the existence of *cis* and *trans* isomers, adopting the ideas presented by Fitzsimmons, *et al.*[27] It is not quite clear under what experimental conditions the different isomers are formed.

A fairly large splitting is also observed for the $Cl_2(C_6H_5)PO$ adduct. Again a *trans* isomer is indicated. The same seems to apply for the 1:1 adduct with dioxane, even though no real comparison is possible for this compound. The postulation of *trans* isomers for the above-mentioned complexes will have to be confirmed either by determination of dipole moments or by vibrational spectroscopy according to Beattie and Rule.[30]

Another interesting facet is shown in the last group of compounds. All complexes formed with bidentate donor groups exhibit quadrupole splittings even though the interaction is apparently quite strong as indicated by the negative stretching frequency shifts. The reason for the occurrence of splitting can again be seen in the distortion around tin caused by the rigid donor group. In this connection it is found that the C–N vibration is shifted to higher frequency upon complex formation. This has been observed and discussed previously.[31]

The stereoisomers methyl fumarate and methyl maleate show very similar Mössbauer data; however the *trans* isomer has been found to exhibit a weak but noticeable room-temperature effect, indicating possibly a polymeric structure.[22]

In conclusion, it can be said that Mössbauer spectroscopy presents a convenient tool for the investigation of donor–acceptor complexes of the described type. Information concerning the donor–acceptor interaction can be obtained from isomer shift and quadrupole splitting data. In addition, intermolecular association and the occurrence of *trans* isomers in a class of compounds where *cis* isomers appear to dominate can be detected quite nicely. The occurrence of quadrupole splittings appears to be the rule for tin(IV) chloride complexes with O-donor ligands rather than the exception. The consequence is that Greenwood's concept loses its experimental basis for hexacoordinated compounds as well as previously reported for tetracoordinated compounds.[24] The electric field gradient on the tin nucleus giving rise to the quadrupole splitting can be caused by weak donor–acceptor interaction as well as by steric hindrance due to bulky ligand groups whereby a clear distinction between both effects is often not possible. The present work also points to the limitations to Mössbauer spectroscopy for the study of tin compounds. For a meaningful understanding of Mössbauer parameters in terms of structure and bonding, support from other physical methods such as vibrational spectroscopy and X-ray diffraction is needed.

Acknowledgment.—Financial support by the National Research Council of Canada is gratefully acknowledged.

[30] I. R. Beattie and L. Rule, *J. Chem. Soc.*, 3267 (1964).

[31] W. Gerrard, M. F. Lappert, H. Pyszora, and J. W. Wallis, *ibid.*, 2182 (1960).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF MICHIGAN, ANN ARBOR, MICHIGAN 48104

Fluorophosphine Ligands. VI. Difluorophosphine Oxide, Sulfide, and Selenide

BY L. F. CENTOFANTI[1a] AND R. W. PARRY[1b]

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The interaction of PF_2I and H_2X has been examined and explained in terms of nucleophilic attack by H_2X on PF_2I. The structure of PF_2HSe, prepared from H_2Se and PF_2I, has been established by means of the ^{31}P, ^{19}F, and ^{1}H nmr spectra. When PF_2HSe is maintained in glass at room temperature for several weeks, SiF_4 and a red solid are obtained. PF_2HTe could not be produced from H_2Te and PF_2I in a reaction comparable to that used for preparing PF_2HSe. Reduction occurred during attempts to prepare PF_2HTe. Association observed in PF_2HO and PF_2HS is explained in terms of a P–X–P interaction and is related to compound decomposition. PF_2HSe shows little association and is moderately stable.

The recently synthesized compounds PF_2HO[2,3] and PF_2HS[2] exhibit association in the liquid phase. It has been suggested[3] that the decomposition observed for PF_2HO can be correlated with the large amount of association observed in its liquid phase. This proposal is examined further here through the preparation and characterization of PF_2HSe and the evaluation of both the degree of association and the extent of decomposition for the group of molecules of formula PF_2HX (X = O, S, Se).

1. Preparation and Characterization of PF_2HSe.—PF_2HSe was prepared by the reaction between H_2Se and PF_2I in the presence of mercury

$$PF_2I + H_2Se \xrightarrow{Hg} HF_2PSe + [HI]$$

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[1] (a) Department of Chemistry, Emory University, Atlanta, Ga. 30322. (b) Department of Chemistry, University of Utah, Salt Lake City, Utah 84112.

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

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

The method could be used to prepare the previously reported[2] HF_2PS. In a typical experiment a yield of 51% was obtained by using H_2S instead of H_2Se.

In the P^{31} nmr spectrum of PF_2HSe a pair of triplets was observed. The signal was first split into a doublet from coupling with the proton [$J_{PH} = 706$ cps, δ(relative to orthophosphoric acid) −79.2 ppm]; each member of the doublet was then further split by the two fluorines into triplets ($J_{P-F} = 1187$ cps). The fluorine nmr showed the expected doublet of doublets [δ(relative to trifluoroacetic acid) −34.0 ppm, $J_{PF} = 1187$ cps, $J_{HPF} = 90$ cps]. The proton nmr spectrum confirmed the phosphorus and fluorine spectra giving a doublet, each member of which was split into a triplet [δ(relative to TMS) −9.2 ppm, $J_{PH} = 702$ cps, $J_{FPH} = 90$ cps]. The coupling constants leave no doubt that the structure is HF_2PSe with the proton attached to the phosphorus.

The infrared spectrum also confirms the structure assigned [data are presented as frequency of line in cm^{-1} and estimate of intensity and shape where s is strong, m is medium, w is weak, v is very, sh is sharp, and br is broad (probable assignment is shown in parentheses)]: 2444.5 m (ν_{sym}(P–H)); 1001.6 s, sh (δ_{sym}(P–H)), typical PQR structure, P–R separation 10–15 cm^{-1}; 950 w, 901.7 vs (ν_{asym}(P–F)); 893.9 vs (ν_{sym}(P–F)); 547 m, br (ν_{sym}(P–Se)); 401.3 w, typical PQR structure, P–R separation 10–15 cm^{-1} (δ_{sym} (PF_2)); 294 w, br.

The mass spectrum shown in Table I, although somewhat complicated by the number of selenium isotopes, can be fitted nicely to the compound HF_2PSe. The vapor pressure values [0.8° (245.6 mm); −26.5° (66.5 mm); −41.9° (27.3 mm); −90.3° (0.9 mm)] can be expressed by the equation

$$\log P(\text{mm}) = \frac{-1387}{T} + 7.453$$

where T is in degrees Kelvin. The entropy of vaporization at the normal boiling point is 20.9 cal/mol deg. Little association is apparent; extrapolated bp 30.3°; mp (sealed tube) −79.9 to −81.5°.

The compound HF_2PSe is more stable than HF_2PO and decomposes by a different reaction than that observed for the oxide. After remaining at 25° for 3 months in a glass container, HF_2PSe was 84% decomposed in accordance with the equation

$$2HF_2PSe + SiO_2 \longrightarrow SiF_4 + \text{red-gray insoluble solid}$$

When an attempt was made to prepare HF_2PTe by a process comparable to that used for preparing HF_2PSe the following reaction was observed

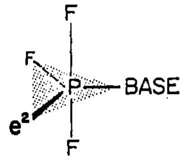
$$PF_2I + 3H_2Te \longrightarrow PH_3 + [HI] + [2HF] + 3Te$$

2. Factors Involved in the Reaction of Difluorophosphines with Nucleophiles.—Nucleophilic attack on phosphorus(III) is relatively easy when compared to similar attack on carbon atoms. This can be explained in terms of the greater polarizability of the phosphorus atom and the larger size of the phosphorus.[4,5] Larger size results in lower initial repulsion of the approaching nucleophile. Many bases react with phosphines forming new compounds of relatively low stability. Compound formation is frequently followed by HX elimination if a proton is available on the attacking nucleophile and a halogen is available on the phosphorus

$$(CH_3)_3N + PF_3 \rightleftarrows (CH_3)_3NPF_3 \quad \text{(no loss of RF or HF)}$$

$$(CH_3)_2NH + PF_3 \longrightarrow [(CH_3)_2\overset{H}{N}PF_3] \longrightarrow (CH_3)_2NPF_2 + HF$$

The trigonal bipyramid postulated as an intermediate can be visualized as



Intermediates of this type are not only of chemical interest but several similar compounds have considerable biological importance.[6] For the specific

TABLE I

MASS SPECTRUM OF F_2HPSe

m/e	Possible assignment	Rel peak height
19	F^+	1.6
20	HF^+	2.9
31	P^+	8.0
32	PH^+	1.6
47	SiF^+	2.5
50	PF^+	14.0
51	HPF^+	3.0
66	SiF_2^+	1.6
69	PF_2^+	31.2
70	HPF_2^+	4.1
76	$^{76}Se^+$	4.7
77	$^{77}Se^+$	4.3
78	$^{78}Se^+$	12.0
80	$^{80}Se^+$	24.6
81	^{80}SeH	2.1
82	$^{82}Se^+$	4.7
107	$^{76}SeP^+$	2.5
108	$^{77}SeP^+$	2.0
109	$^{78}SeP^+$	6.3
111	$^{80}SeP^+$	13.0
113	$^{80}SeP^+$	2.3
126	$^{76}SePF^+$	2.7
127	$^{77}SePF^+$	2.7
128	$^{78}SePF^+$	7.0
130	$^{80}SePF^+$	14.1
131	$^{80}SePFH^+$	1.8
132	$^{82}SePF^+$	2.5
144	. . .	1.8
146	$^{76}SePF_2^+$	19.8
147	$^{77}SePF_2^+$	17.1
148	$^{78}SePF_2^+$	35.8
149	$^{78}SePF_2H^+$	47.1
150	$^{80}SePF_2^+$	100
151	$^{80}SePF_2H^+$	18.3

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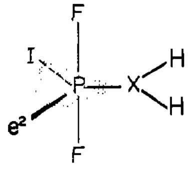
(4) J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, **84**, 16 (1962).

(5) R. F. Hudson, "Structure and Mechanism in Organo-Phosphorus Chemistry," Academic Press, New York, N. Y., 1965.

(6) B. C. Saunders, "Some Aspects of the Chemistry and Toxic Action of Oganic Compounds Containing Phosphorus and Fluorine," University Press, Cambridge, England, 1957.

case of PF_2I and H_2X ($X = S$ or Se) the X atom would serve as the nucleophile



and elimination of HI would then result in the formation of PF_2XH. A proton shift to the electron pair would give the final product. The overall equation describing this process is

$$F_2PI + H_2X \longrightarrow F_2PHX + [HI]$$

Mercury reacts with the HI.

A second intermediate which cannot be ruled out is a five-coordinate phosphorus with the proton bonding initially through the electron pair of the phosphorus. The X group would also serve as a Lewis base to form a secondary bond to the phosphorus.[7]

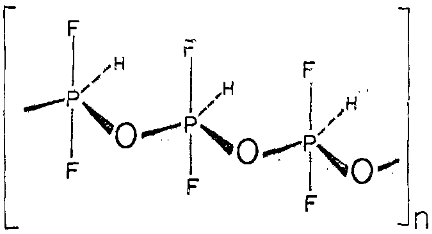
3. Association in PF_2HX.—The boiling point of F_2HPO (55°)[1] is very high when compared to that of F_3PO (−39.8°). Extensive molecular interaction is implied by these differences in volatility. Hydrogen bonding would be a possibility in F_2HPO but not in F_3PO. On the other hand, the infrared spectral shifts between gaseous and solid phases of F_2PHO are not those usually expected for hydrogen bonding. For example, the P–H stretching frequency appears at 2503.1 cm^{-1} in the gas phase but at a *higher* frequency, 2570.8 cm^{-1}, in the solid phase. Usually the X–H stretching frequency is lowered by hydrogen bonding. The unexpected shift of P–H to higher frequencies on going from gas to solid phase is exactly analogous to the shift found in the related compound PF_2H[8] and to the shift in PF_2HS. The Trouton constant of PF_2HS is 25.5 (Table II) implying association. In contrast, the spectrum of PF_2HSe shows no changes in the P–H region on going from solid to vapor phase and the compound shows a normal Trouton constant of 20.9 (Table II). The P–O stretching frequency drops from 1380 cm^{-1} in the gas phase to 1310 cm^{-1} in the solid phase. Although this shift is in the right direction, it cannot be attributed to hydrogen bonding in F_2HPO, since a comparable shift is observed in F_3PO on going from gas (1415 cm^{-1}) to solid phase (1385 cm^{-1}). In the latter case, no hydrogen bonding is possible. Recall further that the Trouton constant for PF_2HSe is near normal (equal to about 21) for a nonassociated species while both PF_2HO and PF_2HS show a high Trouton constant, implying association.

Table II

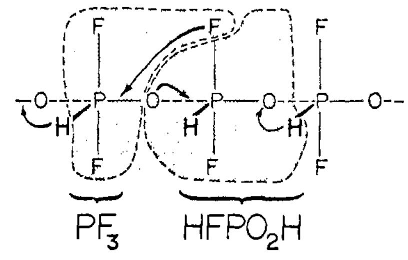
	Gas		Solid		Trouton constant, cal/mol deg
	P–H	P–X	PH	PX	
PF_2HO	2503	1380	2570	1310	26.3[1]
PF_2HS	2458	705	2471	*a*	25.5[1]
PF_2HSe	2444	547	2445	515	20.9[b]

[a] The PS region of PF_2HS(s) was complex and contained several peaks; no assignment was made. [b] Calculated from extrapolated boiling point.

In view of the foregoing facts, the association in PF_2H, PF_2HO, and PF_2HS appears to be similar to that which Miller and Rogers[9] observed in dialkylphosphine oxides (R_2HPO). They also found that the P–O frequency increased when going from solid to solution and that the P–H frequency decreased. They explained these spectral changes for R_2HPO in terms of a postulated $P^+–O^-–P^+–O^-$ interaction. This interaction (of a modified dipole type) would offer a plausible explanation for the shifts observed in the fluorophosphines of interest here. The association found in PF_2H would involve interaction between phosphorus atoms and fluorine atoms ($P^+–F^-–P^+$). The association expected for PF_2HO could involve oxygen as the linking atom.



4. Decomposition of PF_2HX.—Pure PF_2HO decomposes to PF_3 and H_2FPO_2: $2PF_2HO \rightarrow PF_3 + HFPO_2H$. The reaction occurs readily in the liquid phase but only very slowly in the gas phase suggesting that intermolecular association is important in the decomposition process. Assuming that liquid-phase association is a result of the P–X–P type of interaction ($X = O$ or F), one can visualize the following type of transition state



The failure of PF_2HSe to disproportionate through a process comparable to that followed by PF_2HO can

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[7] An alternative mechanism for the reaction of PF_2I and HX in the presence of Hg might involve the prior formation of P_2F_4. This would be followed by the reaction of P_2F_4 with HX: K. D. Morse, Ph.D. Dissertation, University of Michigan, 1966; R. W. Rudolph, R. C. Taylor, and R. W. Parry, *J. Am. Chem. Soc.*, **88**, 3729 (1966). The mechanism is shown by

$$2PF_2I + 2Hg \longrightarrow P_2F_4 + Hg_2I_2 \quad (a)$$

$$F_2P–PF_2 + HX \longrightarrow F_2PH + F_2PX \quad (b)$$

If HX were H(HS) or H_2S, reaction b would be

$$F_2PPF_2 + H_2(S) \longrightarrow F_2PH + F_2PSH \quad (c)$$

The foregoing reaction sequence would demand the presence of Hg to permit formation of F_2PPF_2 in step a. It has been shown in this work that yields of F_2PHS in the absence of mercury are comparable to yields obtained when mercury is present. Furthermore, no direct evidence for F_2PPF_2 was ever obtained. It now appears that any mechanism demanding the prior formation of F_2PPF_2 can be eliminated.

[8] R. W. Rudolph and R. W. Parry, *Inorg. Chem.*, **4**, 1339 (1965).

[9] C. D. Miller, R. C. Miller, and W. Rogers, *J. Am. Chem. Soc.*, **80**, 1562 (1958).

now be rationalized by the lack of association in PF_2HSe. Still, PF_2HSe did decompose to produce a red solid. The process is perhaps suggestive of the reaction between PF_2I and H_2Te in which solid Te was obtained as a product

$$PF_2I + H_2Te \longrightarrow [PF_2HTe] + [HI]$$
$$\xrightarrow{+2H_2Te} PH_3 + [2HF] + 3Te$$

Although a firm classification for the decomposition of F_2PHSe cannot be achieved until the stoichiometry is established with more certainty, it is believed that the process is a redox reaction in which selenide is oxidized. More evidence on the nature of the solid is now being sought.

5. Trends in the Decomposition of PF_2HX.—From the information summarized above it appears that two types of decomposition processes are associated with the molecule PF_2HX. The first is a disproportionation reaction in which PF_3 and FPX_2H_2 are products. This process is strongly influenced by molecular association. It goes most easily when X is oxygen and decreases rapidly as X moves from S to Se to Te. No evidence for such a disproportionation was found in F_2PHSe.

The second type of reaction is related to the reducing strength of the species H_2X. As this species becomes a stronger reducing agent, the tendency to reduce phosphorus to lower oxidation states and to oxidize X to higher states increases. Thus, H_2Te is such a strong reducing agent that the compound F_2PHTe could never be isolated. Both PH_3 and Te were products of the reaction between PF_2I and H_2Te. Although F_2PHSe is known, it did decompose with moderate speed through such an oxidation–reduction reaction. F_2PHS seemed to undergo a very slow oxidation–reduction reaction while F_2PHO showed no oxidation–reduction at all.

In view of the opposite trends in stability

(1) toward disproportionation:

$$\underset{\text{most stable}}{F_2PHTe} > F_2PHSe > F_2PHS > F_2PHO$$

(2) toward oxidation reduction:

$$\underset{\text{most stable}}{F_2PHO} > F_2PHS > F_2PHSe > F_2PHTe$$

the stability maximum appearing at F_2PHS is easily rationalized. In observed or operational stability the two decomposition processes are not distinguished; under these conditions, the observed order of stability is $F_2PHS > F_2PHSe > F_2PHO > F_2PHTe$.

Experimental Section

Apparatus.—Standard high-vacuum techniques were used throughout. Mass spectra were run on a Consolidated Electro-Dynamics 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 Mc, respectively. Chemical shifts were obtained by tube interchange. A negative chemical shift means the peak is downfield from the standard. The infrared spectrum was determined with a Beckman IR-12 instrument in a 75-mm gas cell equipped with CsI windows.

Materials.—PF_2I was prepared from the reaction of $(CH_3)_2NPF_2$ and HI.[10] H_2Se and H_2Te were prepared from the reactions of Al_2Se_3 and Al_2Te_3 with H_2O.[11]

Reactions of PF_2I with H_2X. 1. Preparation of PF_2HS.—A 9.0-mmol sample of PF_2I was condensed in a 500-ml reaction bulb containing 1 ml of triply distilled Hg. A 10-mmol sample of H_2S was then added. The mixture was allowed to warm to room temperature and then shaken for 3 hr. After the reaction had occurred, the bulb was frozen with liquid nitrogen and pumped free of noncondensables (H_2). The reaction products were passed through traps at −78, −125, and −196°. A 4.6-mmol sample of PF_2HS identified by its ir spectrum[1] was found in the −125° trap. The unidentified material at −78° was discarded along with the PF_3 and SiF_4 that was found in the −196° trap.

2. Preparation of PF_2HSe.—A 2.0-ml sample of triply distilled mercury was placed in a 500-ml reaction tube which was equipped with a standard taper joint and a stopcock. The bulb was evacuated and 4.68 mmol of PF_2I and 5.86 mmol of H_2Se were condensed into the vessel at −196°. After warming to 25°, the bulb was shaken for 1 hr. The products were then frozen at −196° and the bulb was opened to traps held at −78, −112, and −196°. A small amount of hydrogen passed through the traps. The products condensable at −196° were warmed and allowed to pass through these traps. A 2.36-mmol sample of PF_2HSe was found in the −112° trap. A trace of unidentified material was found in the −78° trap, while the 196° trap contained PF_3 and SiF_4. PF_2HSe was identified by its ir spectrum which was very similar to the spectrum of PF_2HS. Its identification was later confirmed by its mass spectrum and its ^1H, ^{19}F, and ^{31}P nmr spectra which are given in the discussion.

3. Decomposition of PF_2HSe.—A 9.10-mmol sample of PF_2HSe was added to a 500-ml reaction bulb and allowed to remain at room temperature. Decomposition began immediately with the formation of yellow solids on the walls of the flask. After 3 months at room temperature, the bulb was opened and volatile products were distilled through traps held at −130, −160, and −196°. The −130° trap contained 1.44 mmol of PF_2HSe, while the −160° trap held 3.72 mmol of SiF_4. A trace of PF_3 at −196° was discarded.

4. Reaction of PF_2I and H_2Te.—A 1.70-mmol sample of PF_2I and a 1.806-mmol sample of H_2Te were condensed in a 500-ml reaction bulb along with 1 ml of Hg. On warming the reactants, a violent reaction occurred with the formation of a metallic coating (assumed to be Te) on the walls of the bulb. After shaking for 1 hr, the bulb was frozen with liquid nitrogen and opened to traps held at −78, −112, and −196°. A small amount of material held at −78° was identified by its infrared spectrum as PF_2HSe (probably the result of the use of impure Te to make H_2Te) and P_2F_4. The −196° trap held SiF_4, PF_3 (small amounts), and PH_3 identified by their ir spectra. The main reaction of Hg, H_2Te, and PF_2I can be described by

$$PF_2I + 3H_2Te \longrightarrow PH_3 + [HI] + [2HF] + 3Te$$

Bracketed products were not directly observed.

Acknowledgment.—Support of this work by The National Cancer Institute through Grant CA-07989 is gratefully acknowledged. It is also a pleasure to thank Frank Parker for his assistance in obtaining the nmr spectra.

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(10) J. G. Morse, K. Cohn, R. W. Rudolph, and R. W. Parry, *Inorg. Syn.*, **10**, 147 (1967).

(11) G. R. Waitkins and R. Shutt, *ibid.*, **2**, 183 (1946).