Since PF_3 and CO have been clearly demonstrated to be so similar,[7] it is quite reasonable to assume that the three carbonyl groups in $C_4H_6Fe(CO)_3$ are also undergoing a comparable motion. A similar situation could also occur in $C_4H_6Fe(CO)_2(PF_3)$, but with this species, the two configurations which place PF_3 in the equivalent positions would have sufficiently high energies so that their equilibrium concentration would be too low to be detected.

The fluxional nature of the $C_4H_6Fe(CO)_x(PF_3)_{3-x}$ species was quite unexpected. Detecting this fluxional nature in the tricarbonyl would be difficult, but it becomes quite simple with the phosphorus trifluoride substituents. The phosphorus trifluoride ligand behaves as an excellent handle for CO in most situations.

From the published ^{13}CO nmr work on $C_4H_6Fe(CO)_3$,[17] it would be difficult to reach any conclusion relative to a fluxional nature of the compound.

Finally, if the model of a rotation of a group of three roughly orthogonal ligands is a generally correct mechanism for the internal motion in butadieneiron tricarbonyl, it seems quite likely that the same mechanism might be exhibited in other related species. The Berry model[18] has been assumed to be responsible for the stereochemical nonrigidity in trigonal-bipyramidal five-coordinate species. However, it also is reasonable to suppose that the rotation of a group of ligands located on two equatorial sites and an axial site could undergo a motion similar to that in the butadiene complex. We have tentative evidence that two different mechanisms of stereochemical nonrigidity are operative in the higher $CF_3Co(CO)_x(PF_3)_{4-x}$ species.[19]

It is felt that this mechanism requires a coordination number below 6 in order to be operative. A related mechanism for nondissociative exchange has been postulated for the six-coordinate octahedral species.[20] However, in compounds like $Mo(CO)_x(PF_3)_{6-x}$[21] and $R_fMn(CO)_x(PF_3)_{5-x}$,[22] there is no sign of isomerization among the species. In these, there may not be adequate room for the rotation to occur.

A referee has pointed out that there may be an analogy between the isomerization discussed by Nesmeyanov[23] in an allyl compound and that shown here. A rotation of the plane of the butadiene followed by a tilting of that plane is effectively the same motion that we have discussed, but approached from the other end of the molecule. It should be made clear, however, that there are no signs of nonequivalent rotation isomers for these butadiene complexes of the type found by Nesmeyanov.[23]

Acknowledgment.—J. D. W. wishes to thank the National Science Foundation for assistance in the form of an NSF traineeship. We also wish to thank the Atomic Energy Commission for financial assistance.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF ALBERTA, EDMONTON, ALBERTA, CANADA

Preparation and Properties of Some Oxygen-, Sulfur-, and Nitrogen-Bridged Phosphoryl and Thiophosphoryl Difluorides

BY T. L. CHARLTON AND R. G. CAVELL

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The preparation and characterization of $(SPF_2)_2O$, $(SPF_2)_2S$, $(OPF_2)O(SPF_2)$, $(OPF_2)_2NCH_3$, $(SPF_2)_2NCH_3$, and the trimethylamine adducts $(OPF_2)_2NH\cdot(CH_3)_3N$ and $(SPF_2)_2NH\cdot(CH_3)_3N$ are described. Results of mass and infrared spectral studies are given. Reactions of the trimethylamine adducts with hydrogen chloride result in cleavage of the P–N bonds rather than liberation of the N–H compounds. The N–H compounds are observed, however, in the mass spectrometer.

Introduction

Many diphosphorus compounds are known in which the phosphorus atoms are linked by a difunctional bridging unit such as oxygen, sulfur, or monosubstituted nitrogen.[1–6] The only known pentavalent fluorophosphorus compounds of this type however are difluorophosphoric acid anhydride,[7,8] the analogous chlorofluoro compound,[9] and μ-oxo-bis(difluorophosphine).[10] Re-

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cently, mention has been made of the double-sulfur-bridged compound $(F_2PS_2)_2$ but no details have as yet appeared.[11]

We now wish to report the synthesis and properties of a number of sulfur-, oxygen-, and monosubstituted-nitrogen-bridged phosphoryl and thiophosphoryl difluorides, one of which has recently been reported elsewhere.[12]

Experimental Section

Standard vacuum techniques using Pyrex-glass apparatus were employed throughout. Stopcocks were lubricated with Apiezon "N" grease. Gas-phase infrared spectra were obtained with a Perkin-Elmer 421 dual-grating instrument over the range 4000–300 cm^{-1}. The cell windows (KBr) were coated with a very thin film of paraffin wax for the determination of the spectrum of the reactive $(OPF_2)_2O$. Raman spectra were obtained with a Perkin-Elmer LR1 instrument using a microcell of our own design, mass spectra with an AEI MS-9 double-focusing mass spectrometer, and nmr spectra with Varian A56/60 or HA100 instruments. Proton spectra were measured at 60 MHz with chemical shifts given relative to tetramethylsilane. Fluorine spectra were measured at 94.0 or 56.4 MHz with chemical shifts given relative to $CFCl_3$. Vapor pressures were measured with a glass spiral microtensimeter[13] using the null-point technique with both ascending and descending temperatures.

Materials.—Iodothiophosphoryl difluoride,[14] difluorodithiophosphoric acid,[15] and difluorophosphoric acid anhydride[8] were prepared as previously described. Dimethylaminophosphoryl and thiophosphoryl difluorides were prepared by aminolysis of $OPCl_3$ or $SPCl_3$ followed by fluorination with antimony trifluoride.[16] Methylamino- and aminophosphoryl and -thiophosphoryl difluorides were prepared as described elsewhere.[17] Difluorophosphoric acid (Columbia Chemical Co.) was fractionated under vacuum before use. Chlorophosphoryl and chlorothiophosphoryl difluorides were prepared by partial fluorination of phosphoryl or thiophosphoryl trichlorides with antimony trifluoride followed by vacuum fractionation. All other chemicals wre reagent grade and were used without purification.

Preparation of μ-Oxo-bis(thiophosphoryl difluoride), $(SPF_2)_2O$. (a) **From Iodothiophosphoryl Difluoride and Oxygen.**—Iodothiophosphoryl difluoride (0.22 g, 0.98 mmol) was condensed in a 75-cm reaction tube which was then filled with excess oxygen (as air, from which all material condensable at −196° had been removed). Fractionation of the volatile products after 2 weeks at 70° gave $(SPF_2)_2O$ (0.07 g, 0.33 mmol) condensing at −95°, traces of OPF_3 condensing at −196°, and unreacted SPF_2I (0.05 g, 0.23 mmol) condensing at −81°. Molecular iodine was collected in the least volatile fraction. Separation of $(SPF_2)_2O$ from traces of SPF_2I under vacuum was very difficult and very pure samples of $(SPF_2)_2O$ were obtained only after repeated distillation from a LeRoy still.[18] The yield of $(SPF_2)_2O$ was 88% based on SPF_2I consumed. Higher reaction temperatures and longer reaction times gave more complete consumption of SPF_2I at the expense, however, of more pronounced decomposition of the desired product.

(b) **From Difluorodithiophosphoric Acid and Dimethylaminophosphoryl Difluoride.**—Difluorodithiophosphoric acid (0.13 g, 0.97 mmol) and dimethylaminophosphoryl difluoride (0.07 g, 0.57 mmol) were sealed in a 25-cm^3 reaction tube. After 4 days at room temperature, fractionation of volatile products gave only $(SPF_2)_2O$ (0.10 g, 0.48 mmol) in 99% yield. A yellow crystalline solid remained in the reaction vessel.

Table I

Mass Measurement of Parent Ions

Ion	m/e Obsd	m/e Calcd[a]
$(SPF_2)_2O$	217.8803	217.8802
$(SPF_2)O(OPF_2)$	201.9031	201.9031
$(SPF_2)_2S$	233.8572	233.8575
$(OPF_2)_2NH$[b]	184.9421	184.9419
$(SPF_2)_2NH$[b]	216.8971	216.8973
$(OPF_2)_2NCH_2$	197.9495	197.9492
$(SPF_2)_2NCH_3$	230.9118	230.9120

[a] m/e values calculated for ions involving sulfur are calculated for the ^{32}S isotope. [b] This ion was observed as the ion with the greatest m/e in the spectrum of the trimethylammonium adduct introduced *via* the direct probe.

(c) **From Difluorophosphoric Acid and Dimethylaminothiophosphoryl Difluoride.**—Difluorophosphoric acid (0.41 g, 4.05 mmol) and dimethylaminothiophosphoryl difluoride (0.33 g, 2.88 mmol) were combined in a 25-cm^3 reaction tube and heated to 70° for 1 hr. Fractionation of the volatile products gave OPF_3 (0.077 g, 0.74 mmol), the thiophosphoryl anhydride, $(SPF_2)_2O$ (0.186 g, 0.85 mmol), and a mixture of dimethylaminothiophosphoryl and -phosphoryl difluorides (0.09 g). A clear, colorless, nonvolatile liquid residue remained in the reaction vessel.

The compound μ-oxo-bis(thiophosphoryl difluoride) is a colorless, volatile liquid which has been kept in sealed glass tubes for several months at normal temperatures without decomposition. It was characterized by vapor density molecular weight (calcd for $(SPF_2)_2O$, 217.9; found, 216.8) and mass spectroscopy, including accurate mass measurement of the parent ion (see Table I). Vapor pressure data, given in Table II, obey the equation

$$\log P_{\mathrm{mm}} = 7.734 - (1566/T) \qquad (1)$$

from which an extrapolated boiling point of 49.5°, a heat of vaporization of 7166 cal/mol, and a Trouton constant of 22.2 eu are obtained.

Preparation of μ-Thio-bis(thiophosphoryl difluoride), $(SPF_2)_2S$.—The reaction of dimethylaminothiophosphoryl difluoride with an excess of difluorodithiophosphoric acid at 70° in a sealed tube as described above (b) proved to be the most effective synthetic route to μ-thio-bis(thiophosphoryl difluoride). The crude product was effectively removed from the excess SPF_2SH by a −63° trap. A light yellow solid, presumably $(CH_3)_2NH_2^+S_2PF_2^-$ according to ^1H and ^{19}F nmr spectra, remained in the reaction vessel. Even large excess concentrations of acid and several days of reaction did not result in complete consumption of the $SPF_2N(CH_3)_2$ which condenses along with the desired product in crude vacuum fractionation. Repeated distillation from the LeRoy still gave pure samples of $(SPF_2)_2S$.

The compound μ-thio-bis(thiophosphoryl difluoride) is a colorless, volatile liquid. It appears to be quite stable at room temperatures and samples have been stored for several months in sealed glass tubes without apparent change. It was characterized by vapor density molecular weight (calcd for $(SPF_2)_2S$, 233.9; found, 235.6) and mass spectroscopy, including accurate mass measurement of the parent ion (see Table I). Vapor pressure data, given in Table II, obey the equation

$$\log P_{\mathrm{mm}} = 7.808 - (1930/T) \qquad (2)$$

which yields an extrapolated boiling point of 118.4°, a heat of vaporization of 8830 cal/mol, and a Trouton constant of 22.5 eu.

The Preparation of Difluorophosphoryl-μ-oxo-thiophosphoryl

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TABLE II
VAPOR PRESSURE DATA

				$(SPF_2)_2O$				
Temp, °C	−38.3	−37.8[a]	−33.6[a]	−28.2	−22.4[a]	−17.7	−13.6[a]	
Pressure, mm								
Obsd	11.2	12.1	15.4	22.3	31.2	41.4	51.0	
Calcd[b]	11.7	12.1	15.8	22.0	30.9	40.3	50.4	
Temp, °C	−7.8	−3.6[a]	2.5	7.4[a]	12.6	18.0[a]	23.9	
Pressure, mm								
Obsd	70.1	86.8	115.2	142.8	179.7	220.5	280.9	
Calcd[b]	68.2	84.3	113.3	142.4	179.9	227.5	290.7	
				$(SPF_2)_2S$				
Temp, °C	0.0	7.9[a]	11.1	16.2[a]	20.1	25.4[a]	30.2	35.5[a]
Pressure, mm								
Obsd	5.7	8.9	10.5	13.8	16.9	20.7	27.3	37.0
Calcd[c]	5.6	8.8	10.5	13.8	16.9	22.2	28.0	36.1
Temp, °C	40.8	45.4[a]	51.8					
Pressure, mm								
Obsd	46.2	57.8	75.2					
Calcd[c]	46.0	56.4	74.3					
				$(SPF_2)_2NCH_3$				
Temp, °C	0.0	7.1[a]	12.1	17.3[a]	20.7	25.9[a]	30.1	35.7[a]
Pressure, mm								
Obsd	2.6	4.7	5.7	8.3	9.3	14.3	15.6	20.5
Calcd[d]	2.8	4.4	5.9	8.0	9.6	12.7	15.9	21.1
Temp, °C	40.2	44.7[a]	51.6					
Pressure, mm								
Obsd	26.1	31.4	44.8					
Calcd[d]	26.3	32.6	44.8					

[a] Pressures measured while cooling sample from maximum temperature attained. [b] Pressures calculated from eq 1. [c] Pressures calculated from eq 2. [d] Pressures calculated from eq 3.

Difluoride.—Hydrothiophosphoryl difluoride[19] (0.622 g, 6.08 mmol) and $(OPF_2)_2O$ (1.30 g, 6.97 mmol) were sealed in a 25-cm^3 reaction tube and heated to 70° for 7 days. Fractionation of the volatile products gave a mixture of OPF_3 and PF_3 (0.205 g) collected at −196°, SPF_2H (0.248 g, 2.43 mmol) collected at −116°, $(OPF_2)_2O$ (0.62 g, 3.34 mmol) collected at −65°, OPF_2OH (0.282 g, 2.74 mmol) collected at −81°, and $(SPF_2)O(OPF_2)$ (0.391 g, 1.93 mmol) collected at −95°. A quantity of light yellow solid residue remained in the reaction vessel.

A reaction of SPF_2SH with $(OPF_2)_2O$ carried out in a manner similar to the above also gave $(SPF_2)O(OPF_2)$ but the resulting mixture of compounds was too difficult to separate.

TABLE III
PREPARATION OF AMINO-BRIDGED BIS(PHOSPHORYL AND THIOPHOSPHORYL DIFLUORIDES)

Compd	$EPF_2N(H)R$ taken, mmol	EPF_2Cl taken, mmol	$(CH_3)_3N$ taken, mmol	Yield of compd, mmol (%)	Other products
$(SPF_2)_2NCH_3$	2.24	2.46	2.58	2.01 (89.6)	SPF_3–SPF_2Cl–$(CH_3)_3N$ mixture (0.06 g)
$(OPF_2)_2NCH_3$	4.97	5.19	5.11	3.59 (72.2)	OPF_2Cl–OPF_3–$(CH_3)_3N$ mixture (0.19 g)
$(SPF_2)_2NH(CH_3)_3N$	4.38	5.0	4.78	...	SPF_2Cl (2.86 mmol)–SPF_2NH_2 (1.56 mmol) mixture

The mixed oxy–thio compound $(SPF_2)O(OPF_2)$ was characterized by its infrared, mass, and nmr spectra. The ^{19}F nmr spectrum showed two distinct chemical shift regions: one at ϕ 41.0 ppm ($^1J_{PF}$ = 1177.1, $^3J_{PF}$ = 3.5, and $^4J_{FF}$ = 2.7 Hz) associated with the thiophosphoryl difluoride group and one at ϕ 79.4 ppm ($^1J_{PF}$ = 1057.2, $^3J_{PF} \leq 0.5$, $^4J_{FF}$ = 2.7 Hz) associated with the difluorophosphoryl group. Although the mass spectral cracking pattern could not be obtained because of the lack of purity of the sample, accurate mass measurement of the parent ion confirmed the presence of a compound with the formula $SP_2O_2F_4$ (Table I).

Preparation and Characterization of N-Methylbis(difluorophosphoryl)- and N-Methylbis(difluorothiophosphoryl)amine.—Equimolar ratios of methylaminophosphoryl or -thiophosphoryl difluoride, phosphoryl or thiophosphoryl chlorodifluoride, and trimethylamine were condensed into a 50-cm^3 reaction tube equipped with a stopcock. Reaction (no reaction was observed in the absence of trimethylamine) occurred immediately on warming the contents of the tube to room temperature. The desired products were trapped at −45°. Quantities and yields are given in Table III. The compounds are colorless, moderately volatile liquids which are stable at ordinary temperatures. They were characterized by mass spectroscopy including accurate mass measurement of the parent ion (Table I). Analysis of the sulfur compound confirmed the formula $(SPF_2)_2NCH_3$. *Anal.* Calcd for $CH_3F_4NP_2S_2$: H, 1.30; N, 6.06; F, 32.9. Found: H, 1.59; N, 6.30; F, 32.0 (P:S = 1.0:0.98). Vapor pressure data for $(SPF_2)_2NCH_3$ (given in Table II) obey the equation

$$\log P_{\text{mm}} = 8.009 - (2065/T) \qquad (3)$$

which gives an extrapolated boiling point of 129.5°, a heat of vaporization of 9449 cal/mol, and a Trouton constant of 23.5 eu. The oxygen analog was insufficiently volatile for convenient vapor pressure study.

Preparation and Characterization of the Trimethylammonium Adducts of Bis(difluorophosphoryl)- and Bis(difluorothiophosphoryl)amide.—Equimolar proportions of aminophosphoryl or -thiophosphoryl difluoride, phosphoryl or thiophosphoryl chlorodifluoride, and a twofold molar quantity of trimethylamine were

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

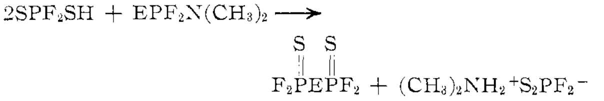
condensed into a 50-cm^3 reaction vessel. Reaction occurred immediately on warming to room temperature to form solid and liquid products. The adducts were obtained as nonvolatile oils by subliming trimethylammonium chloride out of the reaction products. No reaction was observed in the absence of trimethylamine. The use of a unimolar ratio led to incomplete consumption of the aminophosphorus and chlorophosphorus compounds which were then recovered by fractionation. Quantities are given in Table III. Mass spectroscopic analysis of the nonvolatile oils gave parent ions corresponding to $(EPF_2)_2NH$ (E = S, O), the accurate masses of which are given in Table I.

Reaction of $(SPF_2)_2NCH_3$ with HCl.—$(SPF_2)_2NCH_3$ (0.096 g, 0.42 mmol) and HCl (0.176 g, 0.48 mmol) were sealed in a 10-cm^3 reaction tube. When no reaction was observed after several hours at room temperature or at 70° the reaction tube was heated to 150° for 16 hr. The volatile products were then fractionated to give $(SPF_2)_2NCH_3$ (0.062 g, 0.27 mmol) which condensed at −65° and a mixture of HCl and SPF_2Cl which condensed at −196° (0.02 g). A solid white residue and traces of an involatile, colorless liquid remained in the reaction tube.

Reaction of $(SPF_2)_2NH\cdot N(CH_3)_3$ with HCl.—$(SPF_2)_2NH\cdot N(CH_3)_3$ (0.279 g, 1.01 mmol) and HCl (0.033 g, 0.90 mmol) were sealed in a 10-cm^3 reaction tube. When no apparent reaction occurred at room temperatures, the mixture was heated to 150° for 16 hr. Fractionation of the volatile products gave mainly SPF_3 with a trace of SPF_2Cl. A colorless liquid residue which remained in the tube was identified as unchanged $(SPF_2)_2NH\cdot N(CH_3)_3$.

Results and Discussion

A. Sulfur- and Oxygen-Bridged Compounds.—The reaction of difluorodithiophosphoric acid with either dimethylaminophosphoryl or -thiophosphoryl difluoride was the most convenient generalsyn thetic route to two bridged thiophosphoryl difluorides. The reactions follow the equation



$$2SPF_2SH + EPF_2N(CH_3)_2 \longrightarrow F_2\overset{S}{\overset{\|}{P}}E\overset{S}{\overset{\|}{P}}F_2 + (CH_3)_2NH_2{}^+S_2PF_2{}^- \qquad (4)$$

(where E = O, S) which is also the method used recently by other workers to prepare the oxygen-bridged compound μ-oxo-bis(thiophosphoryl) difluoride.[12]

While the synthesis of $F_2P(S)SP(S)F_2$ from SPF_2SH and $SPF_2N(CH_3)_2$ appears to be simply a straightforward cleavage of the P–N link by an acid to form amine and the bridged compound, other reactions that we have attempted indicate that the system does not provide a general synthetic route to all possible bridged compounds. The second successful reaction summarized in eq 4, that of difluorodithiophosphoric acid with dimethylaminophosphoryl difluoride, yields the symmetric bridged compound $(SPF_2)_2O$ rather than the nonsymmetric bridged compound $F_2P(S)SP(O)F_2$. Since it seems reasonable to expect the latter from a straightforward cleavage mechanism, it appears that this reaction involves additional complications which are not presently apparent. Alternate routes to this disulfur compound in the nonsymmetric bridged form have so far been unsuccessful.

In an effort to detect the nonsymmetric product $F_2P(S)SP(O)F_2$ expected from the above reaction of dithiodifluorophosphoric acid with dimethylaminophosphoryl difluoride, the reaction was carried out in an nmr tube and followed from the early stages. Only starting materials, the $S_2PF_2{}^-$ ion, and the symmetric compound $(SPF_2)_2O$ were observed in the spectra taken at periodic intervals throughout the course of the reaction. Since the unsymmetric compound would likely have a characteristic and readily distinguishable spectrum, it is necessary to conclude that no appreciable concentration of this compound was formed. It may however be involved as an intermediate which rapidly rearranges into the symmetric isomer since we have shown below that compounds of this type do rearrange in this manner.

The reaction of difluorophosphoric acid with dimethylaminothiophosphoryl difluoride did not yield the symmetric compound $(OPF_2)_2S$ nor the nonsymmetric isomer $F_2P(O)OP(S)F_2$. Rather a 40% yield of $(SPF_2)_2O$ was obtained along with an appreciable quantity of $OPF_2N(CH_3)_2$ further demonstrating the lack of generality of eq 2. The appearance of $OPF_2N(CH_3)_2$ in the products indicates that the reactions are more complex than initially expected. This reaction was also carried out in an nmr tube but, as before, no evidence for the expected nonsymmetric compound $F_2P(O)OP(S)F_2$ nor its symmetric isomer $(OPF_2)_2S$ was obtained. Further study of these complex reactions is required.

We have successfully synthesized one of the possible nonsymmetric compounds in the system, namely, $F_2P(O)OP(S)F_2$. It was obtained from the reaction of $(OPF_2)_2O$ with SPF_2H and also by the reaction of $(OPF_2)_2O$ and SPF_2SH. A relatively pure sample of this compound in an nmr tube rearranges to $(SPF_2)_2O$ and $(OPF_2)_2O$ upon heating to 100° for several days. This rearrangement may be responsible for the isolation of only symmetric bridged compounds from the reaction of the acids with the amino compounds. Although this rearrangement appears to be relatively slow for the pure compounds, it is possible that it is assisted by acid or base present in the reaction mixtures.

An alternative route to μ-oxo-bis(thiophosphoryl difluoride), $(SPF_2)_2O$, is the reaction of iodothiophosphoryl difluoride, SPF_2I, with elemental oxygen

$$2SPF_2I + 0.5O_2 \longrightarrow (SPF_2)_2O + I_2 \qquad (5)$$

This method is not particularly useful because the reaction is slow and incomplete (at temperatures which do not lead to excessive decomposition of the iodofluoride) and the separation of SPF_2I from $(SPF_2)_2O$ is difficult. It was not possible to convert SPF_2I to $(SPF_2)_2S$ with elemental sulfur.

Reaction of iodothiophosphoryl difluoride with copper oxide gave an approximately 50% yield of $(OPF_2)_2O$ and then only after heating the initially formed product quite strongly. It is possible that the reaction proceeded to the formation of a copper complex with the desired $(SPF_2)_2O$ which is so strongly bound that only decomposition resulted when the adduct was heated in an effort to dislodge the phosphorus compound. A similar reaction[10] gave a good yield of $(F_2P)_2O$ probably because this is a much weaker complexing agent. Other nonmetallic oxides such as antimony(V) oxide were also ineffective. Although silver carbonate converts $(CF_3)_2PI$ into $[(CF_3)_2P]_2O$,[3] its reaction with SPF_2I gave only OPF_3 (in about 15% yield) and no other volatile products even after heating the reaction mixture quite strongly.

Cuprous sulfide did not react with iodothiophosphoryl difluoride. Difluorodithiophosphoric acid even after 10 days at 150° gave only SPF_3 when treated with iodothiophosphoryl difluoride although both of these reactions might have been expected to yield $(SPF_2)_2S$. Reaction of elemental sulfur with $(F_2P)_2O$[10] did not produce any pentavalent thiophosphoryl compound although this reaction is known to proceed readily with organophosphines.[20]

B. Nitrogen-Bridged Compounds.—Both the phosphoryl and thiophosphoryl N-methyl-bridged compounds are easily prepared by the trimethylamine-assisted condensation reaction

$$EPF_2N(H)CH_3 + EPF_2Cl + (CH_3)_3N \longrightarrow (EPF_2)_2NCH_3 + (CH_3)_3NH^+Cl^- \quad (6)$$

(E = S, O) with only symmetrically substituted compounds being attempted. No reaction occurs in the absence of trimethylamine, probably because of the reduced basicity of the $N(H)CH_3$ group resulting from the strong electron-withdrawing properties of the EPF_2 group.

The analogous reactions of the aminophosphorus compounds did not yield the N–H-bridged derivative but rather an additional molar equivalent of trimethylamine was consumed to give involatile, relatively intractable oils which are best formulated as the trimethylamine adducts of the N–H compounds as in

$$EPF_2NH_2 + EPF_2Cl + 2(CH_3)_3N \longrightarrow (EPF_2)_2NH\cdot N(CH_3)_3 + (CH_3)_3NH^+Cl^- \quad (7)$$

where E = S, O. The observed consumption of 1.1 mmol of SPF_2NH_2 and 0.9 mmol of SPF_2Cl by 2.0 mmol of amine agrees reasonably well with idealized stoichiometry (eq 7) especially considering the difficulty of handling the relatively involatile components of the system.

Hydrogen chloride did not displace the $(EPF_2)_2NH$ compound from the adduct but rather split the N–P bonds. The parent N–H-bridged compound was observed, however, in the mass spectrometer upon volatilizing the adduct directly into the ionization chamber by means of the direct probe. The formation of an adduct rather than the N-hydro compound is analogous to the behavior of $[(CF_3)_2P]_2NH$, which also forms a trimethylamine adduct,[6] and this behavior suggests that the hydrogen is fairly acidic due to electron withdrawal by the EPF_2 group. The trifluoromethylphosphinoamine was, however, readily dissociated at 25° whereas much higher temperatures appear to be required for the phosphoryl and thiophosphoryl difluoride analogs.

C. Mass Spectra.—The mass spectral cracking patterns are given in Table IV and the metastable transitions in Table V. Most of the compounds exhibit straightforward cracking patterns with the molecular ion as the most intense feature in the spectrum. The compounds $(SPF_2)_2S$ and $(SPF_2)_2NH\cdot(CH_3)_3N$ show PF_2^+ as the strongest ion in the spectrum. The strongest ion in the spectrum of $(OPF_2)_2NCH_3$ is $OPF_2NCH_3^+$; the molecular ion is extremely weak. Decomposition of the ionized molecule by elimination of a CH_2N fragment to yield the rather unexpected ion observed at *m/e* 171 (a process suggested by the metastable peak at *m/e* 146.9) may account for the absence of a strong molecular ion peak. The mass spectra of the trimethylamine adducts of $(EPF_2)_2NH$ show the parent N–H compound as well as ions arising from the fragmentation of trimethylamine.

Two additional unusual fragmentations, demonstrated by the appropriate metastable peaks, were observed. The fragmentation

$$(SPF_2)_2O^+ \longrightarrow S_2^+ + (PF_2)_2O \quad (8)$$

is supported also by the appearance of a substantial S_2^+ peak (confirmed by mass measurement). The thio-bridged compound, however, did not form the thio-bridged diphosphine $(F_2P)_2S$ but rather undergoes the elimination of PF_3

$$(SPF_2)_2S^+ \longrightarrow S_3PF^+ + PF_3 \quad (9)$$

D. Infrared Spectra. The spectra of the molecules synthesized in this study exhibit a general similarity to each other and to the reported Raman spectrum of $(OPF_2)_2O$[8] as might be expected in view of the structural similarity of the compounds. The observed bands, together with the infrared spectrum of $(OPF_2)_2O$ which is herein reported for the first time, are shown in Tables VI and VII along with assignments of prominent features. Qualitative assignments are relatively easily made by analogy with related systems[7,8,21–24] assuming, as usual, that the vibrations can be considered independently of each other.

Prominent characteristic spectral features are to be expected from the terminal fluorine, oxygen, and sulfur atoms and also from the bridge unit. In a pentavalent tetracoordinate fluorophosphorus molecule P–F stretching frequencies are found in the range 900–1000 cm^{-1}. Thus the bands at 923 and 952 cm^{-1} in the spectrum of $(SPF_2)_2S$ and at 974 and 949 cm^{-1} in the spectrum of $(SPF_2)_2O$ are best associated with P–F stretching frequencies. The very strong band at 1037 cm^{-1} in the spectrum of $(SPF_2)_2O$ which is not reproduced in the spectrum of $(SPF_2)_2S$ is likely due to the asymmetric P–O–P bridge stretching frequency. Likewise, the

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Table IV

Mass Spectral Cracking Patterns

m/e	Rel intens[a]	Assignment[b]	*m/e*	Rel intens[a]	Assignment[b]
$(SPF_2)_2O$			$(SPF_2)_2S$		
220	3.5	M + 2[c]	236	2.9	M + 2
219	0.7	M + 1	235	0.5	M + 1
218	35.6	$(SPF_2)_2O$	234	23.4	$(SPF_2)_2S$
148	1.3	FPOP(S)F	165	1.7	S_3PF_2
135	2.6	F_2POPF	148	0.7	146 + 2
133	0.7	S_2PF_2	146	5.6	S_3PF
120	3.5	SPF_3	133	3.9	S_2PF_2
101	10.7	SPF_2	120	0.5	SPF_3
98	0.7	FPSO	114	2.4	S_2PF
85	0.8	OPF_2	101	8.1	SPF_2
82	0.8	SPF	82	2.9	SPF
69	16.3	PF_2	69	28.5	PF_2
66	1.4	OPF	66	1.0	64 + 2
64	14.2	S_2	64	10.9	S_2[e]
63	0.7	SP	63	2.4	PS
57	1.0		50	2.4	PF
56	1.0		32	2.2	S
50	1.1	PF			
47	1.5	PO			
32	1.9	S			
$(SPF_2)_2NCH_3$			$(OPF_2)_2NCH_3$		
233	2.1	M + 2			
232	0.8	M + 1	198	5.0	$O_2P_2F_4NCH_2$
231	21.7	$S_2P_2F_4NCH_3$	180	1.6	$O_2P_2F_3NCH_3$
216	1.0	$(SPF_2)_2N$	171	6.5	$O_2P_2F_4H$
198	1.9	$F_4P_2SNCH_2$	168	2.4	OP_2F_4N
166	1.1	$F_4P_2NCH_2$	114	47.8	OPF_2NCH_3
148	1.5	$F_3P_2NCH_3$	112	7.0	OPF_2NCH
130	12.4	SPF_2NCH_3	97	1.2	PF_2NCH_2
129	1.4	SPF_2NCH_2	94	2.1	$OPFNCH_2$
128	1.6	SPF_2NCH	86	6.7	OPF_2H
110	4.9	$SPFNCH_2$	85	3.6	OPF_2
102	4.4	SPF_2H	69	12.7	PF_2
101	8.6	SPF_2	67	1.0	OPFH
98	2.5	F_2PNCH_3	66	0.9	OPF
97	1.8	F_2PNCH_2	47	1.4	PO
96	1.8	F_2PNCH			
82	1.1	PSF			
79	0.9	$PFNCH_3$			
78	3.3	$PFNCH_2$			
69	13.9	PF_2			
64	3.9	S_2, PFN			
63	1.4	PS			
60	1.7	$PNCH_3$			
50	1.7	PF			
46	1.1	PNH			
32	1.5	S			

unique strong band at 501 cm^{-1} in the spectrum of $(SPF_2)_2S$ is probably best assigned to the P–S–P asymmetric stretching frequency. The assignment of the 1037-cm^{-1} band in $(SPF_2)_2O$ to the P–O–P asymmetric stretching frequency suggests that the strong band at 1075 cm^{-1} in the infrared spectrum of $(OPF_2)_2O$ should be assigned to this vibration in preference to the value of 987 cm^{-1} assigned previously.[3] This latter band, which in the infrared region appears as a strong band at 993 cm^{-1}, along with the strong band at 899 cm^{-1}, is probably best assigned to the P–F stretching frequency. Our alternative assignment is further supported by the appearance of a strong infrared band in the vicinity of 1055 cm^{-1} in the spectrum of $SPF_2OP(O)F_2$ which is best assigned to the asymmetric P–O–P stretch indicating a smooth decrease of this bridge frequency from 1075 in $(OPF_2)_2O$ to 1037 cm^{-1} in $(SPF_2)_2O$ following the increase of mass and decrease of electronegativity of the EPF_2 group.

Our Raman measurements of $(OPF_2)_2O$ confirm those reported earlier[3] indicating that the 1080-cm^{-1} band is weak in the Raman spectrum in contrast to its strength in the infrared spectrum thus accounting for previous neglect of this band in the assignment scheme. The reason for the greatly different intensities is however not immediately clear.

The symmetric P–O–P stretching band is even less easily assigned. The band[3] at 687 cm^{-1} in $(CF_3)_2POP$-

TABLE IV (*Continued*)

m/e	Rel intens[a]	Assignment[b]	m/e	Rel intens[a]	Assignment[b]
$(OPF_2)_2NH \cdot (CH_3)_3N$[d]			$(SPF_2)_2NH \cdot (CH_3)_3N$[d]		
185	23.7	$O_2P_2F_4NH$	219	1.2	M + 2
168	1.4	OP_2F_4N	217	12.9	$S_2P_2F_4NH$
166	5.2	$O_2P_2F_3NH$	134	2.0	P_2F_3NH, PS_2F_2H
165	5.2	$O_2P_2F_3N$	128	0.7	SP_2FNH
146	1.4	$O_2P_2F_2N$	118	0.8	
102	16.9	O_2PF_2H	115	0.8	SPF_2N
86	0.7	OPF_2H	107	1.3	
85	14.2	OPF_2	101	3.4	SPF_2
84	5.0	PF_2NH	97	2.4	SPFNH
83	5.2	PF_2N	96	1.2	SPFN
82	3.1	O_2PF	84	1.2	PF_2NH
81	1.8	OPFNH	82	1.0	SPF
69	7.1	PF_2	77	1.6	SPN
67	0.7	OPFH	69	24.4	PF_2
66	1.1	OPF	66	4.4	64 + 2
63	2.4	O_2P	65	2.9	PFNH
50	1.0	PF	64	33.6	S_2, PFN
47	2.7	PO	63	2.1	PS
			50	2.2	PF

[a] Intensities are expressed relative to the total ionization defined as Σ_n(intensity) for all ions with masses greater than 30 whose intensities are greater than 2% of the base peak. [b] Only the ^{32}S iostope is considered unless otherwise noted. [c] The symbol M refers to the molecular ion. [d] The strongest part of the spectrum is due to the $(CH_3)_3N$ fragmentation pattern. Only phosphorus-containing fragments are given here for simplicity. [e] Identity confirmed by mass measurement (calcd for $^{32}S_2$, *m/e* 63.9441; found, *m/e* 63.9443).

TABLE V

METASTABLE TRANSITIONS

Compound	Transition	Obsd	Calcd[a]
$(SPF_2)_2O$	$(SPF_2)_2O^+ \rightarrow S_2^+ + (PF_2)_2O$	18.8	18.8
$(SPF_2)_2S$	$(SPF_2)_2S^+ \rightarrow S_3PF^+ + PF_3$	91.0	91.1
$(SPF_2)_2NCH_3$	$(SPF_2)_2NCH_3^+ \rightarrow SPF_2NCH_3^+ + SPF_2$	73.0	73.2
$(OPF_2)_2NCH_3$	$(OPF_2)_2NCH_2^+ \rightarrow PF_2NP(O)F_2^+ + CH_2O$	142.5	142.5
	$(OPF_2)_2NCH_3^+ \rightarrow O_2P_2F_4H^+ + NCH_2$	146.9	146.9
$(SPF_2)_2NH \cdot (CH_3)_3N$	$(SPF_2)_2NH^+ \rightarrow SPF_2NSPF^+ + HF$	178.7	178.8
	$FP(S)N(H)P(S)F_2^+ \rightarrow FPN(H)PF_2^+ + S_2$	90.6	90.7
	$PF_2N^+ \rightarrow PF_2^+ + N$	57.4	57.4
	$(CH_3)_2NCH_2^+ \rightarrow C_3H_6N^+ + H_2$	54.2	54.1
	$C_3H_8N^+ \rightarrow C_2H_5N^+ + CH_3$	31.9	31.9
	$(SPF_2)_2NH^+ \rightarrow S_2^+ + (PF_2)_2NH$	18.8	18.9
	$C_3H_8N^+ \rightarrow C_2H_6^+ + CH_2N$	15.5	15.5
$(OPF_2)_2NH \cdot (CH_3)_3N$	$(OPF_2)_2NH^+ \rightarrow PF_2NP(O)F_2^+ + OH$	152.6	152.6
	$(OPF_2)_2NH^+ \rightarrow OPFNP(O)F_2^+ + HF$	147.2	147.2
	$OPFN(H)P(O)F_2^+ \rightarrow (OPF)_2N^+ + HF$	128.4	128.4
	$PF_2N^+ \rightarrow PF_2^+ + N$	57.3	57.4
	$(CH_3)_2NCH_2^+ \rightarrow C_3H_6N^+ + H_2$	54.2	54.1
	$(CH_3)_3NH^+ \rightarrow (CH_3)_2NH^+ + CH_3$	33.8	33.8
	$(CH_3)_2NCH_2^+ \rightarrow C_2H_6^+ + CH_2N$	15.5	15.5

[a] Values calculated for ^{32}S isotope of sulfur-containing compounds.

$(CF_3)_2$ and the band[10a] at 715 cm^{-1} in F_2POPF_2 have been assigned to the symmetric P–O–P stretching absorptions. Therefore it seems reasonable to associate the medium-intensity band at 734 cm^{-1} in $(OPF_2)_2O$ to the symmetric P–O–P stretch in agreement with other workers' assignments[25,26] for the analogous molecule $P_2O_3Cl_4$. Although a definite conclusion is presently impossible, it is unlikely that this vibration occurs as low as 480 cm^{-1} as suggested by Robinson.[8] A strong band is indeed observed at 489 cm^{-1} in the infrared spectrum of $(OPF_2)_2O$ which seems more reasonably associated with PF_2 deformations. If our *tentative* assignments are correct, then it appears that the symmetric bridge stretching frequency increases with formal oxidation state of phosphorus, and the stronger bridge bond in the pentavalent system may be due to greater π contributions.

Nitrogen-bridged compounds show a strong band in the 1100-cm^{-1} region similar to that found in the EPF_2-NR_2 compounds.[17] These bands, at 1185 cm^{-1} in $(OPF_2)_2NCH_3$ and at 1072 cm^{-1} in $(SPF_2)_2NCH_3$, are reasonably assigned to P–N–P asymmetric stretching absorptions in agreement with the assignment of bands in the 850–950-cm^{-1} region to this vibration in the trivalent bridged compounds $(F_2P)_2NCH_3$[4] and

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Table VI

Infrared Spectra (cm^{-1}) of Some Oxygen- and Sulfur-Bridged Difluorophosphorus Compounds

$(OPF_2)_2O$	$(SPF_2)_2O$	$(SPF_2)_2S$	$SPF_2OP(O)F_2$[a]	Assignment
1795 vw[c]	1873 vw	...	...	
...	1639 vw	...	...	
1570 vw	1574 vw	...	...	
1405 s	...	...	1410 s	$\nu(P=O)$
...	1404 vw	...	...	
1330 m	1332 vw	...	...	
...	1308 w	...	...	
1185 w	1195 w	...	...	
...	1117 w, sh	...	...	
...	...	1030 vw	...	
1075 vs	1037 vs	...	1055 vs	$\nu_{as}(P-O-P)$
...	...	991 vw	...	
993 vs	974 vs	952 vs[b]	980 vs, br	$\nu_{as}(P-F)$
957 vw, sh	949 m, sh	934 m, sh	945 m, sh	
899 s	...	923 s[b]	...	$\nu_s(P-F)$
...	850 w, sh	835 vw	...	
822 vw	847 m	...	...	
...	797 vw	795 vw	790 m	
734 m	...	760 vw	...	
...	...	745 w	...	
...	711 sh	...	...	
...	708 s	703 s	705 w	$\nu(P=S)$
...	644 vw	...	645 w	
...	607 vw	...	...	
520 sh	576 vw	526 vw	...	
...	...	501 s	...	$\nu_{as}(P-S-P)$
489 s	...	...	500 w, br	
...	469 m	...	445 m	
431 vw	416 m[b]	406 vw	...	
...	387 vw	368 m	...	
...	357 vw	339 m	...	

[a] Only a partial listing of definitely identified bands is given since the compound was not obtained in the pure state. [b] Band shows typical PQR rotational structure. [c] Abbreviations: br, broad; m, medium; s, strong; sh, shoulder; v, very; w, weak.

Table VII

Infrared Spectra (cm^{-1}) of Some Nitrogen-Bridged Difluorophosphorus Compounds

$(OPF_2)_2NCH_3$	$(SPF_2)_2NCH_3$	$(OPF_2)_2NH \cdot (CH_3)_3N$	$(SPF_2)_2NH \cdot (CH_3)_3N$	Assignment
...	...	3390 br, w	3420 br, w	
...	...	3045 br, m	...	$\nu(CH_3)$
2975 vw[a]	2975 vw	2970 w, sh	2980 br	
...	...	2740 br, m	2730 br	
...	...	2520 w	2518 w	
...	...	2470 w	2470 w	
...	...	1486 m	1477 m	
...	...	1460 w, sh	1453 w, sh	
...	...	...	1415 w, sh	
1387 s	...	1360 s	...	$\nu(P=O)$
1368 s	...	...	...	
...	...	1292 s	1300 vs, br	
1229 w	1207 m	1239 m	...	$\nu(CN)$
...	...	1143 m	1045 vw	
1185 m	1072 s	987 m	980 m	$\nu_{as}(P-N-P)$
975 vs	951 vs	943 m	...	$\nu(PF)$
935 m	931 w, sh	884 s, br	850 vs, br	
877 m	915 vs	842 s	...	
...	788 vw	...	...	
...	...	750 w	727 vw	
...	697 m	...	659 vs	$\nu(P=S)$
...	689 m	...	...	
663 vw	...	...	...	
500 s	...	500 s	...	
...	455 w	...	442 m	
423 w	429 m	...	414 m	
388 w	385 w	...	...	
...	365 m	...	...	

[a] Abbreviations: br, broad; m, medium; s, strong; sh, shoulder; v, very; w, weak.

$[(CF_3)_2P]_2NCH_3$.[6] Again shifts to higher energy are suggested for the pentavalent compounds perhaps indicating stronger bonding in these systems. The P–N–P asymmetric stretch in the trimethylamine adducts appears to be most reasonably assigned to the bands at 980–1000 cm^{-1}.

The notably greater reluctance of hydrogen chloride to cleave the P–N bond in pentavalent phosphorus compounds as compared to the ease of P–N bond cleavage by hydrogen halides in the trivalent phosphorus compounds may reflect a greater P–N bond strength in the pentavalent system in agreement with the infrared interpretation. The possibility of kinetic control of the cleavage of the P–N bond in pentavalent phosphorus compounds must not be overlooked.

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Notes

CONTRIBUTION FROM ROCKETDYNE,
A DIVISION OF NORTH AMERICAN ROCKWELL CORPORATION,
CANOGA PARK, CALIFORNIA 91304

Oxidation–Reduction in the Chlorine Monoxide–Arsenic Pentafluoride System[1]

BY C. J. SCHACK AND D. PILIPOVICH

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Dichlorine oxide (or chlorine monoxide) has been reported to form a complex with AsF_5 at −78° and at about −50° to form an odd-electron molecule, $ClOAsF_5$, through elimination of Cl_2.[2] Inference of the structure as being the postulated odd-electron molecule was drawn from the observed reaction stoichiometry and the fact that the postulated odd molecule reacted with NO_2 to give $ClNO_3$. No additional data concerning the complex have appeared. Inasmuch as we had projected a reaction study based on "$ClOAsF_5$," an effort was made to verify its formation. However, it was found that the original report was erroneous in that the known $ClO_2^+AsF_6^-$ and not "$ClOAsF_5$" is produced by this reaction.

Experimental Section

Materials.—Chlorine monoxide was prepared from Cl_2 and yellow HgO using a modified procedure.[3] Arsenic pentafluoride was purchased from Ozark-Mahoning and used without purification after gas chromatography indicated a purity of better than 99.5%. Chloryl fluoride was prepared from $KClO_3$ and F_2[4] and purified by fractional condensation. Nitrogen tetroxide was purchased from the Matheson Co. and purified by fractional condensation. Phosphorus dichloride trifluoride was formed[5] from PF_3 and Cl_2.

Apparatus.—Experiments were conducted in two vacuum systems, one constructed of glass and the other of stainless steel–Teflon. Solids were handled in an inert-atmosphere glove box. Infrared spectra were taken on a Perkin-Elmer 137 Infracord using 5-cm gas cells fitted with AgCl windows and were also taken as Halocarbon oil mulls or neat solids between AgCl plates. Debye–Scherrer powder X-ray diffraction patterns were obtained with a GE XRD5 instrument using Cu Kα radiation. Vapor-phase chromatography of reactants and products was carried out on a column packed with 50% w/w of Halocarbon 4-11V oil and Kel-F low-density molding powder according to Dayan and Neale.[6]

Reactions of Cl_2O and AsF_5.—Measured quantities of Cl_2O (117 cm^3, 5.22 mmol) and AsF_5 (85.0 cm^3, 3.79 mmol) were separately condensed into the reactor (glass or Teflon tubes) at −196°. The temperature was changed to −78° and it was observed that the mixed reactants gradually developed a dark red color. Pumping on the mixture after a few hours at −78° resulted in the recovery of some of the starting materials and much Cl_2. Subsequent warming of the reaction to ambient temperature gave additional small amounts of gaseous materials and a white solid. Little or no gases not condensable at −196° were observed throughout the reaction. In all, 111 cm^3 of volatile products was obtained. Infrared and gas chromatographic analyses indicated these products to be a mixture of AsF_5 (17.5 cm^3, 0.78 mmol) and Cl_2 (93.5 cm^3, 4.17 mmol) with a trace of ClO_2 and no Cl_2O. The observed reactant:product ratio of $Cl_2O:AsF_5:Cl_2$ was 5.00:2.89:4.01. Similar reaction ratios were obtained when Cl_2O was used as the excess reagent. The solid product showed three infrared bands: 1280 (m, doublet), 1040 (w, doublet), and 690–700 cm^{-1} (s, broad).

Preparation of $ClO_2^+AsF_6^-$.—Chloryl fluoride (111 cm^3, 4.96 mmol) and AsF_5 (63.7 cm^3, 2.84 mmol) were separately condensed into a Teflon ampoule at −196°. After 1 hr at room temperature, the unreacted gases were removed and measured (48.0 cm^3, 2.14 mmol). An infrared spectrum showed only $FClO_2$. The white solid product had an infrared spectrum identical with that of the solid from the Cl_2O–AsF_5 reaction. In addition, both solids fumed in air and exploded on contact with water. Powder X-ray patterns of both solids were obtained and were identical. The observed spacings and relative intensities are given in Table I.

Reaction of $ClO_2^+AsF_6^-$ and NO.—A weighed sample of $ClO_2^+AsF_6^-$ (0.38 g, 1.48 mmol) was treated with NO (66.0 cm^3, 2.95 mmol) for approximately 1 hr at ambient temperature. The volatile products of the reaction were separated by fractional condensation and consisted of Cl_2 contaminated with a trace of ClNO (17.5 cm^3, 0.78 mmol) and NO_2 (32.2 cm^3, 1.44 mmol). Unreacted NO was not detected. The white solid product left in the reactor was identified as $NO_2^+AsF_6^-$ by its infrared spectrum.[7] A similar reaction of the $ClO_2^+AsF_6^-$ obtained from the Cl_2O reaction and NO also rapidly gave Cl_2, NO_2, and $NO_2^+AsF_6^-$ in approximately the same stoichiometry but in lower over-all yield as expected for $ClO_2^+AsF_6^-$ contaminated with $AsOF_3$.

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