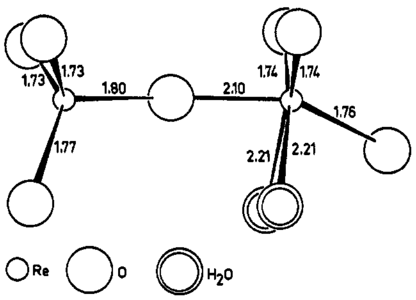

Figure 4.—Configuration and bond distances in ångströms of the primary hydrolysis product of Re_2O_7: dirhenium diaquoheptoxide, $Re_2O_7(OH_2)_2$ ("solid perrhenic acid").[32]

If the dimensions of the molecule, as given in Figure 4, are compared with the bond distances in Re_2O_7, a close resemblance is evident. Of special theoretical interest is the fact that the kind of distortion of the octahedra is analogous in both compounds.

The mechanism of the partial hydrolysis of rhenium(VII) oxide to $Re_2O_7(OH_2)_2$ can be assumed to be similar to the evaporation mechanism. The Re–O bonds which are cleaved hydrolytically are the same which are broken in the process of evaporation: Re(1)–O(1), Re(2)–O(8) plus either Re(1)–O(2), Re(2)–O(9) or Re(1)–O(3), Re(2)–O(10). If Figures 3 and 4 are compared, the structural relationships among Re_2O_7(s), Re_2O_7(g), and $Re_2O_7(OH_2)_2$ can be visualized.

Thermal Vibrations.—The temperature factor coefficients are significantly larger for the tetrahedrally coordinated Re atoms than for those in the octahedra (see Tables I and II). The shortest axes of the vibration ellipsoids for the octahedral Re atoms were found to be along the directions in which the metal atoms are displaced from the centers of the octahedra. These features are physically reasonable, and they are observed almost identically in two crystallographically independent polyhedra. In view of the esd's the parameter differences of Table II are to be regarded as possibly significant. The oxygen atoms O(6), O(7), and O(13), representing terminal atoms in the tetrahedra, show substantially (and possibly significantly) higher temperature factors than the rest.

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The Synthesis of Trifluorophosphazo Compounds

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Trifluorophosphazosulfuryl fluoride, $PF_3{=}NSO_2F$, trifluorophosphazophosphoryl fluoride, $PF_3{=}NP(O)F_2$, and trifluorophosphazothiophosphoryl fluoride, $PF_3{=}NP(S)F_2$, are prepared by the reaction between phosphorus dichloride trifluoride, PF_3Cl_2, and sulfuramidic fluoride, FSO_2NH_2, phosphoramidic difluoride, $F_2P(O)NH_2$, and thiophosphoramidic difluoride, $F_2P(S)NH_2$, respectively. Some properties of these new compounds, including $F_2P(S)NH_2$, have been studied.

Trichlorophosphazophosphoryl difluoride, $PCl_3{=}NP(O)F_2$, and several of its derivatives[1] and trichlorophosphazosulfuryl fluoride, $PCl_3{=}NSO_2F$,[2] have recently been reported. However, attempts to exchange the chlorine atoms bound to the phosphorus with fluorine have been unsuccessful.[2] A method has now been found for the preparation of perfluorinated phosphazosulfuryl and -phosphoryl compounds

$$PF_3Cl_2 + \begin{matrix} FSO_2NH_2 \\ F_2P(E)NH_2 \end{matrix} \longrightarrow \begin{matrix} PF_3{=}NSO_2F \\ PF_3{=}NP(E)F_2 \end{matrix} + 2HCl$$

where E = O or S. Thiophosphoramidic difluoride, a new compound and the precursor to trifluorophosphazothiophosphoryl difluoride, is prepared by ammonolysis of μ-oxo-bis(thiophosphoryl difluoride), $F_2P(S)OP(S)F_2$, in a manner similar to the synthesis of phosphoramidic difluoride from pyrophosphoryl fluoride.

Experimental Section

Reagents.—The amidic compounds FSO_2NH_2[2] and POF_2NH_2[3] were prepared by the literature methods. Established methods were used to synthesize pyrophosphoryl fluoride[4] and μ-oxo-bis(thiophosphoryl difluoride).[5] Lecture bottles of PF_3 and Cl_2 were

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(1) O. Glemser, H. W. Roesky, and P. R. Heinz, *Inorg. Nucl. Chem. Letters*, **4**, 179 (1968).
(2) J. K. Ruff, *Inorg. Chem.*, **6**, 2108 (1967).
(3) S. Kongpricha and C. Preusse, *ibid.*, **6**, 1915 (1967).
(4) E. A. Robinson, *Can. J. Chem.*, **40**, 1725 (1962).
(5) W. E. Hill, to be submitted for publication.

obtained from the Ozark-Mahoning Co. and the Matheson Co., respectively. PF_3Cl_2 was prepared by the direct combination of Cl_2 with a slight excess of PF_3. It was purified by trap to trap distillation, being retained at −126° while the remaining PF_3 passed through.

Technique.—All volatile materials were manipulated within a standard Pyrex vacuum apparatus. In cases when this method was impractical, reagents were handled in the presence of an inert, dry atmosphere.

Synthesis of $PF_3{=}NSO_2F$.—The synthesis was performed by weighing 0.826 g (8.34 mmol) of FSO_2NH_2 into a 50-ml Pyrex reactor equipped with a Fischer-Porter Teflon valve for an inlet. PF_3Cl_2 (8.38 mmol) was distilled into the reactor at −196°. The mixture was allowed to warm slowly to room temperature and stand for 0.5 hr. The volatile products were slowly passed through traps set at −45 and −196°. The former retained 1.22 g of $PF_3{=}NSO_2F$ (6.61 mmol, 80.2% yield) and the −196° trap held 13.3 mmol of HCl and small quantities of PF_5 and POF_3. A nonvolatile oil remained in the reactor.

Synthesis of $PF_3{=}NP(O)F_2$.—This synthesis was achieved in much the same way using $F_2P(O)NH_2$ and PF_3Cl_2 (10.2 mmol each) in the same reactor described above. After an initial contact at −196°, the mixture was warmed slowly to room temperature and then stirred for 15 min. The mixture was distilled. The product (8.6 mmol, 84.3% yield) was found in a trap held at −45°. A trap at −196° retained 20.2 mmol of HCl along with traces of POF_3, PF_5, and POF_2Cl.

Synthesis of $F_2P(S)NH_2$.—Ammonia was slowly bubbled through a stirred solution of 5.56 g (25.5 mmol) of $F_2P(S)OP(S)F_2$ dissolved in 50 ml of anhydrous ether in a 100-ml round-bottom flask held at −20°. After the ammonia was delivered, the mixture was allowed to warm to ambient temperature and stand for 0.5 hr. A nitrogen overpressure was kept over the solution at all times. About half of the ether was stripped away by a rotary evacuator. The remainder of the mixture was fractionated by trap to trap distillation. The product (1.32 g, 11.3 mmol), which contained a trace of ether, was collected at −45°. Further purification was achieved by passage through a Dow-11 silicone on Chromosorb W chromatograph column at 100°. The solid resisdue which remained in the reactor was identified as NH_4^+-$POSF_2^-$ by its infrared spectrum as well as its ^{19}F and ^{31}P nmr spectra.

Synthesis of $PF_3{=}NP(S)F_2$.—The reactants $F_2P(S)NH_2$ and PF_3Cl_2 (2.02 mmol) each were charged into the reactor and allowed to react in the same manner as in the $PF_3{=}NP(O)F_2$ synthesis. The products were passed through traps at −45, −80, and −196°. $F_3P{=}NP(S)F_2$ (0.92 mmol, 46% recovery) was found in the −80° trap while HCl (3.55 mmol) and a small quantity of POF_3 were retained in the −196° trap. The −45° trap held a small amount of $F_2P(S)NH_2$.

Analytical Data.—Hydrogen and nitrogen was determined by combustion using an F & M Model 185 analyzer. For phosphorus, the compounds were burned in an oxygen flask. The residue was absorbed in 6 *N* HNO_3 and the phosphate was determined spectrophotometrically as the phosphovandomolybdate.[6] Fluorine was analyzed by reduction of the compounds with lithium in *n*-propylamine followed by distillation of the fluoride as H_2SiF_6 and titration with thorium nitrate. *Anal.* Calcd for $PF_3{=}NSO_2F$: F, 41.06; N, 7.57; P, 16.74. Found: F, 40.9; N, 7.52; P, 16.2. Calcd for $PF_3{=}NP(O)F_2$: F, 50.80; N, 7.48; P, 33.15. Found: F, 50.9; N, 7.57; P, 32.5. Calcd for $PF_3{=}NP(S)F_2$: F, 46.80; N, 6.90; P, 30.54. Found: F, 46.3; N, 6.18; P, 30.2. Calcd for $PF_2(S)NH_2$: F, 32.48; N, 11.97. Found: F, 31.8; N, 11.6.

Infrared Spectra.—These spectra were taken in the NaCl region with a Perkin-Elmer Infracord spectrometer using a 10-cm path length gas cell. Spectra were recorded at pressures up to 20 mm. The absorption frequencies and assignments are given in the Discussion.

Nmr Spectra.—The ^{19}F and ^1H spectra were taken with a Varian Model V4310 spectrometer operating at 40 Mc. The ^{31}P spectra were obtained at 12.8 Mc. Samples were measured at room temperature in 5-mm o.d. Pyrex tubes using CCl_3F as an internal fluorine standard and tetramethylsilane and H_3PO_4 as external hydrogen and phosphorus standards, respectively. The results are discussed below.

Mass Spectra.—A Consolidated Engineering Corp. Model 61-620 spectrometer with a heated inlet system and operating at 100 eV was used. Generally unreliable cracking data were obtained except for the compounds $PF_3{=}NP(O)F_2$ and $PF_3{=}NP(S)F_2$. For these cases the results are tabulated as follows as mass number (species) and relative abundance, respectively; the molecular ions are assigned a relative intensity equal to 100.0%: $PF_3{=}NP(O)F_2$: 31 (P^+), 13.4; 45 (PN^+), 4.0; 47 (PO^+), 11.8; 50 (PF^+), 14.8; 64 (FPN^+), 9.3; 69 (PF_2^+), 94.8; 83 (F_2PN^+), 28.6; 85 (POF_2^+), 150.0; 88 (PF_2^+), 12.0; 102 (F_3PN^+), 12.8; 104 (POF_3^+), 171.0; 107 (PF_4^+), 8.0; 152 ($P_2F_4N^+$), 4.0; 168 ($P_2F_4NO^+$), 61.0; 187 (p^+),[7] 100.0. $PF_3{=}NP(S)F_2$: 14 (N^+), 2.2; 31 (P^+), 7.6; 32 (S^+), 16.5; 46 (SN^+), 21.8; 50 (PF^+), 5.8; 63 (PS^+), 3.1; 69 (PF_2^+), 79.1; 82 (FPS^+), 8.6; 88 (PF_2^+), 7.8; 96 ($FPSN^+$), 5.8; 101 (F_2PS^+), 7.4; 107 (PF_4^+), 14.3; 115 (F_2PSN^+), 32.6; 120 (PSF_3^+), 4.7; 133 ($P_2F_3N^+$), 9.4; 152 ($P_2F_3N^+$), 37.2; 171 ($P_2F_5N^+$), 11.7; 184 ($P_2F_4NS^+$), 9.5; 203 (p^+), 100.00; 205 (i^+),[7] 4.4.

Molecular Weights.—The molecular weights of 182 for $PF_3{=}NSO_2F$ (calcd 185.0), 187.8 for $PF_3{=}NP(O)F_2$ (calcd 187.0), 201.8 for $PF_3{=}NP(S)F_2$ (calcd 203.1), and 114.2 for $F_2P(S)NH_2$ (calcd 117.1) were obtained by vapor density measurements using a 208.2-ml Pyrex bulb. A value of 200 for $PF_3{=}NP(S)F_2$ was also obtained by effusiometry[8] using the spectrometer using mass 203 as the reference peak.

Vapor Pressure Measurements.—These measurements were performed by a literature method.[9] Cathetometers were employed for measuring the pressure indicated by a mercury manometer and for observing the null point of the spoon gauge. All vapor pressures listed below for $PF_3{=}NP(S)F_2$ are precise to within 0.2 mm. The temperatures were measured with a potentiometer using a copper-constantan thermocouple. The accuracy of these measurements is ±0.1°. The sample temperature was regulated by a water bath. Some observed pressures for $PF_3{=}NP(S)F_2$ are: −33.7°, 22.1 mm; −18.4°, 38.1 mm; −2.7°, 59.4 mm; 17.0°, 94.2 mm; 24.7°, 122.4 mm. Over this temperature range the data obey the equation: $\log P = -(944/T) + 5.27$. The vapor pressure of $PF_3{=}NSO_2F$ at 24.5° is 11.5 mm; that of $PF_3{=}NP(O)F_2$ at 26.0° is *ca.* 39 mm, while that of $F_2P(S)NH_2$ at 23.5° is 9.6 mm.

Melting Points.—Melting points were observed visually by immersing the samples, contained in 5-mm o.d. Pyrex tubes, in alcohol cold baths. The baths were held in a dewar flask with an unsilvered strip, and the rate of warming was *ca.* 0.25°/min. Temperature measurements were taken with the apparatus described above. The results are: $PF_3{=}NSO_2F$, −26.0 ± 0.5°; $PF_3N{=}P(O)F_2$, 5.2 ± 0.9; $PF_3{=}NP(S)\ F_2$, −49.5 ± 1.5°; $PF_2(S)NH_2$, −80.6 ± 0.7°.

Results and Discussion

The compounds $PF_3{=}NSO_2F$, $PF_3{=}NP(O)F_2$, and $PF_3{=}NP(S)F_2$ represent a new class containing the $PF_3{=}N-$ moiety and are prepared in generally high yields by the reaction between PF_3Cl_2 and the corresponding amidic compounds. These are colorless

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[6] I. M. Kolthoff, P. J. Elving, and E. B. Sandell, "Treatise on Analytical Chemistry," Part II, Vol. 5, Interscience Publishers, Inc., New York, N. Y., 1961, p 370.

[7] p and i are symbols for the molecule ion and the ^{34}S isotope, respectively.

[8] (a) M. Eden, B. E. Burr, and A. W. Pratt, *Anal. Chem.*, **23**, 1735 (1951); (b) P. D. Zemany, *J. Appl. Phys.*, **23**, 924 (1952).

[9] S. G. Foord, *J. Sci. Instr.*, **11**, 126 (1934).

liquids. The first two decompose slowly at ambient temperature, and, consequently, completely reliable characterization data were difficult to obtain. The decomposition products were oils indicating polymerization, but the oils were not analyzed. The low volatility of both liquid $PF_3{=}NSO_2F$ and $PF_3{=}NP(O)F_2$ compared to that of $PF_3{=}NP(S)F_2$ indicates that the sulfuryl and the phosphoryl compounds may be associated in the liquid state, although vapor density measurements suggest that all are monomeric in the gaseous state. Thiophosphoramidic difluoride is also a colorless liquid.

The infrared spectra show characteristic absorption bands. For example, the spectrum of $PF_3{=}NSO_2F$ exhibits a strong and broad band at 1357 cm^{-1} assigned to the P=N stretching frequency.[10] The S=O asymmetric and symmetric stretching frequency absorption bands are at 1434 (vs) and 1220 (vs) cm^{-1}.[11] The band attributed to the PF_3 group P—F stretching motion is at 1015 (vvs) cm^{-1} and that at 818 (vs) cm^{-1} is assigned to the S–F stretching frequence. Another unassigned absorption band is at 735 (ms) cm^{-1}. The spectra of both $PF_3{=}NP(O)F_2$ and $PF_3{=}NP(S)F_2$ show bands at 1439 and 1412 cm^{-1} (vs, broad and complex), respectively, assigned to the P=N stretching vibrations while the band at 1353 (s) cm^{-1} is presumably due to the P=O stretching frequency in the former. The PF_3 group P—F stretching motion is attributed to that at 1010 (vvs) cm^{-1} in the spectrum of $PF_3{=}NP(O)F_2$ and to that at 1005 (vvs) cm^{-1} in the spectrum of the corresponding thio derivative. The P—F stretching motions of the phosphoryl and thiophosphoryl groups are probably due to the bands lying at the lower frequencies, *i.e.*, at 962 (ms) and 885 (vvs) cm^{-1} in the former spectrum and at 928 (ms) cm^{-1} with a shoulder at 908 cm^{-1} in the latter. Derivatives having the $-OP(O)F_2$ and the $-OP(S)F_2$ groups have two bands in the same general regions.[12] Because infrared spectra were not measured below 670 cm^{-1}, an assignment for the P=S frequency cannot be given, although a strong band is observed at 775 cm^{-1} in the spectrum of $PF_3{=}NP(S)F_2$. A broad, medium-intensity, unassigned absorption is observed at 720 cm^{-1} in the spectrum of $PF_3{=}NP(O)F_2$. The spectrum of $F_2P(S)NH_2$ is also characteristic. Absorption bands are observed at 3584 (mw) and 3460 (mw) cm^{-1}, assigned to the asymmetric and symmetric N—H stretching frequencies; at 1541 (m) cm^{-1}, N—H deformation;[10] at 1003 (vs, PQR), 962 (s, complex), and 889 (vs) cm^{-1}, P—N and P—F stretchings; and at 670 (mw) cm^{-1}, P=S stretch. A typical spectrum, that of $PF_3{=}NP(S)F_2$, is shown in Figure 1. No other bands for the above compounds were observed in the NaCl region.

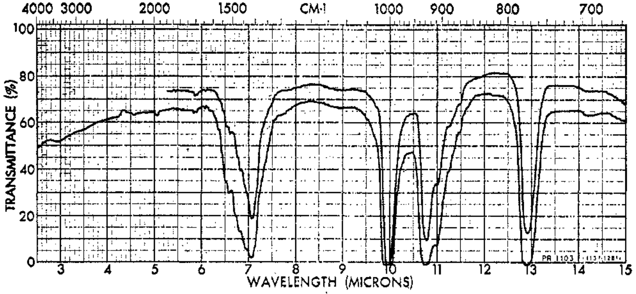

Figure 1.—Infrared spectrum of $PF_3{=}NP(S)F_2$ at 10 and 4 mm.

The nmr spectra of these compounds are diagnostic. The ^{19}F spectrum of $F_3P{=}NSO_2F$ exhibits a doublet (J_{PNSF} = 16 cps) of quadruplets (J_{FPNSF} = 4 cps) centered at ϕ 60.9 due to the fluorine bound to the sulfur atom and a doublet (J_{PF} = 1090 cps) of doublets (J_{FPNSF} = 4 cps) centered at ϕ 86.7 due to the three identical fluorines attached to the phosphorus atom. The area ratio of the low-field resonance to that at high field is very close to 1:3. Reliable spectra of $PF_3{=}NP(O)F_2$ could not be obtained owing to decomposition of samples within the nmr tubes. The fluorine spectrum of $PF_3{=}NP(S)F_2$ contains two sets of doublets, one centered at ϕ 38.0 (J = 1112 cps) assigned to the $P(S)F_2$ fluorine nuclear absorptions and the other at ϕ 85.2 (J = 1045 cps) due to the PF_3 group fluorine. The members of both doublets are split further in a complicated but symmetric fashion, but the resolution does not permit interpretation of the complex splitting. Last, the spectrum of $F_2P(S)NH_2$ has a doublet centered at ϕ 42.7 (J = 1078 cps). The ^{31}P spectrum of this compound shows a triplet at −847 cps (J = 1090 cps) while the proton trace indicates a broad resonance at −177 cps. FPNH and PNH coupling could not be observed.

Efforts were made to obtain mass spectra of these compounds, but only $PF_3{=}NP(O)F_2$ and $PF_3{=}NP(S)F_2$ survived without detectable decomposition in the inlet system. Both show some similar fragments although the intensities of these ions vary considerably by comparison. High-intensity molecule ions are observed in both cases. Absorptions due to the molecule ion less a fluorine atom are also present. The ions, $P(E)F_3^+$ (along with fragments of this species) and PF_4^+ are detected. The ion SN^+, presumably due to a rearrangement reaction, is found in the spectrum of $PF_3{=}NP(S)F_2$. All the other ions present are the expected fragments of these compounds.

In conclusion the spectral and elementary analyses support the proposed structures for the trifluorophosphazo compounds as well as that given for $F_2P(S)NH_2$.

Acknowledgment.—The author thanks Mr. Joseph E. West at Rohm and Haas Co., Redstone Research Laboratories, for obtaining the nmr spectra.

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(11) M. Lustig, C. L. Bumgardner, F. A. Johnson, and J. K. Ruff, *Inorg. Chem.*, **3**, 1165 (1964).

(12) M. Lustig, *ibid.*, **7**, 2054 (1968).