this region.[19-21] The resonances at −43.8 and −54.6 ppm are in the regions associated with OSO_2F and SO_2F groups, respectively.[15,22,23] Under high resolution each of these singlets was split into a pair of doublets arising from coupling of the two nonequivalent F atoms with the third one. Although no nitrogen coupling was observed, the resonance attributed to the −C(O)F group was broadened indicating that quadrupole interactions may be important. Broadening of nmr signals for F on −C(O)F have been observed in compounds containing −C(O)F groups bonded to nitrogen.[24] The larger J value observed for coupling of F on $-OSO_2F$ with F on −C(O)F suggests that through-space interactions may be important since F on OSO_2F is four atoms removed from F on −C(O)F. Such through-space interactions have been found to be important in the perfluoroalkyl derivatives of sulfur hexafluoride.[25] In the case of $FSO_2N(OCF_3)C(O)F$, three resonances were also observed at +68.3, +6.6, and −50.4 ppm relative to CCl_3F. The areas were in the ratio of 3:1:1 and are in the regions associated with the $-OCF_3$, −C(O)F, and $-SO_2F$ groups, respectively. The high-resolution spectrum showed a high-field pair of doublets arising from coupling of two nonequivalent F atoms with those of the $-OCF_3$ group. The resonance at 6.6 ppm was observed as a broadened quintet in the ratio 1:4:6:4:1 arising from two overlapping quartets due to coupling of the −C(O)F fluorine atom with those of the $-OCF_3$ and $-SO_2F$ groups. The low-field resonance appeared as two partially superimposed quartets due to coupling of the F atom on the $-SO_2F$ group with those on the −C(O)F and $-OCF_3$ groups. $(FSO_2NC(O)F)_2$ exhibited two resonances of equal intensity located at +9.08 and −57.4 ppm attributed to F atoms in the −C(O)F and $-SO_2F$ groups, respectively. No fine structure was observed. Although the results of infrared, nmr, and chemical analyses indicate that the empirical formula is $(FSO_2NC(O)F)_n$, they do not show that n equals 2. The conclusion that n equals 2 follows after a consideration of rules of chemical valence, comparison of observed with expected volatility, and the fact that the material is uncolored indicating that it is probably not a free radical.[26]

It is interesting to note that apparently **only** one isomeric form of each new compound reported here is formed in isolable quantities. The fact that the carbonyl stretching frequency is invariant at 1888 cm^{-1} lends support to the argument that this must arise from a −C(O)F group since in perfluoracyl fluorosulfates[27] the C=O stretch is found at 1845–1850 cm^{-1}. However, in fluoroformyl fluorosulfate this stretch is shifted to 1910 cm^{-1}.[13] The nmr spectra leave essentially no doubt as to the absence of >NF in these compounds since >NF resonances in general occur at higher fields than the resonances assigned here to −C(O)F, *e.g.*, for $C_2F_5N(F)C(O)F$, $CF_3N(F)SF_5$,[28] and $FN(SO_2F)_2$,[16] >NF resonances occur at ϕ 49.4, 48.2, and 28.5, respectively.

The compounds are hydrolyzed by traces of moisture. Hydrolytic attack probably occurs first at the fluorocarbonyl group followed by very slow hydrolysis of the fluorosulfuryl group.[23]

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Contribution from the Department of Chemistry,
University of Alberta, Edmonton, Alberta, Canada

Fragmentation and Rearrangement Processes in the Mass Spectra of Fluoroalkylphosphorus Compounds. II. Compounds Containing Two or More Phosphorus Atoms

By R. G. CAVELL and R. C. DOBBIE

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The mass spectra of five fluoroalkylphosphorus compounds containing two or more phosphorus atoms have been obtained and partial fragmentation patterns deduced. Rearrangement to give ions with P–F bonds was detected in all of the spectra.

Introduction

It has been demonstrated that trifluoromethylarsenic[1] and -phosphorus[2] compounds rearrange under electron impact in the mass spectrometer, with the migration of fluorine from carbon to arsenic or phosphorus. The mass spectra of some fluoroalkyl com-

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TABLE I

MASS SPECTRA OF TRIFLUOROMETHYLPHOSPHORUS COMPOUNDS

m/e	Ion	I, %[b]
	$(CF_3)_2PP(CF_3)_2$	
338^a	$C_4F_{12}P_2$	10.6
319	$C_4F_{11}P_2$	5.8
269^a	$C_3F_9P_2$	1.0
231^a	$C_3F_7P_2$	0.8
169^a	C_2F_6P	1.9
150^a	C_2F_5P	1.2
131^a	C_2F_4P	5.0
119^a	CF_4P	10.9
100^a	CF_3P	6.8
93	CFP_2	0.7
81^a	CF_2P	1.8
69^a	CF_3	30.1
	PF_2	16.5
62^a	CFP	0.6
	P_2	1.8
50^a	CF_2	1.0
31^a	CF	4.2
	$(CF_3)_2POP(CF_3)_2$	
354^a	$C_4F_{12}P_2O$	3.8
285^a	$C_3F_9P_2O$	2.4
235^a	$C_2F_7P_2O$	3.1
185^a	C_2F_6PO	0.4
	CF_5P_2O	0.5
169	C_2F_6P	2.2
150	C_2F_5P	1.5
135^a	CF_4PO	1.4
	P_2F_3O	21.2
131	C_2F_4P	0.9
119	CF_4P	2.7
116	P_2F_2O	1.4
100^a	CF_3P	4.9
97	P_2FO	0.7
81	CF_2P	1.6
69^a	CF_3	13.5
	PF_2	17.1
62	CFP	0.9
	$(CF_3)_2POP(CF_3)_2$ (*Contd*)	
50^a	CF_2	0.7
	PF	1.0
47^a	PO	14.1
31^a	CF	1.7
	P	2.2
	$(CF_3)_2PSP(CF_3)_2$	
370^a	$C_4F_{12}P_2S$	2.5
351	$C_4F_{11}P_2S$	1.0
301^a	$C_3F_9P_2S$	16.5
251^a	$C_2F_7P_2S$	4.8
201^a	C_2F_6PS	0.8
	CF_5P_2S	2.1
163^a	C_2F_4PS	0.8
	CF_3P_2S	1.5
151^a	CF_4PS	0.7
	P_2F_3S	1.2
150	C_2F_5P	0.8
131	C_2F_4P	0.4
119^a	CF_4P	4.9
113^a	C_2F_3S	0.3
	CF_2PS	5.0
	P_2FS	1.3
100^a	CF_3P	3.0
94^a	CFPS	0.7
	P_2S	0.3
82	PFS	0.5
81	CF_2P	1.5
75	CPS	1.0
69^a	CF_3	15.4
	PF_2	10.7
63^a	CFS	1.8
	PS	14.0
62	CFP	0.7
50^a	CF_2	1.0
	PF	0.7
31^a	CF	3.6
	P	0.4
	$(CF_3P)_4$	
400^a	$C_4F_{12}P_4$	14.2
331^a	$C_3F_9P_4$	4.1
281^a	$C_3F_8P_3$	1.5
	$C_2F_7P_4$	2.2
231^a	$C_2F_6P_3$	1.1
	CF_5P_4	2.2
193^a	$C_2F_4P_3$	1.4
	CF_3P_4	2.0
181^a	$C_2F_5P_2$	1.0
	CF_4P_3	2.9
143^a	$C_2F_3P_2$	1.1
	CF_2P_3	5.5
	FP_4	4.4
131^a	C_2F_4P	0.8
	CF_3P_2	4.5
124^a	CFP_3	1.4
	P_4	2.0
119	CF_4P	3.5
112^a	CF_2P_2	0.8
105	C_2FP_2	1.4
100^a	CF_3P	0.9
93^a	CFP_2	4.6
	P_3	7.3
81	CF_2P	1.0
74	C_2FP	0.6
69^a	CF_3	7.2
	PF_2	15.2
62^a	CFP	2.4
	P_2	0.5
55	C_2P	0.4
50^a	PF	0.9
31^a	CF	0.8
	P	0.3
	$(CF_3P)_4S$	
432^a	$C_4F_{12}P_4S$	12.6
413	$C_4F_{11}P_4S$	0.4
400	$C_4F_{12}P_4$	0.5
	$(CF_3P)_4S$ (*Contd*)	
363^a	$C_3F_9P_4S$	3.8
313^a	$C_2F_7P_4S$	0.9
281^a	$C_3F_8P_3$	1.4
262	$C_3F_7P_3$	0.5
232^a	$C_2F_6P_2S$	2.6
231^a	$C_2F_6P_3$	1.1
225	$C_2F_4P_3S$	0.5
213^a	$C_2F_5P_2S$	0.9
	CF_4P_3S	2.3
181^a	C_3F_6P	1.0
	CF_4P_3	0.5
163^a	CF_3P_2S	8.0
	$C_2F_3P_2$	0.4
143^a	CF_2P_3	0.8
	FP_4	0.3
131	CF_3P_2	2.8
125	CFP_2S	0.8
119	CF_4P	1.6
113^a	CF_2PS	0.9
	FP_2S	8.9
112	CF_2P_2	0.5
100^a	CF_3P	0.7
94^a	CFPS	3.0
	P_2S	2.1
93^a	CFP_2	2.4
	P_3	3.8
81	CF_2P	0.7
75	CPS	3.6
69^a	CF_3	3.6
	PF_2	7.3
63^a	PS	13.6
62	CFP	1.3
50^a	CF_2	0.3
	PF	0.7
32	S	0.7
31^a	CF	0.5
	P	0.3

[a] The identity of these peaks was established by mass measurement under high resolution. [b] Intensities are expressed relative to the total ionization, defined as ΣI_n, where n refers to all ions with mass greater than 30 whose intensity is greater than 2% of the base peak.

pounds containing more than one phosphorus atom have now been studied.

Experimental Section

All of the mainpulations were carried out in a Pyrex vacuum system. Mass spectra were recorded on an AEI MS-9 instrument operating at an ionizing voltage of 70 ev, samples being introduced as vapors through a heated inlet system at 185°. Perfluorotributylamine was used as a standard for mass measurement. The diphosphine, $(CF_3)_2PP(CF_3)_2$,[3] the diphosphine oxide,[4] diphosphine sulfide,[5] and tetrakistrifluoromethylphosphine, $(CF_3P)_4$,[6] were prepared by the literature methods. The cyclic polyphosphine sulfide, $(CF_3P)_4S$, recently reported by Burg,[7] was prepared by the action of silver sulfide on diiodotrifluoromethylphosphine at 100° or by the reaction of dichlorotrifluoromethylphosphine with hydrogen sulfide, assisted by trimethylamine. The compounds were identified by infrared, vapor pressure, and molecular weight measurements and by precise mass measurement of the parent ion in the mass spectrum.

Results and Discussion

The compounds studied were the diphosphine, $(CF_3)_2PP(CF_3)_2$, the diphosphine oxide and sulfide, $(CF_3)_2POP(CF_3)_2$ and $(CF_3)_2PSP(CF_3)_2$, the cyclic tetramer, $(CF_3P)_4$, and the cyclic phosphine sulfide, $(CF_3P)_4S$. The mass spectra, together with the results of high-resolution studies, are shown in Table I. Some metastable ions observed in the spectra are listed in Table II. As in the study of trifluoromethyl phosphorus halides and hydrides,[2] rearranged ions were found which contributed between 23 and 49% to the total ionization.

The cracking pattern of the diphosphine, deduced from exact mass measurements and observation of the appropriate metastable peaks, is shown in Figure 1. The parent ion, which had a relative intensity comparable to that observed in the spectra of the halogeno- and hydridophosphines,[2] fragmented with loss of F or

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Table II

Metastable Ions in the Mass Spectra of Trifluoromethylphosphorus Compounds

Compound	m/e Obsd	m/e Calcd	Transition		
$(CF_3)_2PP(CF_3)_2$	214.0	214.1	$C_4F_{12}P_2^+$	$\rightarrow C_3F_9P_2^+$	$+ CF_3$
	167.5	167.3	$C_4F_{11}P_2^+$	$\rightarrow C_3F_7P_2^+$	$+ CF_4$
	89.3	89.5	$C_4F_{11}P_2^+$	$\rightarrow C_2F_6P^+$	$+ C_2F_5P$
	84.4	84.5	$C_4F_{12}P_2^+$	$\rightarrow C_2F_6P^+$	$+ C_2F_6P$
	66.6	66.6	$C_4F_{12}P_2^+$	$\rightarrow C_2F_5P^+$	$+ C_2F_7P$
	63.8	63.8	$C_3F_9P_2^+$	$\rightarrow C_2F_4P^+$	$+ CF_5P$
	53.9	53.8	$C_4F_{11}P_2^+$	$\rightarrow C_2F_4P^+$	$+ C_2F_7P$
	52.6	52.6	$C_3F_9P_2^+$	$\rightarrow CF_4P^+$	$+ C_2F_5P$
$(CF_3)_2PSP(CF_3)_2$	258.0	258.1	$C_4F_{11}P_2S^+$	$\rightarrow C_3F_9P_2S^+$	$+ CF_2$
	245.0	244.9	$C_4F_{12}P_2S^+$	$\rightarrow C_3F_9P_2S^+$	$+ CF_3$
	209.3	209.3	$C_3F_9P_2S^+$	$\rightarrow C_2F_7P_2S^+$	$+ CF_2$
	179.6	179.5	$C_4F_{11}P_2S^+$	$\rightarrow C_2F_7P_2S^+$	$+ C_2F_4$
	161.0	161.0	$C_2F_7P_2S^+$	$\rightarrow 201^+$	$+ 50$
	56.5	56.4	$C_2F_7P_2S^+$	$\rightarrow CF_4P^+$	$+ CF_3PS$
	47.1	47.0	$C_3F_9P_2S^+$	$\rightarrow CF_4P^+$	$+ C_2F_5PS$
$(CF_3)_2POP(CF_3)_2$	229.3	229.4	$C_4F_{12}P_2O^+$	$\rightarrow C_3F_9P_2O^+$	$+ CF_3$
	193.5	193.8	$C_3F_9P_2O^+$	$\rightarrow C_2F_7P_2O^+$	$+ CF_2$
	121.5	121.5	$C_2F_7P_2O^+$	$\rightarrow C_2F_6P^+$	$+ POF$
	77.5	77.6	$C_2F_7P_2O^+$	$\rightarrow 135^+$	$+ 100$
	60.3	60.3	$C_2F_7P_2O^+$	$\rightarrow CF_4P^+$	$+ CF_3PO$
	16.4	16.4	135^+	$\rightarrow PO^+$	$+ 88$
$(CF_3P)_4$	273.7	273.9	$C_4F_{12}P_4^+$	$\rightarrow C_3F_9P_4^+$	$+ CF_3$
	238.6	238.6	$C_3F_9P_4^+$	$\rightarrow 281^+$	$+ 50$
$(CF_3P)_4S$	319.0	319.0	$C_4F_{11}P_4S^+$	$\rightarrow C_3F_9P_4S^+$	$+ CF_2$
	304.8	305.0	$C_4F_{12}P_4S^+$	$\rightarrow C_3F_9P_4S^+$	$+ CF_3$
	269.8	270.0	$C_3F_9P_4S^+$	$\rightarrow C_2F_7P_4S^+$	$+ CF_2$
	217.8	217.5	$C_3F_9P_4S^+$	$\rightarrow C_3F_8P_3^+$	$+ PSF$
	190.1	189.9	$C_3F_8P_3^+$	$\rightarrow C_2F_6P_3^+$	$+ CF_2$
	114.5	114.5	$C_2F_6P_2S^+$	$\rightarrow CF_3P_2S^+$	$+ CF_3$
	73.3	73.2	$C_3F_9P_4S^+$	$\rightarrow CF_3P_2S^+$	$+ C_2F_6P_2$
	61.2	61.1	$C_2F_6P_2S^+$	$\rightarrow CF_4P^+$	$+ CF_2PS$
	34.5	34.5	$CF_3P_2S^+$	$\rightarrow CPS^+$	$+ PF_3$

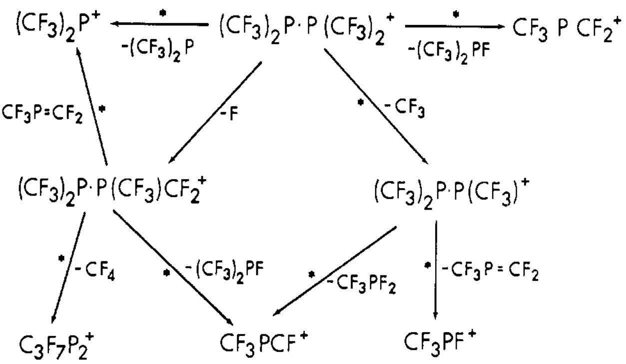

Figure 1.—Fragmentation pattern of tetrakistrifluoromethyldiphosphine, $(CF_3)_2PP(CF_3)_2$.

CF_3. In addition, however, the ion was also found to cleave at the P–P bond, symmetrically to give $(CF_3)_2P^+$ (*m/e* 169, 1.9%), or with the transfer of a fluorine atom to the remote phosphorus atom to give $CF_3PCF_2^+$ (*m/e* 150, 1.2%), ejecting a molecule of fluorobis(trifluoromethyl)phosphine, $(CF_3)_2PF$. The latter process was demonstrated by the observation of a metastable peak at 66.6 amu (calcd 66.6).

Elimination of CF_3PF_2 from the diphosphorus ion $(CF_3)_2PP(CF_3)^+$ was observed in the transition

$$(CF_3)_2PP(CF_3)^+ \longrightarrow CF_3PCF_2^+ + CF_3PF_2 \qquad (1)$$

demonstrated by the appropriate metastable peak. The principal rearrangement ions were CF_3PF^+ (*m/e* 119, 10.9%) and PF_2^+ (*m/e* 69, 16.5%). The former arose from $C_3F_9P_2^+$ by loss of C_2F_5P, possibly as the molecule $CF_3P{=}CF_2$, which has been postulated to be a reaction intermediate in the hydrolysis of some bis(trifluoromethyl)phosphino derivatives.[8]

The mass spectrum of the diphosphine sulfide, $(CF_3)_2PSP(CF_3)_2$, was more complex, several of the ions of higher *m/e* value being doublets. A complete breakdown pattern could not be obtained as some of the metastable ions did not define the transition unambiguously. A partial fragmentation scheme is shown in Figure 2. The parent ion, which was of low intensity, lost CF_3, followed by CF_2 to give the ion $C_2F_7P_2S^+$ (*m/e* 251, 4.8%), for which two structures, A and B, may be proposed

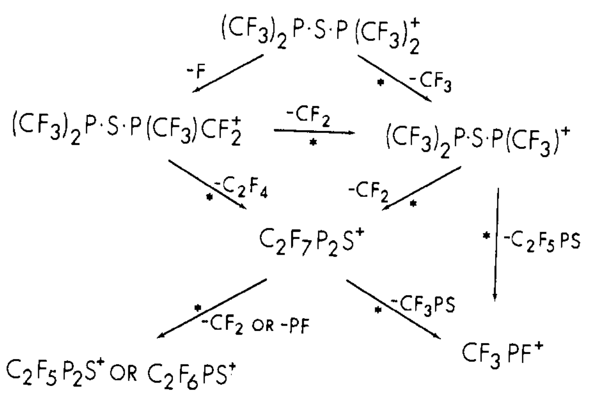

Figure 2.—Fragmentation pattern of tetrakistrifluoromethyldiphosphine sulfide, $(CF_3)_2PSP(CF_3)_2$.

$(CF_3)_2PSPF^+$	$CF_3PSP(CF_3)F^+$
A	B

Since the peak in the mass spectrum at *m/e* 201, formed from $C_2F_7P_2S^+$ by loss of a fragment of 50 amu, was a doublet containing both $C_2F_6PS^+$ and $CF_5P_2S^+$, it is suggested that ions of both structures A and B were present, for A could readily lose PF, while both A and B could eliminate CF_2 from one of the CF_3 groups in the manner proposed for the trifluoromethylphosphines[2]

$$\begin{tikzcd}[row sep=small] & (CF_3)_2PS^+ + PF & (2) \\ A \arrow[ur] \arrow[dr] & & \\ & FPSP(CF_3)F^+ + CF_2 & (3) \\ B \arrow[ur] \arrow[dr] & & \\ & CF_3PSPF_2^+ + CF_2 & (4) \end{tikzcd}$$

As in the mass spectrum of the diphosphine, there was an intense rearrangement ion at *m/e* 119 (CF_3PF^+, 4.9%) which was shown by observation of the appropriate metastable ion to be produced as

$$C_2F_7P_2S^+ \longrightarrow CF_3PF^+ + CF_3PS \qquad (5)$$

Structure B was preferred to A for the parent ion of this transition, since no abnormal fragmentation would then be required. The elimination of "CF_3PS," which is not a known compound, is analogous to the elimination of the phosphoalkene, $CF_3P{=}CF_2$, observed in the mass spectrum of the diphosphine (eq 1). Although P_2S^+ (*m/e* 94, 0.3%) was only of low intensity, PS^+ (*m/e* 63, 14.0%) was one of the more intense peaks in the spectrum. Examination of the ion at *m/e* 63 under high resolution showed it to be a

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[8] H. Goldwhite, R. N. Haszeldine, and R. G. Rowsell, *Chem. Commun.*, 83 (1965).

doublet, also containing CFS^+ (1.8%). The origin of this novel rearrangement ion is not known.

A partial fragmentation scheme for the diphosphine oxide is shown in Figure 3. About half of the total ionization was made up of rearranged ions. The parent ion lost CF_3 followed by CF_2 to give $C_2F_7P_2O^+$ (*m/e* 235, 3.1%). A metastable peak indicated that this ion in turn lost 100 amu to give a doublet at *m/e* 135, shown to consist of CF_4PO^+ (1.4%) and $P_2F_3O^+$ (21.2%), both rearranged ions, with the latter forming the base peak of the spectrum. As in the corresponding sulfide, this pointed to two structures, C and D, for the parent ion (*m/e* 235) of the transition.

$$\underset{\text{C}}{(CF_3)_2POPF^+} \qquad \underset{\text{D}}{CF_3POP(CF_3)F^+}$$

An ion of structure C could eliminate a molecule of C_2F_4 from the adjacent trifluoromethyl groups, as observed in the halogenobis(trifluoromethyl)phosphines[2]

$$(CF_3)_2POPF^+ \longrightarrow F_2POPF^+ + C_2F_4 \qquad (6)$$

This would be unlikely for an ion of structure D, although loss of CF_3P would now be possible

$$CF_3POP(CF_3)F^+ \longrightarrow CF_3P(F)O^+ + CF_3P \qquad (7)$$

The ion of structure D would then give rise to the rearranged ion CF_3PF^+ (*m/e* 119, 2.7%), formed from $C_2F_7P_2O^+$ by loss of CF_3PO in a manner analogous to that of eq 5. It is interesting to note that PO^+ (*m/e* 47, 14.1%) was an intense peak probably formed by elimination of CF_4 from $CF_3P(F)O^+$ rather than by elimination of PF_3 from $P_2F_3O^+$; no detectable amount of CFO^+ (*m/e* 47) was present.

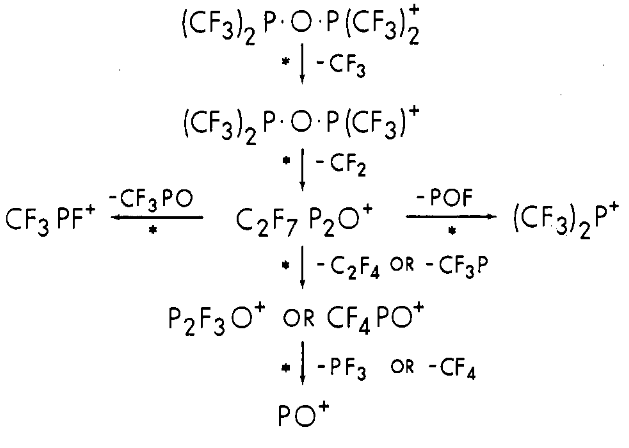
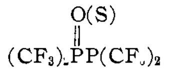


Figure 3.—Fragmentation pattern of tetrakistrifluoromethyldiphosphine oxide, $(CF_3)_2POP(CF_3)_2$.

Notably the mass spectra of the diphosphine sulfide and oxide showed no ions corresponding to the loss of sulfur or oxygen atoms with retention of the diphosphine unit. Thus the mass spectra confirm the original formulation of these compounds as trivalent phosphorus derivatives with sulfur or oxygen bridging[4,5] rather than the isomeric structure with a phosphorus–phosphorus bond



$$(CF_3)_2\overset{O(S)}{\overset{\|}{P}}P(CF_3)_2$$

The cyclic tetramer, $(CF_3P)_4$, showed a parent ion (*m/e* 400, 14.2%) only slightly less intense than the rearrangement ion PF_2^+ (*m/e* 69, 15.2%) which formed the base peak of the spectrum. Although over 20 metastable ions were observed, precise identification of the corresponding transitions could not be made as many of the ions in the spectrum were doublets or triplets. It was clear, however, that primary loss of CF_3 from the parent ion was followed by elimination of either CF_2 or PF to give the doublet at *m/e* 281. Fragmentation at the C–P bonds took place before extensive breakdown of the polyphosphine skeleton, and species such as $CF_5P_4^+$ (*m/e* 231, 2.2%), $CF_3P_4^+$ (*m/e* 193, 2.0%), FP_4^+ (*m/e* 143, 4.4%), and P_4^+ (*m/e* 124, 2.0%) were observed.

The base peak in the mass spectrum of the tetraphosphine sulfide, $(CF_3P)_4S$, was PS^+ (*m/e* 63, 13.6%) although the parent ion (*m/e* 432, 12.6%) was only slightly less intense. A partial fragmentation pattern, shown in Figure 4, demonstrates that the first step in the breakdown under electron bombardment was loss of CF_3 followed by elimination of CF_2 to give $C_2F_7P_4S^+$ (*m/e* 313, 0.9%), or of PFS to give $C_3F_8P_3^+$ (*m/e* 281, 1.4%). A number of ions and metastable peaks were common to the tetraphosphine sulfide and the cyclic tetramer, produced mainly by breakdown of $C_3F_8P_3^+$ in each case. However, the cyclic sulfur compound also showed fragment ions in which the P–S bond was retained so that there appeared to be two parallel breakdown pathways.

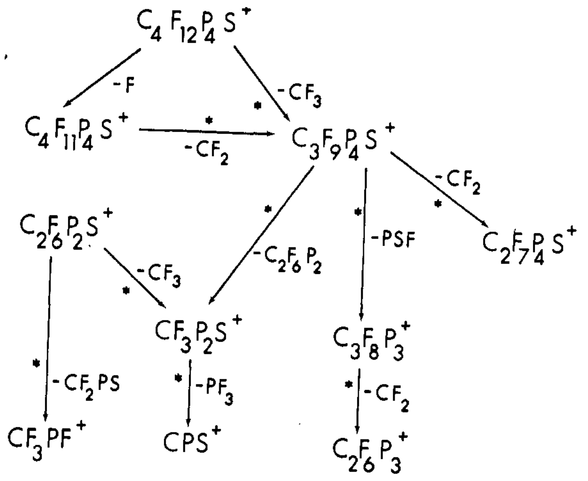


Figure 4.—Fragmentation pattern of the cyclic tetraphosphine sulfide, $(CF_3P)_4S$.

The low intensity of the parent ion in the diphosphine oxide and sulfide compared to that of the other three compounds may indicate a stabilization of the parent ion by a P–P bond.

With the exception of the diphosphine, initial loss of CF_3 was followed by elimination of CF_2 to give a rearranged ion with a P–F bond. This is in contrast to the halogenobis(trifluoromethyl)phosphines[2] which gave the analogous rearranged ions (PFX^+) by loss of a fluorine atom followed by elimination of C_2F_4.

Since most of the compounds[2-6] are known to be stable at 185° (the temperature of the heated inlet system) the possibility that the rearrangements were caused by pyrolysis can be dismissed. It is probable that, as suggested earlier,[2] the rearrangements proceed through the interaction of the nonbonding p-orbital electrons on the fluorine atom with vacant d orbitals on the phosphorus. In the present case the transfer of fluorine to a distant phosphorus atom also appears to occur in transitions such as

$$(CF_3)_2PP(CF_3)_2^+ \longrightarrow CF_3PCF_2^+ + (CF_3)_2PF$$

which may indicate that the fluorine atoms of a CF_3 group attached to one phosphorus can interact with the d orbitals of the distant phosphorus atom.

Finally, this work should act as a warning that fluorocarbon derivatives are not solely characterized by normal bond breaking in the mass spectrometer since rearrangement of fluorine atoms can occur readily in phosphorus and arsenic compounds. Similar rearrangements may be anticipated in other fluorocarbon nonmetal and metal derivatives.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN 53706

Synthesis and Characterization of the Alkylhydridotrifluorophosphoranes CH_3PF_3H and $C_2H_5PF_3H$[1]

BY RUTH A. GOODRICH AND P. M. TREICHEL

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The compounds CH_3PF_3H and $C_2H_5PF_3H$ have been prepared by the reaction of the respective alkyltetrafluorophosphorane with trimethyltin hydride. These compounds are considerably more stable than HPF_4 and H_2PF_3 and may be manipulated and stored in Pyrex apparatus without decomposition. Infrared spectra and ^1H and ^{19}F nmr spectra at low temperatures confirm an equatorial-substituted trigonal-bipyramidal geometry for both alkylhydridofluorophosphoranes. At room temperature the nmr spectra indicate a substantial averaging of axial and equatorial fluorine atom environments owing to intramolecular exchange processes.

Ivanova and Kirsanov reported in 1961 the synthesis of three arylhydridotrifluorophosphoranes, $ArPF_3H$ (Ar = *p*-chlorophenyl, *p*-tolyl, and phenyl), by the oxidative reaction of KHF_2 with the respective aryldichlorophosphine.[2] The same reaction with alkyldichlorophosphines is reported in a patent[3] to yield alkylhydridotrifluorophosphoranes *in situ*. These products were not characterized, however, but were allowed to react with secondary amines giving a series of compounds of the general formula $RPF_2(NR'_2)H$ (R = CH_3, C_2H_5; R' = CH_3, C_2H_5, n-C_4H_9). We wish now to report the synthesis and characterization of CH_3PF_3H and $C_2H_5PF_3H$ as relatively stable entities from the exchange reactions of CH_3PF_4 and $C_2H_5PF_4$, respectively, with $(CH_3)_3SnH$. These reactions are analogous to the reaction which we have recently reported for the preparation of HPF_4 and H_2PF_3.[4]

Evidence is also presented for the formation of $(CH_3)_2NPF_3H$ from the exchange reaction between $(CH_3)_2NPF_4$ and $(CH_3)_3SnH$. This compound could not be obtained in pure form, however.

Synthesis

A Pyrex-glass vacuum system of standard construction was used in this work. Stopcocks were greased with Apiezon-N grease. Quantities of volatile materials were measured in a calibrated volume on the line. Substances of low volatility were weighed in an ampoule and then transferred to the line.

Methyl- and ethyltetrafluorophosphoranes were prepared by the reaction of PF_5 and the respective tetraalkyltin compounds.[5] These starting materials were shown to be pure by comparison of observed vapor pressures with similar data for samples known to be pure. The vapor pressure data for pure CH_3PF_4 and $C_2H_5PF_4$, previously unreported, are given in Table I. Dimethylaminotetrafluorophosphorane was prepared by the method reported by Demitras, Kent, and MacDiarmid;[6,7] purity was verified by vapor pressure measurements (obsd, 40 mm at 0°; lit.,[8] 40 mm).

Trimethyltin hydride and triethyltin hydride were prepared from lithium aluminum hydride and the respective trialkyltin chloride or bromide.[9,10] Purity was ascertained by comparison of vapor pressures of samples with known values ($(CH_3)_3SnH$:

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