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# CHEMISTRY OF PHOSPHORUS FLUORIDES

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Abstract-Phosphorus tri- and pentafluorides were prepared in high yield and conversion by reaction of the respective chlorides and CaF<sub>2</sub> at 300-400°. The pentafluoride is a very strong acceptor molecule and forms complexes with amines, ethers, nitriles, sulphoxides and other organic bases. The 19F spectra of the complexes are fully consistent with an octahedral model, and the P-F coupling constants, similar to that in  $PF_6^-$ , suggest a relative insensitivity of hybridization to the type of donor molecule. In accord with the strong acceptor properties, the pentafluoride is an excellent catalyst for ionic polymerizations. Especially noteworthy is the PFs-catalysed polymerization of tetrahydrofuran to a very high  $(M_n^- = 280,000)$  molecular weight elastomer. Phosphorus trifluoride, unlike the pentafluoride, exhibits no significant acceptor properties. However, the trifluoride does undergo a curious disproportionation,  $3MF + 5PF_3 \rightarrow 3MPF_6 + 2P$ , that may involve an  $MPF_4$  intermediate.

### Synthesis

We have found that phosphorus fluorides can be prepared in high yield and purity directly from calcium fluoride and the phosphorus chlorides. Calcium fluoride reacts exothermally with PCl<sub>5</sub> at 300-500° to form CaCl<sub>2</sub> and PF<sub>5</sub>. In a sealed reaction vessel (metal) and in a flow system (glass) wherein gaseous  $PCl_5$  was carried in an inert gas, conversions of PCl<sub>5</sub> to PF<sub>5</sub> ranged from 85 to 98 per cent. Purities were estimated to range from 85 to 98 per cent. Principal impurities were POF<sub>3</sub> (and SiF<sub>4</sub> when reaction was effected in glass equipment) and chlorine. Chlorine was readily removed by treatment with sulphur trioxide. Similarly,  $PCl_3$  and  $CaF_2$  gave  $PF_3$  in 77 per cent yield at 350°.

Phosphorus pentafluoride was also prepared in good yield by "chlorofluorination" of  $PF_3$  with  $CaF_2$  and chlorine at 350° in a sealed vessel. This chlorofluorination is probably complex since each of the steps outlined below are either known reactions or were demonstrated in this study:



# Acceptor properties of PF<sub>5</sub>

Phosphorus pentafluoride exhibits the general acceptor properties of the classic Lewis acid, BF<sub>3</sub>. Complexes of PF<sub>5</sub> with such bases as ethers, sulphoxides, amines, amides and esters were prepared, and data for these complexes are listed in Table 1. The PF<sub>5</sub> complexes are much less stable than the analogous BF<sub>3</sub> complexes. For example, unlike the BF<sub>3</sub> amine complexes that can be recrystallized from water, all of the PF<sub>5</sub> complexes are decomposed rapidly by water and by alcohols. The relationship is the reverse to that which pertains in the hydrolytic stability of  $BF_4^-$  and

 $PF_6^-$ . The lower stability of the  $PF_5$  complexes may be due at least partially to steric factors, the importance of which is well established in  $BF_3$  complexes.<sup>(1)</sup> The P<sup>5+</sup> atom is only slightly larger than  $B^{3+}$  and yet must accommodate two more fluorine atoms in its complexes. Direct evidence for a steric factor was found in ether and amine complexes:  $PF_5 O(C_2H_5)_2$  is largely dissociated at 25° whereas  $PF_5 O(CH_2)_4$  can be distilled at 116°/0.15 mm. Two hindered amines, triethylamine and 2,4,6-trimethylpyridine, showed only partial association with PF<sub>5</sub> at 25°.

Evidence for the structure of the PF<sub>5</sub> complexes was obtained from the <sup>19</sup>F magnetic resonance spectra (40 Mc/s) of acetonitrile solutions of the sulphoxide, amine, oxime, amide and thioamide complexes. All of these consisted of two sets of a doublet and quintuplet of relative intensities four and one, respectively; the two sets arise from <sup>31</sup>P-<sup>19</sup>F coupling. The doublet-quintuplet fine structure is the predicted pattern for an octahedral structure in which there are four equivalent, coplanar fluorine atoms and one apical fluorine atom. The <sup>31</sup>P-<sup>19</sup>F coupling constants varied slightly (710-765 c/s) from complex to complex and averaged about 740 c/s, as compared to 710 c/s for  $PF_{6}$ . Since M-F coupling constants appear to reflect<sup>(2,3)</sup> the fractional p character of M–F hybrid bonds (only p electrons are effective in the coupling), the near identity of  $J_{P-F}$  in  $PF_6^-$  and  $PF_5$  base suggests similar hybridization in these fluorides. The F-F coupling constants averaged about 55 c/s.

The doublet-quintuplet fine structure was not observed in the <sup>19</sup>F spectra of PF<sub>5</sub> dissolved in ethers, esters and nitriles; only a doublet was observed at 25°. In the case of  $PF_5 (C_2H_5)_2O$  dissolved in ether, the expected pair of doublets (broadened) but not the pair of quintuplets were resolved at  $-78^{\circ}$ . On warming, the doublets merged into single peaks. Loss of fine structure is attributed to the rapid equilibrium:

$$PF_5 + base \Longrightarrow PF \cdot base$$

that would yield effective equivalence of fluorine atoms and yet preserve <sup>31</sup>P-<sup>19</sup>F coupling, because no P-F bonds are cleaved in this scheme. Such a rapid equilibrium is consistent with the very weak donor properties of the above-cited bases.

In accord with the strong acceptor properties of PF<sub>5</sub>, the fluoride is an outstanding catalyst, particularly in ionic polymerizations. Examples of organic monomers readily polymerized are vinyl ethers and sulphides, isobutylene, styrene, butadiene, dihydropyran and epoxides. Phosphorus pentafluoride, unlike boron trifluoride, is especially effective for the polymerization of tetrahydrofuran. Bulk polymerization of tetrahydrofuran at 30° in the presence of PF<sub>5</sub> yielded very high molecular weight ( $M_n^- =$ 180,000-280,000) elastomeric solids. Phosphorus oxyfluoride is not a catalyst for these polymerizations.

# Acceptor properties of PF<sub>3</sub>

Arsenic and antimony trifluorides have been shown to function as Lewis acids by the formation of  $MAsF_4^{(4.5)}$  and  $MSbF_4^{(6)}$  salts and by formation of molecular complexes<sup>(6,7)</sup> with organic bases. Thus, phosphorus trifluoride was expected to exhibit

<sup>&</sup>lt;sup>(1)</sup> H. C. BROWN and co-workers, cf. H. C. BROWN, J. Chem. Soc. 1248 (1956).

 <sup>(</sup>a) H. S. GUTOWSKY, D. W. MCCALL and C. P. SLICHTER, J. Chem. Phys. 21, 279 (1953).
 (a) E. L. MUETTERTIES and W. D. PHILLIPS, J. Amer. Chem. Soc. 81, 1084 (1959).
 (a) A. A. WOOLF and N. N. GREENWOOD, J. Chem. Soc. 2200 (1950).

<sup>&</sup>lt;sup>(5)</sup> E. L. MUETTERTIES and W. D. PHILLIPS, J. Amer. Chem. Soc. 79, 3686 (1957).
<sup>(6)</sup> H. J. EMELEUS, Fluorine Chemistry Vol. 1, p. 55. Academic Press, New York (1950).
<sup>(7)</sup> A. BESSON, C.R. Acad. Sci., Paris 110, 1258 (1890); E. L. MUETTERTIES. Unpublished work.

acceptor properties although to a lesser degree than the lower members of the Group V trifluorides. However, we could find no evidence for molecular complex formation and only indirect evidence for fluorophosphites.

Fluorophosphites had been previously suggested by several investigators.\* We found that KF and CsF do, in fact, absorb  $PF_3$  at ~150° but the product is not  $MPF_4$ but a mixture of MPF<sub>6</sub> and red phosphorus. Thus, these alkali metal fluorides induce a rather remarkable low temperature disproportionation of PF<sub>3</sub> with formation of the very stable hexafluorophosphate salts the presumed driving force of the reaction:

$$3MF + 5PF_3 \rightarrow 3MPF_6 + 2P$$

This reaction may proceed through an MPF<sub>4</sub> intermediate.<sup>†</sup>

Phosphorus trifluoride is only slowly absorbed by water, a weak base, but it is rapidly absorbed by concentrated aqueous base. This attack by OH- ion may well involve intitial formation of PF<sub>3</sub>OH<sup>-</sup>. However, attempts to detect intermediate fluorophosphites by following the <sup>19</sup>F spectrum (for appearance of a doublet due to  $^{31}P_{-}^{19}F$  coupling) of aqueous KOH solution during PF<sub>3</sub> absorption were unsuccessful; only fluoride ion was detected. Thus, fluorophosphites, if they exist, are hydrolytically unstable as is the tetrafluoroarsenite anion.<sup>(4)</sup>

# Fluorine exchange

Several fluorides, AsF<sub>3</sub>, SbF<sub>3</sub> and SbF<sub>5</sub>, closely related to PF<sub>3</sub> and PF<sub>5</sub> show a marked tendency to undergo fast intermolecular exchange either in the pure state or with covalent fluorides.<sup>(3)</sup> However, we found, from nuclear magnetic resonance studies, that neither PF<sub>3</sub> nor PF<sub>5</sub> undergo fast exchange either in the pure state or in the presence of a number of fluorides that are known to catalyse fluorine exchange. A major distinction between  $PF_5$  and  $SbF_5$  and between  $PF_3$  and  $AsF_3$  or  $SbF_3$  is the degree of molecular association; for example,  $PF_5$  (b.p.  $-80^\circ$ ) is essentially non-associated whereas SbF<sub>5</sub> (b.p. 150°) is highly associated through fluorine bridge bonding. These properties and exchange behaviours are consistent with an earlier observation that there is some correlation between ease of intermolecular fluorine processes and the degree of molecular association in a fluoride.(3,12)

# EXPERIMENTAL

#### Materials and physical methods

Reagent grade calcium fluoride was dried at 300-500° before use. Commercial samples of phosphorus chlorides and chlorine were used directly without purification. The organic bases were purified by standard techniques. Tetrahydrofuran employed in the polymerization studies was refluxed over KOH, then over LiAlH<sub>4</sub> and was finally distilled from LiAlH<sub>4</sub> under an atmosphere of nitrogen immediately prior to use.

The nuclear magnetic resonance spectra were obtained with a Varian high resolution spectrometer and electromagnet at 40 Mc/s and 56.4 Mc/s and fields of ~7,500 and 14,000 gauss, respectively. For the fluorine exchange studies, the fluorides were sealed in quartz capillaries (2 mm i.d.).

\* BERTHELOT<sup>(8)</sup> and MOISSAN<sup>(9)</sup> proposed that fluorophosphites are formed when PF<sub>3</sub> is absorbed by aqueous bases; however, no products were isolated or characterized.  $\dagger$  The fluorides, AsF<sub>3</sub><sup>(4-5)</sup>, IF<sub>5</sub><sup>(10)</sup> and TeF<sub>6</sub><sup>(11)</sup> react exothermally with KF, RbF, and CsF to form MAsF<sub>4</sub>,

MIF, and M<sub>2</sub>TeF<sub>8</sub> salts but none of these fluorides react with sodium fluoride even under forcing conditions. Similarly, we found that PF<sub>3</sub> will not react with sodium fluoride.

<sup>(8)</sup> M. BERTHELOT, C.R. Acad. Sci., Paris 100, 81 (1885).

<sup>(9)</sup> H. MOISSAN, C.R. Acad. Sci., Paris 99, 655 (1884).

(10) H. J. EMELIUS and A. G. SHARPE, J. Chem. Soc. 2206 (1949); E. L. MUETTERTIES. Unpublished work. (11) E. L. MUETTERTIES, J. Amer. Chem. Soc. 79, 1004 (1957).

(12) E. L. MUETTERTIES and W. D. PHILLIPS, J. Amer. Chem. Soc. 79, 322 (1957).

Synthesis of PF<sub>5</sub> and PF<sub>3</sub>

A "Hastelloy C"-lined pressure vessel was heated to 200-300°, evacuated, cooled and then charged with 80 g CaF<sub>4</sub> and 50 g PCl<sub>5</sub>. The vessel was heated to 400° for 3 hr and then cooled. Volatile product was distilled directly into a cooled  $(-78^\circ)$  stainless steel cylinder. Molecular weights derived from gas density of the crude product ranged from 115 to 121 (theory, 126). Removal of chlorine impurity by treatment of the gas with SO<sub>3</sub> raised the molecular weight values to  $\sim 124$ . The remaining impurities were largely POF<sub>3</sub> and SiF<sub>4</sub>. Mass spectrometric analyses consistently gave low values for  $PF_{5}$  content due to hydrolysis within the spectrometer. Analytical determination of phosphorus and fluorine indicated purities in the 92–98 per cent range. Conversions of  $PCl_{5}$  to crude  $PF_{5}$  in nine seperate runs ranged from 85-98 per cent.

A 64 mm Pyrex tube,  $2\frac{1}{2}$  ft. in length, was packed with 400 g of  $\frac{3}{16}$  in. calcium fluoride pellets in the centre 7 in. section. The reactor system was then baked out in a split furnace at 400° for 12 hr. The entrance to the reactor was connected to a small flask fitted with a nitrogen gas inlet and filled with about 70 g of phosphorus pentachloride. To the exit end of the reactor was connected a cold trap and a gas bubbler. The cold trap was cooled with liquid nitrogen. A slow stream of nitrogen gas was then passed through the reactor while the flask containing the phosphorus pentachloride was heated to sublime the chloride into the reaction zone. The reaction was exothermic and the reaction mass temperature was maintained at about 400° by control of the furnace input and of the rate of flow of phosphorus pentachloride. The gaseous product was collected in a liquid nitrogen trap and, at the completion of the reaction, it was transferred to a stainless steel cylinder. In the course of the reaction the section of the Pyrex tube enclosing the reaction zone was slightly etched due to the reaction:

$$2PF_5 + SiO_2 \rightarrow 2POF_3 + SiF_4$$

In all of the runs, infra-red analysis indicated that the major product (ca. 80-90 per cent) was phosphorus pentafluoride. The only impurities indicated were phosphorus oxyfluoride and silicon tetrafluoride. A summary of four runs using the above procedure is given below:

Amount of PCl <sub>s</sub> sublimed (g)	Yield of crude PF₅(%)	Conversion of PCl <sub>5</sub> to crude PF <sub>5</sub> (%)	Reaction time (hr)
98	68	64	6
65	87	63	1.33
70	98	98	1
100	98	98	1.25

Phosphorus trifluoride was prepared from PCl<sub>3</sub> and CaF<sub>2</sub>. Reaction of PCl<sub>3</sub> (180 g) and excess  $CaF_{a}$  (234 g) in a "Hastelloy C"-lined pressure vessel at 350° for 8 hr yielded ~107 per cent of the theoretical volatile product indicating incomplete reaction. The crude product was roughly separated and the low boiling fraction was distilled. About 89 g (77 per cent yield) of  $PF_3$ , boiling at  $-101^\circ$ , was obtained.

#### Chlorination and chlorofluorination of phosphorus trifluoride

Phosphorus trifluoride (30.2 g) and chlorine (24 g) were distilled into a 500 ml stainless steel cylinder which was cooled with liquid nitrogen. The mixture was then allowed to warm to room temperature over a period of about 30 min while the cylinder was slowly rotated. An exothermic reaction was not detected. In 24 hr, it was apparent that much of the product in the reaction was a solid. The cylinder was allowed to stand for a further period of five days and then was evacuated to about 1 mm pressure. The cylinder was opened and found to contain 47.7 g of a white solid that fumed in air and analysed approximately for a mixture of  $PCl_4 + PF_6^{-(13)}$  (or  $PCl_4 + F^{-*}$ . The <sup>19</sup>F magnetic resonance spectrum of a pyridine solution of this solid consisted of a doublet that was identical to that of PF6- (NH4PF6 solution).<sup>(3)</sup>

\* KOLDITZ<sup>(14)</sup> has reported PCl<sub>4</sub>+F<sup>-</sup> to be a product of the thermal decomposition of PCl<sub>4</sub>+PF<sub>6</sub><sup>-</sup>. <sup>(13)</sup> L. KOLDITZ, Z. Anorg. Chem. 284, 144 (1956). <sup>(14)</sup> L. KOLDITZ, Z. Anorg. Chem. 286, 307 (1956).

					An	alytical da	ta					
Adduct	Carbo	(%) uc	Hydro£	çen (%)	Phospho	rus (%)	Fluorir	1e (%)	Nitroge	sn (%)		
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	m.p.('C)	0.p.(^C)
PF <sub>5</sub> ·(CH <sub>3</sub> ) <sub>3</sub> N	19-47	20-08	4-90	5-09	16.74	16-50	<b>5</b> 1-33	51-69	7-57	7-82	214-215	170 <sup>0-15</sup> mm
PF <sub>5</sub> ·C <sub>5</sub> H <sub>5</sub> N	29·28	29-94	2.46	2-94	15.11	13-62	46.32	46.61	6.83	7-27	179-182	
PF <sub>5</sub> ·(CH <sub>3</sub> ) <sub>2</sub> NCHO	18-01	18.13	3.54	3-69	15.56	15.27	47-72	47-51	7.04	7-31	118-120	50 <1mm
PF <sub>5</sub> ·(CH <sub>3</sub> ) <sub>2</sub> NCHS	16-74	16.88	3.28	3.70	14.40	14-03	1		6.51	6.50	190 d	
PF <sub>5</sub> ·(CH <sub>3</sub> ) <sub>2</sub> CNOH	18-01	18-36	3-54	3-87	15.56	14.99	47-72	46-33			þ	
PF <sub>5</sub> ·(CH <sub>3</sub> ) <sub>2</sub> SO	11.77	13.65	2.96	3.55	14.75	15.14	46-54	45.78	15.71	16.37	q	
									(S)	(S)		
PF <sub>5</sub> ·(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O		Ι		(0-958	:1-00 PF	:(C <sub>2</sub> H <sub>5</sub> ),C	) at 5°)	I	:	:	1	dis.
PF <sub>5</sub> ·(CH <sub>2</sub> ) <sub>4</sub> O	24-25	24-49	4·08	5.62			1	١		1	55	116-118 <sup>0.15mm</sup>
PF <sub>5</sub> ·(CH <sub>2</sub> ) <sub>5</sub> O				_	(~1:1 PF	; (CH <sub>2</sub> ),	O at 25°)	-			45-46	dis.
CH,		·							_			
-<												
PF, 0					(~1:1 PF	' <sub>5</sub> :C,H <sub>10</sub> O	at 25°)					70-80 <sup>85 m ш</sup> (dis.)
										_		

TABLE 1.--PF<sub>5</sub> COMPLEXES

In an attempt to isolate the molecular species  $PF_3Cl_2$ , the above procedure was followed except that immediately after mixing the product was transferred to a low temperature still. Distillation covering the period of 2.5 hr produced the following fractions: (1) 25 weight per cent b.p.  $-40-0^\circ$ , (2) 70 weight per cent b.p.  $0-5^\circ$ , and (3) 5 weight per cent of liquid residue. Fraction (2) corresponded approximately in boiling point to the literature value for  $PF_3Cl_2$  but its boiling point dropped slowly at total reflux suggesting that slow disproportionation was occuring in the still.

The  $PF_s$ -Cl<sub>a</sub> reaction was also examined by following the pressure as a function of time (Table 2, 0.52 mole of each reagent at 25° in a 500 ml stainless steel vessel).

Time (hr)	Pressure (atm)	Non-volatiles weight (%)
0.5	2.9	
1	3.0	<1
2	3.3	-
19	6.1	39
45	7.5	76
65	6.9	79
90	6.6	81
115	6.4	81
140	6.3	82

TABLE 2.—PF3-Cl REACTION

These data may be interpreted in terms of a very fast reaction of  $PF_3$  and  $Cl_2$  to give  $PF_3Cl_2$  followed by two slow reactions, one that leads to a pressure decrease,

$$2PF_{a}Cl_{a}(l) \rightarrow PCl_{a} + PF_{a}(c)$$

and one that gives a pressure increase,

$$2PF_{s}Cl_{s}(l) \rightarrow PCl_{s}(c) + PF_{s}(g)$$

At the end of 140 hr, the volatile fraction was essentially all PF<sub>5</sub>, and the solid, non-volatile product was largely  $PCl_4+PF_6^-$  with small amounts of  $PCl_5$  or  $PCl_4+F^-$ .

A mixture of 81.2 g of PF<sub>8</sub>, 65.5 g of Cl<sub>2</sub> and 123 g of CaF<sub>2</sub> was charged into a 1 l., Hastelloy rocker pressure vessel and heated for 8 hr at  $350^{\circ,(15)}$  The gaseous product weighed 116 g and its density corresponded to an average molecular weight of 115 (theory for PF<sub>5</sub>, 126). Elemental analysis of the gas indicated a halogen-phosphorus ratio of 4.95:1 and a fluorine-chlorine ratio of 19:1. The product was largely phosphorus pentafluoride that contained chlorine impurities.

#### Preparation of PF<sub>5</sub> complexes

The complexes of PF<sub>5</sub> with nitrogen or sulphur organic bases were prepared by passing phosphorus pentafluoride slowly into a solution of the base in toluene. In some cases a precipitate was formed immediately and, in others, concentration of the toluene solution was necessary before a significant amount of crystalline complex separated out. In most instances, the complexes were recrystallized from tetrahydrofuran, dimethoxyethane or acetonitrile. The tetrahydrofuran complex<sup>(10)</sup> was prepared by passing phosphorus pentafluoride into tetrahydrofuran while the reaction mass was maintained at 0°. At about the point at which saturation of the tetrahydrofuran occurred, a solid product was formed. This material was then transferred under nitrogen to a vacuum sublimator whose cold finger was maintained near  $-40^{\circ}$ , and with a vacuum of approximately 0.02 to 0.05 mm, the complex sublimed at about 70°. The analytical data and physical properties for these complexes are listed in Table 1. Some complexes were characterized only by the stoicheiometry of the PF<sub>5</sub>·Sase reaction; there were PF<sub>5</sub>·S(CH<sub>2</sub>)<sub>4</sub>, PF<sub>5</sub>·CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub>, PF<sub>5</sub>·CH<sub>3</sub>CN, and 2PF<sub>5</sub>·N<sub>3</sub>O<sub>4</sub>. Stoicheiometries were determined in a vacuum system by reacting a known volume of PF<sub>5</sub> gas with a weighed

(15) E. L. MUETTERTIES, U.S. Pat. 2810629.

(16) E. L. MUETTERTIES, U.S. Pat. 2748145.

amount of liquid base. The decrease in pressure of the phosphorus pentafluoride (within a known volume of the vacuum system) then gave a rough measure of the stoicheiometry of the reaction.

The ease of protonic attack of all the  $PF_s$  complexes was indicated by the observation that (1) molecular weight determinations in water (cryoscopic) and alcohol (ebulliometric) gave values that were fractions of the theoretical value and (2) the <sup>10</sup>F spectra in water and ethanol did not show the fine structure exhibited in acetonitrile solutions. The complexes were not soluble in benzene but molecular weight determination in acetonitrile (ebulliometric) indicated the complexes were simple molecular species, e.g.  $PF_s$  (CH<sub>3</sub>)<sub>2</sub>NCHS, found, 218, calc., 215;  $PF_s$ ·N(CH<sub>3</sub>)<sub>3</sub>, found, 199, calc., 185; and  $PF_s$ ·(CH<sub>3</sub>)<sub>3</sub>NCHO, found, 182, calc., 199.

Mr. A. L. BIDDLE of this laboratory indexed the PF<sub>5</sub>·C<sub>5</sub>H<sub>5</sub>N complex as tetragonal with the parameters  $a_0 = 13.70$  Å,  $c_0 = 11.58$  Å, c/a = 0.845, and z = 8·

Phosphorus oxyfluoride was found to be, at best, a very weak acceptor molecule. This fluoride gave very little heat of reaction (or solution) with typical organic bases. At  $25^{\circ}$ , the solubility of POF<sub>3</sub> in dimethylformamide and in dimethylsulphoxide is very low (5 per cent or less).

### Reactions of PF<sub>3</sub>

The solubility of PF<sub>3</sub> in organic bases was determined in a vacuum system at ~600 mm PF<sub>3</sub> partial pressure and 25°, and the values obtained for dimethyl sulphoxide, dimethylformamide and pyridine were, respectively, 0.01, 0.03, and 0.05 mole/mole of solvent. The <sup>19</sup>F spectrum of a mixed solution of pyridine and liquid PF<sub>3</sub> gave the characteristic PF<sub>3</sub> spectrum; there was no significant perturbation of the <sup>31</sup>P-<sup>19</sup>F coupling constant. Equimolar amounts of pyridine and PF<sub>3</sub> were heated in a stainless steel-lined pressure vessel for 2 hr and these components were recovered unreacted.

Cesium fluoride in contact with an atmosphere of  $PF_8$  in a vacuum system began to slowly absorb the trifluoride at about 130°. Potassium fluoride behaved similarly. X-ray investigation of the solid products indicated the presence of the corresponding metal hexafluorophosphates. The solid products when dissolved in water and filtered yielded a red-brown, insoluble material that proved by the nature of its combustion and by the odor of the combustion products to be amorphous red phosphorus. The filtrate yielded a precipitate with nitron acetate that analytical data indicated to be nitron hexafluorophosphate. (Found: C, 53.71; H, 3.74. Calc. for  $C_{s0}H_{16}N_4HPF_6$ : C, 52.41 H, 4.03%).

This disproportionation reaction was not driven to completion even in pressure vessels at 250°, presumably because the red phosphorus coated the surface of the unreacted metal fluoride. Sodium fluoride showed no evidence of reaction with the trifluoride in a sealed reactor at temperatures as high as 280° (5 hr reaction period).

#### Polymerization of tetrahydrofuran

Phosphorus pentafluoride or the phosphorus pentafluoride-tetrahydrofuran complex readily initiated the polymerization of tetrahydrofuran at temperatures of 10-30°.(17) Uniform conversions to polymer of 60-70 per cent were obtained over a time range of 1-18 hr but molecular weights were usually at a maximum after a period of 5-7 hr. A typical example of a bulk polymerization is as follows: Tetrahydrofuran (89 g) containing the PF<sub>5</sub>-tetrahydrofuran complex (0.24 g) was maintained at 30° for 6 hr under a nitrogen atmosphere. The viscosity rapidly increased and the material gave no evidence of flow after 1.5 hr. The resultant product was heated in water to destroy the catalyst and was then dissolved in tetrahydrofuran and slowly added to ice water in a Waring Blendor. The polymer separated out as a white, shredded solid (60 per cent conversion, inherent viscosity 3.94). High molecular weight polytetrahydrofuran samples usually showed block melting points greater than 150° and ranged as high as 215°. True crystalline melting points of 40-47°, as indicated by the disappearance of polymer crystallites to give amorphous material, were obtained by use of both the X-ray and polarizing hot-stage microscope methods. If 45° is taken as a representative crystalline melting point and if the empirical relationship,  $T_g = \frac{2}{3} T_{mp} - 90$  (in °C), between the amorphous transition temperature and the crystalline melting point is used, one obtains a calculated value of  $-60^{\circ}$  for the amorphous transition temperature. Natural rubber and neoprene have values of  $-72^{\circ}$  and  $-40^{\circ}$ , respectively. Thus, polytetrahydrofuran would appear to be inherently a rubbery polymer. The very high block melting points, in the range 150-200°, reflect primarily the high melt viscosity of the higher molecular weight polymers.

(17) E. L. MUETTERTIES, U.S. Pat. 2856370.

#### Chemistry of phosphorus fluorides

#### Fluorine exchange

Fast intermolecular exchange processes lead to collapse of fine structure in nuclear magnetic resonance spectra. This criterion was employed to detect exchange in PF<sub>5</sub> and PF<sub>5</sub>. Neither PF<sub>5</sub> nor PF<sub>5</sub> were found to undergo fast (10<sup>8</sup> sec<sup>-1</sup>) intermolecular fluorine exchange in the pure liquid state. In the <sup>19</sup>F spectra, the <sup>31</sup>P-<sup>19</sup>F coupling is not lost in liquid PF<sub>5</sub> or PF<sub>5</sub> up to the critical temperature (estimated  $T_c: \sim 15^\circ$ , PF<sub>5</sub> and  $\sim -15^\circ$ , PF<sub>3</sub>). The coupling is also preserved in the gaseous state at 30° in both fluorides. Retention of <sup>31</sup>P-<sup>19</sup>F coupling was also observed in liquid or gaseous PF<sub>3</sub> when this fluoride was in contact with PF<sub>5</sub> (*l*), AsF<sub>3</sub> (*c*) or (*l*), CsF(*c*), BF<sub>3</sub> (*l*), or SF<sub>4</sub> (*l*). The same was true for PF<sub>5</sub> in contact with PF<sub>3</sub> (*t*), AsF<sub>3</sub> (*c*) or (*l*), CsPF<sub>6</sub> (*c*), BF<sub>5</sub> (*l*), IF<sub>5</sub><sup>\*</sup> (*c*) or (*l*), or SF<sub>4</sub>PF<sub>5</sub> (*c*).

\* Liquid IF<sub>5</sub> (an associated liquid) and liquid PF<sub>5</sub> are not miscible.