalent phosphorus.[1,8,13,15,16,22,23]

TABLE IV

INFRARED SPECTRA OF HYDROPHOSPHORYL DIFLUORIDE AND HYDROTHIOPHOSPHORYL DIFLUORIDE[a]

SPF_2H	OPF_2H	Assignment
2458 m[a]	2500 w[c]	ν(P–H)
	1377 s[d]	ν(P=O)
1054 w[a]	1020 w[d]	
1019 vs[b]	993.5 s	δ(P—H)
973 m	...	
958 w	...	
923 vs[b]	932 s[d]	ν(P—F) antisym
895 sh	892 s[c]	ν(P—F) sym
844 vw	...	
709 m	...	ν(P=S)
	510.5 m[c]	
420 w	491 w, sh	
	388 m[c]	
336 w		

[a] All values are in cm^{-1}. Both spectra were measured at room temperature in a 9-cm cell at 10–15 mm pressure. Intensities are given as: s, strong; v, very; m, medium; w, weak. [b] Typical PQR band structure, type A or C with strong, single central Q branch. P–R separation approximately 20 cm^{-1}. [c] Typical PQR band structure, type A or C with strong single central Q branch. P–R separation approximately 30 cm^{-1}. [d] Type B, PQQ'R band with P–R separation of approximately 25 cm^{-1}.

The infrared spectra, which are given in Table IV, also support the pentavalent structure of the compounds. The oxygen compound shows a very strong band at 1377 cm^{-1} which is best assigned to the P=O stretch. The medium-intensity band at 2500 cm^{-1} and the strong band at 993 cm^{-1} shift on deuteration suggesting that these bands are due to P–H stretch and bend, respectively. No band was observed in the 3600-cm^{-1} region which could be assigned to O–H absorption. The infrared data reported here for OPF_2H are in good agreement with those previously reported.[5] The spectrum of the thiophosphoryl compound is similar to that of the oxygen compound. The shifts of the 2458- and 1019-cm^{-1} bands on deuteration confirm that these bands involve motion of hydrogen atoms. Since S–H stretching frequencies are usually observed[10] above 2600 cm^{-1}, the above bands of the thiophosphoryl compounds are best assigned to the P–H stretching and bending vibrations, respectively. The 1600–1200-cm^{-1} region is clear in the thiophosphoryl compound adding further support to the assignment of the 1377-cm^{-1} band in the phosphoryl compound to the P=O stretching vibration. The P=S stretch in the thiophosphoryl compound is probably best assigned to the 709-cm^{-1} band.

The mass spectra of the fluorohydrides, shown in Table V, are similar and confirm the assigned molecular formulas. The most notable feature of the spectra is the appearance of the molecular ion as the *strongest* ion in the spectrum as in the mass spectrum of PF_2H, but in contrast to the mass spectra of the hydrofluorophosphoranes HPF_4 and H_2PF_3 where the molecular ions were not observed.[5] Previously reported[5] mass spectra of OPF_2H do not show the predominance of the molecular ion and show an entirely different intensity pattern from ours. Their spectra show evidence for OPF_3 and SiF_4 impurities, however, which were absent in the present spectra. It is interesting to note that the mass spectrum of OPF_2H shows a metastable peak at *m/e* 50.7 amu, corresponding to the elimination of HF from the molecular ion

$$OPF_2H^+ \longrightarrow OPF^+ + HF$$

(calcd) *m/e* 50.6 amu). No metastable ions were observed in the mass spectrum of SPF_2H.

Pure hydrothiophosphoryl difluoride suffered less than 5% decomposition after heating to 100° in the gas phase for several weeks. The compound did not decompose significantly during its preparation. In contrast, a *pure* sample of the phosphoryl compound was almost completely decomposed to phosphorus trifluoride and phosphorous acid, $OPH(OH)_2$, after 14 days at room temperature in the gas phase. Impure samples decomposed rapidly, and significant decomposition occurred during preparation. The final products of the decomposition, phosphorus trifluoride and phosphorous acid, were not observed during the initial stages, and the initial products, phosphoryl fluoride and difluorophosphoric acid, were not observed in the final

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(22) H.-G. Horn and A. Muller, *Z. Anorg. Allgem. Chem.*, **346**, 266 (1966).

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Table V

Mass Spectra of Hydrophosphoryl Difluoride and Hydrothiophosphoryl Difluoride

SPF_2H			OPF_2H		
m/e	Rel intensity[a]	Ion	m/e	Rel intensity[a,b]	Ion
102	52.9	SPF_2H^+	86	40.8	OPF_2H^+
101	6.9	SPF_2^+	85	10.6	OPF_2^+
83	1.6	$SPFH^+$	69	19.6	PF_2^+
82	3.2	SPF^+	67	8.6	$OPFH^+$
69	28.0	PF_2^+	66	10.2	OPF^+
63	4.2	SP^+	50	1.6	PF^+
50	3.2	PF^+	31	1.2	P^+

[a] Intensities are expressed as per cent total ionization, defined as ΣI_n where n refers to all ions with $m/e > 30$ whose intensity is $>2\%$ of the base peak. [b] A very weak peak at m/e 32 ($<0.5\%$) due to PH^+ was observed. No peaks at m/e 104 (*i.e.*, POF_3 or SiF_4) or m/e 88 (PF_3) were observed.

products. While we have not yet completely evaluated the effects of impurities and other conditions on the course of this complex decomposition, it is reasonable to suggest that the initial decomposition product, OPF_3, formed by some unknown route, reacts with the original hydrophosphoryl difluoride to form difluorophosphoric acid

$$OPF_3 + OPF_2H \longrightarrow PF_3 + F_2PO(OH)$$

and the difluorophosphoric acid in turn is consumed by reaction with the original hydrophosphoryl compound

$$2OPF_2H + F_2PO(OH) \longrightarrow PF_3 + OPF_3 + OPH(OH)_2$$

The sum of these two equations

$$3OPF_2H \longrightarrow 2PF_3 + OPH(OH)_2$$

gives an equation which is in fair agreement with the observed yield of phosphorus trifluoride. This scheme is consistent with the observations summarized in Table I and with the results of the decomposition study but is not proven. The reaction may involve rearrangement to the trivalent isomer, F_2POH, as the initial step.

Hydrophosphoryl difluoride yielded phosphorous acid and silicon tetrafluoride on hydrolysis; the latter is probably due to the reaction of hydrogen fluoride with glass

$$OPF_2H + 2H_2O \longrightarrow OPH(OH)_2 + 2HF$$

$$2HF + {}^1/_2SiO_2 \longrightarrow {}^1/_2SiF_4 + H_2O$$

The hydrolysis of SPF_2H also gave phosphorous acid and in addition hydrogen sulfide. Monothiophosphorous acid, $SPH(OH)_2$, is probably formed initially

$$SPF_2H + H_2O \longrightarrow SPH(OH)_2 + 2HF$$

and subsequently hydrolyzed to phosphorous acid and hydrogen sulfide

$$SPH(OH)_2 + H_2O \longrightarrow OPH(OH)_2 + H_2S$$

probably catalyzed by the hydrofluoric acid in the solution. In both cases the yield of silicon tetrafluoride was not quantitative. Hydrogen was not obtained in any of the hydrolysis reactions showing that the hydrogen atoms are not hydritic. The P–H bond probably maintains its integrity during hydrolysis as in the case of the hydrolysis[24] of PF_2H.

Both compounds have abnormal Trouton constants and notably higher boiling points than those of the parent fluorides, suggesting that they are associated, possibly through weak hydrogen bonding similar to that suggested for difluorophosphine.[1] More convincing support for association is provided by the concentration dependence of the hydrogen chemical shift and by shifts in the infrared frequencies with phase.[17] All of these effects are greatest for the phosphoryl compound where greater hydrogen-bonded association is reasonably expected. We hope to present more detailed evidence in a future publication.

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Hydrolysis of Titanium Tetrafluoride

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The hydrolysis of titanium tetrafluoride in various solutions is described. In a 40% TiF_4 aqueous solution evidence is presented for the polynuclear species $[TiF_4 \cdot Ti(OH)_4(H_2O)_2]$. An F^{19} study of the supernatant liquid from the hydrolysis of the adduct $TiF_4 \cdot 2HC(O)N(CH_3)_2$ showed the presence of $TiF_5 \cdot HC(O)N(CH_3)_2^-$, $TiF_5 \cdot H_2O^-$, and TiF_6^{2-}. The *cis*-$TiF_4 \cdot 2H_2O$ adduct was found as a product in dilute hydrogen fluoride solutions of TiF_4 in water. The hexafluorotitanate ion is stable in water but hydrolyzes in acidic solutions.

Introduction

The species $TiOF_4^{2-}$, $TiOF^+$, $TiOF_2$, and $TiOF_3^-$ were reported to be present in hydrogen fluoride solutions of Ti(IV).[2] It was also noted that the hexafluorotitanate ion was not stable in aqueous solutions but was rapidly hydrolyzed to $TiOF_4^{2-}$ and more slowly to

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