being characteristic of *cis*-M(bipy)$_2$X$_2^+$ and a single band or lack of complexity being characteristic of the trans isomer. As shown in the Results, this criterion has given incorrect assignments. It is probable that the differences observed in this region result from specific crystal-packing effects. Solution infrared spectra of these compounds, which would eliminate these effects, cannot be obtained due to low solubilities in appropriate solvents.

The orginal cis assignment[3] of [Ir(phen)$_2$Cl$_2$]Cl·3H$_2$O prepared by a fusion process was confirmed by optical resolution work.[23] However, Gillard and Heaton[14] were not able to effect resolution using the same resolving agent on their analogous product. The later compound is assigned the cis configuration on the basis of its published powder pattern (Table IV) and our analysis here. Apparently experimental difficulties account for the unsuccessful resolution.

The insensitivity of the powder patterns of bis-phen and bis-bipy complexes to M, X, Y, and *n* is probably due to the bulkiness of the bidentate nitrogen ligands. The principal groups controlling the crystal packing are the phen and bipy ligands and not the comparatively small halogen and nitrate ions or water. This empirical observation may be quite useful in assigning configurations to more complicated systems.

The work reported here points out the problems inherent in assigning structures to analogous systems. Techniques, such as infrared and visible–ultraviolet spectroscopy, may work well in one system (ethylenediamine) and not in another (bipy). Application of these methods, proven in simple systems, to complex molecules of biochemical interest must be done with caution.

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Fluorophosphine Ligands. VIII. The Chemistry of Difluorophosphine Oxide

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F$_2$POPF$_2$ has been found to interact with amines and alcohols in a two-step process. The reaction with amines gives PF$_3$, PF$_2$NR$_2$, and NR$_2$H$_2$HFPO$_2$ and with alcohols gives PF$_3$, HFPO$_2$R, and HFPO$_2$R. The reaction of F$_2$POPF$_2$ with N$_2$F$_4$ gives N$_2$, PF$_5$, PF$_3$O, and colored products. PF$_2$HO has been found to react with amines to give PF$_3$ and NR$_{4-x}$H$_x{}^+$HFPO$_2{}^-$, with PF$_2$OR to give PFHO$_2$R, PF$_3$, and HFPO$_2$H, with PF$_2$N(CH$_3$)$_2$ to give PF$_3$, PF$_2$OPF$_2$, and N(CH$_3$)$_2$H$_2{}^+$HFPO$_2{}^-$, and with BF$_3$ to give a weakly bonded adduct PF$_2$HOBF$_3$. PF$_2$HOBF$_3$ is observed to decompose to BF$_3$ and HFPO$_2$HBF$_3$. No reaction is observed between B$_2$H$_6$ and PF$_2$HO. A mechanism for the various reactions is discussed and explained in terms of association found in PF$_2$HO.

Introduction

Difluorophosphine oxide was first observed by Treichel, Goodrich, and Pierce in the decomposition of HPF$_4$.[1] Charlton and Cavell[2] and Centofanti and Parry[3] were able to prepare the compound in significant enough quantity to characterize the molecule. Difluorophosphine oxide is rather unstable as a liquid and undergoes complete decomposition in about 2 hr.[3] It is believed[4] that this decomposition results from association found in the condensed phases. Investigation of the chemistry of PF$_2$HO has shown that PF$_2$HO is a very reactive molecule. The work is described herein.

Discussion

1. Reaction of HX (X = OR, NR$_2$, etc.) with F$_2$POPF.—It was thought that the reaction of F$_2$POPF$_2$ with various proton sources should result in the preparation of PF$_2$HO and PF$_2$X, by a reaction similar to that observed with HBr: PF$_2$OPF$_2$ + HBr → PF$_2$HO + PF$_2$Br. The general reaction would then be PF$_2$OPF$_2$ + HX → PF$_2$HO + PF$_2$X.

Two proton sources were studied. In both cases the results can be explained in terms of the general reaction given above, followed by a second reaction between PF$_2$HO and PF$_2$X.

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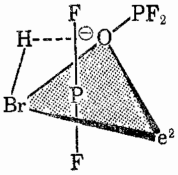
[1] P. M. Treichel, R. A. Goodrich, and S. B. Pierce, *J. Amer. Chem. Soc.*, **89**, 2017 (1967).

[2] T. L. Charlton and R. G. Cavell, *Inorg. Chem.*, **6**, 2204 (1967).

[3] L. F. Centofanti and R. W. Parry, *ibid.*, **7**, 1005 (1968).

[4] L. F. Centofanti and R. W. Parry, *ibid.*, **9**, 744 (1970).

The intermediate of F_2POPF_2 with HX would be expected to be similar to the trigonal bipyramid postulated for PF_2OPF_2 and HBr or PF_3NR_3.[3] Cleavage would occur producing PF_2OH (rearrangement to PF_2HO would occur immediately) and PF_2X. The secondary reaction between PF_2HO and PF_2X could then occur.



Ethyl alcohol and F_2POPF_2 react immediately on warming to give PF_2HO, $PF_2OC_2H_5$, large amounts of PF_3, and less volatile oils. PF_2HO and $PF_2OC_2H_5$ were recovered as a weak complex that was less volatile than either free species. In the case of alcohols the second reaction between PF_2HO and PF_2OR is somewhat slow so that small amounts of PF_2HO and PF_2OR can be recovered. The PF_3 and oils are formed from the interaction of PF_2HO and PF_2OR. This reaction was confirmed by mixing PF_2HO and PF_2OR directly (results given in a later section).

The reaction of HNR_2 with F_2POPF_2 is similar to the reactions of alcohols and is described by $HNR_2 + F_2POPF_2 \rightarrow F_2HPO + F_2PNR_2$. As in the case of alcohols, a second reaction then occurs but is more rapid and goes to completion. The products of the second reaction include PF_3, F_2POPF_2, and $NR_2H_2^+HFPO_2^-$. The sequence was confirmed by allowing PF_2HO and PF_2NR_2 to react directly and is discussed in a later section.

2. Reaction of F_2POPF_2 with N_2F_4.—A violent reaction occurred between F_2POPF_2 and N_2F_4. The reaction can be described as a fluorination of F_2POPF_2 by N_2F_4, a commonly observed reaction of N_2F_4.[5] The products included PF_5, PF_3O, and N_2. The reaction is $F_2POPF_2 + N_2F_4 \rightarrow PF_5 + PF_3O + N_2$.

It is interesting to note that an unidentified, bright red material was observed during separation of the products at low temperature. It was very volatile and almost completely disappeared on warming. Some type of free radical or complex may be responsible for the color.

3. Reactions of PF_2HO with $XN(CH_3)_2$ ($X = H$, CH_3, PF_2).—Difluorophosphine oxide reacts immediately with amines to form solids or oils and PF_3. The solids and oils were identified by nmr as the amine salts of monofluorophosphorous acid; thus the reaction can be described as

$$2PF_2HO + \begin{array}{c} N(CH_3)_3 \\ \text{or} \\ N(CH_3)_2H \end{array} \longrightarrow PF_3 + \begin{array}{c} N(CH_3)_3H^+ \\ \text{or} \\ N(CH_3)_2H_2^+ \end{array} HFPO_2^-$$

In the reaction mentioned earlier between PF_2OPF_2 and $HN(CH_3)_2$, F_2HPO and $PF_2N(CH_3)_2$ were the expected products. Since they were not observed, it was concluded that these two molecules must react to form new products. In a separate experiment, it was found that PF_2HO and $PF_2N(CH_3)_2$ react vigorously at room temperature. Although the reaction was complicated by side reactions, the interaction of PF_2HO and $PF_2N(CH_3)_2$ can be described by the equation

$$3PF_2HO + PF_2N(CH_3)_2 \longrightarrow PF_3 + F_2POPF_2 + NR_2H_2^+HFPO_2^-$$

$NR_2H_2^+HFPO_2^-$ was identified by its phosphorus, fluorine, and proton spectra, which were identical with the spectra observed from the reaction of F_2POPF_2 with HNR_2 and the reaction of PF_2HO with HNR_2.

The ^{31}P nmr spectrum of $NR_2H_2^+HFPO_2^-$ consisted of a doublet of doublets. The signal was first split into doublets from coupling with the fluorines ($J_{PF} = 976$ cps, δ(relative to orthophosphoric acid) 1.4 ppm); each member of the doublet was further split into doublets by the proton attached to the phosphorus ($J_{PH} = 678$ cps). The ^{19}F nmr tracing showed the expected doublets of doublets. The signal first split by the phosphorus into a doublet ($J_{PF} = 986$ cps; δ(relative to $CFCl_3$) 54 ppm). Each member of the doublet was further split into doublets by the proton on the phosphorus ($J_{HPF} = 125$ cps).

The proton spectrum showed unequivocally that the molecule was $NR_2H_2^+HFPO_2^-$. It consisted of three sets of peaks with a relative area of 1:2:6. The first set with an area of 1 was a doublet of doublets and was assigned to the proton attached directly to the phosphorus. The signal was first split by the phosphorus into doublets ($J_{PH} = 681$ cps, δ(relative to TMS) -6.7 ppm). Interaction with fluorines then further split each doublet into doublets ($J_{FPH} = 122$ cps). A broad peak (δ(relative to TMS) -8.9 ppm) with an area of 2 was assigned to the protons attached to the nitrogen directly. The third set of peaks with an area of 6 was found to be a triplet. The peak (δ(relative to TMS) -2.2 ppm) was assigned to the protons attached to the carbon in the amine. The triplet resulted from coupling with the N–H protons ($J_{HNCH} = 5.2$ cps).

The ^{19}F nmr spectrum for $N(CH_3)_3H^+HFPO_2^-$ was identical with that for the $NH_2(CH_3)_2^+$ salt, except for slight changes in chemical shifts and coupling constants. The proton spectrum not only showed the expected changes (coupling constants, chemical shifts, and relative areas), but a loss of coupling was observed for the HCNH interaction. Coupling constants and chemical shifts are summarized in Table I for $NH_2(CH_3)_2^+$-$HFPO_2^-$ and $NH(CH_3)_3^+HFPO_2^-$.

TABLE I
NMR DATA FOR $HFPO_2^-$ SALTS

	$NR_2H_2^+$	NR_3H^+
J_{PF}, cps	986,[a] 976[c]	961[a]
J_{PH}, cps	681,[b] 678[c]	690[b]
J_{HPF}, cps	125,[a] 122[b]	129,[a] 123[b]
J_{HNCH}, cps	5.2[b]	...
$\delta_P(H_3PO_4)$, ppm	1.4	...
$\delta_F(CFCl_3)$, ppm	54	54
δ_{CH}(TMS), ppm	-2.2	-2.5
δ_{NH}(TMS), ppm	-8.9	-11.5
δ_{PH}(TMS), ppm	-6.7	-6.5

[a] From ^{19}F spectra. [b] From ^1H spectra. [c] From ^{31}P spectra.

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[5] C. B. Colburn, *Advan. Fluorine Chem.*, **3**, 92 (1963).

4. Reactions of PF_2HO with PF_2OR.—In the reaction of F_2POPF_2 and alcohols, it was observed that the predicted products (PF_2OR and PF_2HO) could not be completely isolated. From this observation, it was concluded that PF_2OR and PF_2HO underwent interaction to give new products. A mixture of PF_2OCH_3 and PF_2HO was found to react rapidly in the liquid phase at 25° to give PF_3, $HFPO_2H$, and $HFPO_2CH_3$. The products can be explained in terms of two competing reactions

$$2HF_2PO \longrightarrow PF_3 + HFPO_2H$$

$$HF_2PO + PF_2OCH_3 \longrightarrow PF_3 + HFPO_2CH_3$$

The first suggested reaction is well established in the chemistry of F_2HPO. The second is supported by the following facts.

The fluorine-19 nmr initially showed PF_2HO and PF_2OCH_3. Almost immediately, new peaks could be observed in the spectrum. A low-field doublet which could be assigned to PF_3 appeared first. Two sets of peaks, each a doublet of doublets, then began appearing. One set was situated on the low side of PF_2HO and the other on the high side. The low-side doublets could be assigned to $HFPO_2H$, while the upfield side was assigned to $HFPO_2CH_3$.

The proton nmr of a different sample confirmed the ^{19}F nmr. Initially, all peaks could be assigned to PF_2HO and PF_2OCH_3 (if a weak complex is formed, the gross features of the complex must remain similar to the free species). Gradually the triplet of doublets of PF_2HO was replaced by two sets of doublets of doublets and a singlet. In this case, a larger ratio of PF_2OCH_3 had been used so that $HFPO_2CH_3$ would be formed in greater abundance. The lower field doublet of doublets was assigned to $HFPO_2CH_3$, while the upfield doublet of doublets was assigned to $HFPO_2H$. The doublets result from the proton attached to phosphorus in $HFPO_2H$ and $HFPO_2CH_3$, while the singlet is the result of the proton attached to the oxygen in $HFPO_2H$. The spectrum of the CH_3 protons also shows changes with time. Beginning with the doublet of PF_2OCH_3 (POCH coupling), a new doublet slowly appears, resulting from P–O–C–H coupling in $HFPO_2CH_3$. After about 1 hr, a doublet of doublets appeared, probably due to decomposition or reaction of $HFPO_2CH_3$. A summary of coupling constants and chemical shifts is given for $HFPO_2CH_3$ in Table II.

TABLE II

COUPLING CONSTANTS AND CHEMICAL SHIFTS FOR $HFPO_2CH_3$

J_{PF} = 1056 cps	$\delta_F(CFCl_3)$ 67.8 ppm
J_{PH} = 772 cps	δ_{PH}(TMS) −6.8 ppm
J_{POCH} = 12 cps	δ_{CH}(TMS) −3.7 ppm
J_{HPF} = 115 cps	

5. Reactions of PF_2HO with BF_3.—PF_2HO was found to form a weak complex with boron trifluoride. At room temperature in the gaseous state, the complex was completely dissociated. At −78° in the solid state, no dissociation was observed.

The ^1H, ^{31}P, ^{19}F, and ^{11}B nmr spectra were used to confirm the presence of a complex. Although the structural features of each spectrum of the complex remained the same as the free species, several large changes in coupling constants occurred. The ^{31}P nmr spectrum of the complex $PF_2HO \cdot BF_3$ showed a doublet of triplets. The signal was first split by two fluorines (J_{PF} = 1155 cps, δ(relative to H_3PO_4) −2.9 ppm) into a triplet, and then further coupling with the proton split each member of the triplet into doublets (J_{PH} = 990 cps). The ^{19}F spectrum showed a pair of doublets and a singlet. The pair of doublets was assigned to the fluorine attached to phosphorus. The signal was first split by the phosphorus to give a doublet (J_{PF} = 1150 cps, δ(relative to $CFCl_3$) 73.5 ppm); each member of the doublet was then further split by the proton (J_{HPF} = 96 cps). The singlet observed in the fluorine nmr was assigned to the fluorines attached to the boron (δ(relative to $CFCl_3$) 143 ppm). The proton nmr tracing was found to be a triplet of doublets. The signal was first split by the phosphorus into a doublet (J_{PH} = 980 cps δ(relative to TMS) −7.6 ppm), and each member of the doublet was further split into triplets by coupling with the fluorines (J_{FPH} = 97 cps).

Because of earlier evidence that suggested that the decomposition of PF_2HO could be related to the association present, it was hoped that difluorophosphine oxide could be stabilized by the addition of a BF_3 group to the oxygen. On coordination to the oxygen, the associated $(PF_2HO)_n$ species should be broken.

When a mixture of PF_2HO and BF_3 is allowed to sit at room temperature for long periods (~24 hr),[6] the difluorophosphine oxide decomposes in a fashion similar to that observed for the free ligand.[3] The decomposition of the adduct can be explained in terms of (1) dissociation of the adduct, (2) decomposition of PF_2HO, and (3) interaction of the product with BF_3. The equations are summarized as

$$2PF_2HOBF_3 \rightleftarrows 2PF_2HO + 2BF_3$$

$$2PF_2HO \longrightarrow PF_3 + HFPO_2H$$

$$HFPO_2H + BF_3 \longrightarrow HFPO_2H \cdot BF_3$$

The overall reaction would then be

$$2PF_2HOBF_3 \longrightarrow PF_3 + BF_3 + HFPO_2HBF_3$$

$HFPO_2HBF_3$ was identified by its ^1H, ^{31}P, and ^{19}F nmr spectra. The phosphorus nmr spectrum showed a doublet (J_{PF} = 1069 cps, δ(relative to H_3PO_4) −6.1 ppm), each member of which was split into a doublet (J_{PH} = 857 cps). The ^{19}F spectrum consisted of doublets (J_{PF} = 1073 cps, δ(relative to $CFCl_3$) 69.9 ppm) split into doublets (J_{HPF} = 105 cps) and a singlet from the BF fluorines (δ(relative to $CFCl_3$) 143.2 ppm). The proton spectrum showed a doublet (J_{PH} = 856 cps, δ(relative to TMS) −7.2 ppm) further split into doublets (J_{HPF} = 102 cps) and a singlet resulting from the OH proton (δ(relative to TMS) −9.9 ppm). Thus the nmr spectra indicate that the boron trifluoride is coordinated to the oxygen.

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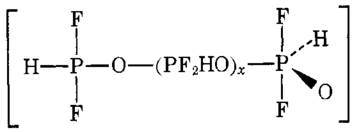
(6) After 24 hr the sample was completely decomposed; shorter periods were not examined so that at present no comparison can be made with the decomposition of pure PF_2HO.

6. The Reactivity of PF_2HO.—The reaction of PF_2OR is very similar to the decomposition of PF_2HO. In the gas phase no detectable reaction was observed over an 8-hr period, but a rapid reaction (0.5–1 hr to completion) occurred in the liquid phase. Conditions were identical with those for the decomposition of PF_2HO.

Several factors can be considered when examining the reactivity of PF_2HO. Three sites are of interest in the molecule: (1) the phosphorus, (2) the oxygen, and (3) the proton. The phosphorus atom can accept an electron pair and assume a pentacoordinate geometry while the oxygen can donate an electron pair. Thus in phosphine oxides the possibility exists that the nucleophile (oxygen) of one molecule will interact with the electrophile (phosphorus) of another. The role of various substituents has not been completely clarified, but PF_2HO exhibits this type of association to the greatest extent.[3] The chemistry is reflected in this association. Most of the reactions observed would result from attack on the associated chain, preferably at the end molecules.[7]



In the case of the observed reactions of PF_2HO, all the reacting molecules (PF_2OCH_3, $NR_{x-3}H_x$, and $PF_2N(CH_3)_2$) can be considered as nucleophiles, while two can also be considered as electrophiles (PF_2OCH_3 and $PF_2N(CH_3)_2$). The reaction between amines and PF_2HO strongly suggests nucleophilic attack either at an end phosphorus in an associated chain or at a proton in the chain. In both cases, the end result would be removal of a proton to give $R_2NH_2{}^+F_2PO^-$. The anion would react with HF_2PO to give PF_3 and $HFPO_2{}^-$ *via* a process similar to that postulated for the decomposition of PF_2HO. The amine thus drives the decomposition of PF_2HO to completion. The intermediate F_2PO^- would resemble the anion (PF_2S^-) which Charlton and Cavell[8] have tentatively identified in the reaction of trimethylamine with PF_2HS.

Because of the ability of PF_2HO to behave as either an electrophile or a nucleophile (as observed in the association of PF_2HO), the reactions with PF_2OCH_3 and $PF_2N(CH_3)_2$ are not as obvious. Either one or a combination of the two processes may be occurring. Work is now in process to clarify the interaction further.

Experimental Section

Apparatus.—Standard high-vacuum techniques were used throughout. Mass spectra were obtained on a Consolidated Electrodynamics Model 21-103B mass spectrometer at 70 eV.

Proton, boron, fluorine, and phosphorus nmr spectra were determined with a Varian Associates HR-100 nmr spectrometer at 100, 32.1, 94.4, and 40.4 MHz, respectively. Chemical shifts were obtained by tube interchange. A negative chemical shift implies that the peak is downfield from the standard.

The infrared spectrum was determined with a Beckman IR-12 in a 75-mm gas cell equipped with CsI windows.

Materials.—PF_2HO was prepared from the reaction of HBr and F_2POPF_2.[3] $HN(CH_3)_2$, $N(CH_3)_3$, and BF_3 were obtained from the Matheson Co. PF_2OCH_3 and $PF_2N(CH_3)_2$ were prepared by the reaction of PF_3 with CH_3OH and $HN(CH_3)_2$, respectively.[9]

Reaction of $HN(CH_3)_2$ with F_2POPF_2.—Dimethylamine (3.41 mmol) was condensed in a 500-ml reaction bulb with 1.71 mmol of F_2POPF_2. On warming the bulb, a reaction occurred with the formation of a solid. The volatile products were led through traps held at −78, −145, and −196°. A small amount of unidentified material at −78° was discarded. A 1.53-mmol sample of $(CH_3)_2NPF_2$ was found in the −145° trap and a 0.17-mmol sample of PF_3 remained in the −196° trap. The solid which remained in the reaction vessel decomposed on heating. Its decomposition products included H_2, PF_3, PH_3, $(CH_3)_2NPF_2$ (identified by ir spectrum and vapor pressure), and yellow solids. In a separate experiment PF_2HO was placed in an nmr tube with excess $(CH_3)_2NPF_2$; an immediate reaction took place as was evidenced by the formation of two phases. The nmr spectrum is considered in the Discussion.

Reaction of PF_2OPF_2 and CH_3OH.—In a typical reaction, 1.24 mmol of CH_3OH and 1.33 mmol of F_2POPF_2 were condensed in a 500-ml reaction flask and allowed to warm to room temperature. A reaction could be observed during the warming period. The products were then distilled through traps held at −78, −112, and −196°. A slightly volatile material was found in the −78° trap, while the −196° trap contained F_2POPF_2, PF_3, SiF_4, and PF_2OCH_3. A small amount of an unidentified oil remained in the flask. A second sample was prepared and the ^{19}F nmr of the material held at −78° was obtained. The nmr spectrum showed that the material was a mixture containing PF_2HO, $HFPO_2H$, and small amounts of PF_2OCH_3. The products are considered in the Discussion.

Reaction of PF_2OPF_2 and C_2H_5OH.—Reaction of equal amounts of PF_2OPF_2 and C_2H_5OH gave results that were similar to those obtained with CH_3OH. During the distillation some product was held in a −30° trap. An ^{19}F nmr of this material showed it to be $PF_2OC_2H_5$ and PF_2HO. This suggests that a weak adduct between the two is formed. The features of the nmr suggest that no pronounced structural changes have occurred in adduct formation.

Reaction of N_2F_4 with F_2POPF_2.—A 1.82-mmol amount of N_2F_4 and 1.93 mmol of F_2POPF_2 were condensed into a 500-ml reaction bulb and allowed to warm to room temperature. No immediate reaction occurred. The reactants were cooled to −196° and then rewarmed several times with no noticeable effect. While the reactants were being separated, a violent reaction occurred. A flame was observed in the bulb, and as the gases were produced from this flame, they were led through traps at −130 and −196°. Large amounts of noncondensable gas passed through the −196° trap (assumed to be N_2 and other products). The −130° trap contained a 1.4-mmol sample of PF_3O, while the −196° trap contained 1.6 mmol of PF_5 and an unidentified bright red solid. Unrecovered products could have been lost with the N_2. On warming and cooling the material at −196°, the color was greatly diminished although it never completely disappeared. Attempts to identify the colored material failed.

Reaction of PF_2HO and $N(CH_3)_3$.—A 2.40-mmol amount of $N(CH_3)_3$ was condensed into a reaction bulb with 4.40 mmol of PF_2HO. The mixture was allowed to warm slowly to room temperature, during which time a violent reaction occurred. After reaching room temperature, the volatile components were led through traps at −78 and −196°. A trace of unidentified material at −78° was discarded while 2.21 mmol of PF_3, identified by ir analysis and vapor pressure, was found at −196°. The PF_3 contained trace amounts of $N(CH_3)_3$. A white solid remained in the reaction bulb. From a mass balance, ^{19}F, ^1H, and ^{31}P

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(7) In examining the characteristics of $(PF_2HO)_x$, the end molecules would appear to be most reactive. One end of the chain would be more nucleophilic while the other end would be more electrophilic than the original molecule. Thus attack would favor the ends of the chain. At present chain lengths are not known.

(8) T. L. Charlton and R. G. Cavell, *Inorg. Chem.*, **8**, 2436 (1969).

(9) References described by R. Schmutzler, *Advan. Fluorine Chem.*, **5**, 31 (1965).

nmr, and a comparison with the reaction of PF_2HO with $PF_2N(CH_3)_2$ or $HN(CH_3)_2$, the solid was identified as $HN(CH_3)_3^+HFPO_2^-$. The reaction could be expressed by $2PF_2HO + N(CH_3)_3 \rightarrow PF_3 + NH(CH_3)_3^+FPHO_2^-$.

Reaction of PF_2HO and $HN(CH_3)_2$.—In a typical reaction, 6.55 mmol of PF_2HO and 2.76 mmol of $HN(CH_3)_2$ were condensed into an nmr tube connected to a 200-ml evacuated flask. The mixture was allowed to warm slowly to room temperature during which time a vigorous reaction occurred. After allowing the mixture to sit at room temperature for several minutes, the volatile components were led through traps held at −78, −140, and −196°. Nothing was found at −78°, while 0.20 mmol of $(CH_3)_2NPF_2$ was recovered at −140°. The −196° trap contained 2.46 mmol of PF_3. These species were identified by their vapor pressure and infrared spectra. An oil remaining in the nmr tube was dissolved in $CHCl_3$ and ^{19}F, ^1H, and ^{31}P nmr spectra showed the oil to be $H_2N(CH_3)_2^+HFPO_2^-$. Thus, the reaction could be described as $2PF_2HO + N(CH_3)_2H \rightarrow PF_3 + NH_2(CH_3)_2^+HFPO_2^-$.

The Reaction of PF_2HO and $PF_2N(CH_3)_2$.—This interaction is complicated by the fact that the products react with the reactants and with each other. Best results were obtained when near stoichiometric amounts of the reactants were used. A 2.63-mmol sample of $PF_2N(CH_3)_2$ was condensed with 6.02 mmol of PF_2HO in a 100-ml reaction bulb. The mixture was slowly warmed to room temperature during which time a violent reaction occurred. After reaching room temperature, the volatile components of the reaction were led through traps held at −105, −140, and −196°. A 0.33-mmol sample of $PF_2N(CH_3)_2$ was found at −105°, while the −196° trap contained 2.61 mmol of PF_3. A 2.12-mmol sample of F_2POPF_2 was recovered at −140°. These species were identified by their infrared spectra and vapor pressures. A white solid remained in the reaction vessel. The solid was identified by its nmr spectrum as $N(CH_3)_2H_2^+HFPO_2^-$.

In a separate experiment, PF_2HO and excess $PF_2N(CH_3)_2$ were condensed into an nmr tube and allowed to warm to room temperature. An immediate reaction occurred. The spectra are considered in the Discussion, and the reaction was identified as $3PF_2HO + PF_2N(CH_3)_2 \rightarrow PF_3 + F_2POPF_2 + N(CH_3)_2H_2^+HFPO_2^-$.

Reaction of PF_2HO and PF_2OCH_3.—A 1.22-mmol sample of PF_2HO was condensed with a 1.22-mmol sample of PF_2OCH_3 into a 500-ml reaction bulb and allowed to stand overnight at room temperature. After 8 hr in the gaseous phase, the products were distilled and found to contain only starting materials. After standing at 23° for 1 hr as a liquid in a smaller volume (75 ml) a reaction occurred. The products were passed through traps at −160 and −196°. The −196° trap contained 0.95 mmol of PF_3 while the −160° trap contained 0.61 mmol of PF_2OCH_3. An oil remained in the reaction flask (the distillation was probably not allowed to run for a long enough period since the oils $HFPO_2H$ and $HFP(O)OCH_3$ should be slightly volatile). A mass balance showed that 1.22 mmol of PF_2HO and 0.61 mmol of PF_2OCH_3 were consumed. A 0.95-mmol sample of PF_3 was recovered. From a mass balance and the ^{19}F and ^1H nmr spectra, which were discussed, the reaction is best stated by the two competing reactions

$$2PF_2HO \longrightarrow PF_3 + PFHO_2H$$

$$PF_2HO + PF_2OR \longrightarrow PF_3 + PFHO_2R$$

Reaction of PF_2HO with BF_3 and with B_2H_6.—A 1.86-mmol sample of PF_2HO and 1.64 mmol of BF_3 were condensed into a 200-ml reaction bulb and allowed to warm to room temperature. At room temperature, the gaseous mixture was found by its infrared spectra to be BF_3 and PF_2HO. At lower temperatures, an adduct was formed between the two and was undissociated at about −78°. The adduct was identified by a mass balance and its ^1H, ^{19}F, ^{31}P, and B^{11} nmr spectra to be PF_3HOBF_3.

In a similar experiment, B_2H_6 and PF_2HO were condensed into a reaction bulb. No adduct formation was observed with B_2H_6 at room temperature or at about −78°.

Decomposition of PF_2HOBF_3.—The above sample of PF_2HO (1.86 mmol) and BF_3 (1.64 mmol) was condensed into a 100-ml reaction bulb and allowed to remain at room temperature for 24 hr. During this period, a reaction occurred. The volatile components were led through traps held at −78 and −196°. A trace of PF_2HO was found at −78° and discarded. At −196° a 1.59-mmol mixture of PF_3 and BF_3 was found, while a nonvolatile oil remained in the reaction bulb. The BF_3–PF_3 mixture was condensed with H_2O (BF_3 rapidly reacted with H_2O). A 1.03-mmol sample of PF_3 was recovered from the water mixture. Thus, from the amount of BF_3 and PF_2HO consumed, the reaction can be described as $2PF_2HOBF_3 \rightarrow PF_3 + BF_3 + PFHO_2H \cdot BF_3$ (oil).

In a separate experiment, the decomposition was run in an nmr tube and the various nmr spectra were used to confirm the identity of the oil as $PFHO_2HBF_3$ (see Discussion).

In a similar experiment, 7.37 mmol of PF_2HO and 4.99 mmol of B_2H_6 were added to a 200-ml reaction bulb and allowed to sit at room temperature for 3 hr. The products were separated and all the B_2H_6 was recovered, while the PF_2HO had decomposed to PF_3 and $HFPO_2H$. A trace of H_2 and F_2POPF_2 was also observed in the products. Thus, the main reaction was only the decomposition of PF_2HO.

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