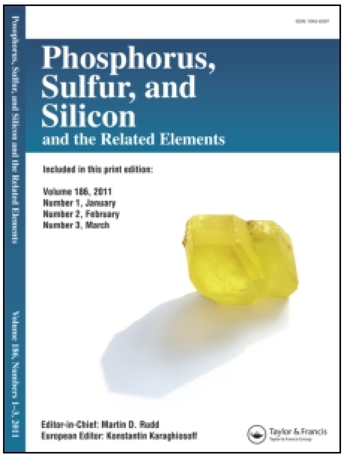

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Odom, J. D. and Zozulin, A. J.(1981) 'THE REACTION OF NITRIC OXIDE WITH PHOSPHINE AND SEVERAL DIFLUOROPHOSPHINE MOLECULES', Phosphorus, Sulfur, and Silicon and the Related Elements, 9: 3, 299 — 305
To link to this Article: DOI: 10.1080/03086648108078254
URL: http://dx.doi.org/10.1080/03086648108078254

Phosphorus and Sulfur, 1981, Vol. 9, pp. 299–306
0308-664X/81/0903–0299$06.50/0

THE REACTION OF NITRIC OXIDE WITH PHOSPHINE AND SEVERAL DIFLUOROPHOSPHINE MOLECULES

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(*Received February 22, 1980; in final form April 21, 1980*)

The reaction of nitric oxide with phosphine and several difluorophosphines (PF_2X where X = F, Cl, Br, I, H and PF_2) has been investigated. The products of these reactions include nitrogen, nitrous oxide and the corresponding phosphine oxide. In cases where X = *H* or PF_2 a complex mixture of phosphorus containing compounds has been obtained. When X = I the previously uncharacterized phosphoryl difluoride iodide has been isolated and identified. A reaction scheme which accounts for the observed products is also presented.

INTRODUCTION

Nitric oxide is a versatile molecule which undergoes many different types of reactions. It is known to function as both a Lewis acid and a Lewis base, as well as an oxidizing and reducing agent.[1,2] In a series of investigations, Drago and co-workers demonstrated that NO behaves as a Lewis acid toward a substantial number of Lewis bases including primary and secondary amines.[3–8] The structure of the adduct has been postulated[1] to be the type

$$\mathrm{B{:}\ddot{\underset{..}{N}}{-}\ddot{\underset{..}{O}}{:}} \quad (\mathrm{B = Lewis\ Base})$$

which could be a species involved in the transition state or could be an intermediate. The oxidation of phosphines and phosphites by NO has also been reported,[6,9–11] and the results[11] of a kinetic study of the reaction of triethyl phosphite with NO is consistent again with the initial formation of an unstable species BNO.

$$(RO)_3P + NO \longrightarrow [(RO)_3PNO]$$

It has been reported that methylphosphine and phosphine do not react with NO in the gas phase.[10] There have been no previous studies concerning the reaction of NO with PF_2X compounds (X = F, Cl, Br, I, H, PF_2) and, in the course of this research, we also had cause to reinvestigate the reaction of PH_3 and NO. The reaction of NO with ammonia was also carried out and the results of this study are reported herein.

RESULTS AND DISCUSSION

Several factors must be considered in discussing the reactions of nitric oxide with phosphine and halodifluorophosphines. These are as follows:

a) Ammonia and nitric oxide undergo no reaction.

b) Trifluorophosphine, chloro-, and bromodifluorophosphine react with NO only under the influence of ultraviolet irradiation.

c) Phosphine and trifluorophosphine react with a large excess of NO to yield the same products as the 1:2 reaction.

d) Phosphine and trifluorophosphine do not react with N_2O.

e) Nitrogen gas was produced in all reactions.

f) Nitrogen and nitrous oxide cannot be produced from pure NO under our experimental conditions.

g) Difluorophosphine and tetrafluorodiphosphine undergo a more complex reaction.

Previous studies involving the interaction of nitric oxide with phosphines have reported either the formation of the phosphine oxide or no reaction.[6,9–11] For example, trimethylphosphine and dimethylphosphine react with NO to form the respective phosphine oxide and N_2O. It has been reported that phosphine and methylphosphine do not react with NO.[10] There is little doubt that the initial interaction between an organophosphine and NO is an acid-base reaction where the organophosphine acts as a Lewis base and NO acts as a Lewis acid. Further reaction of this complex with another molecule of NO results in the subsequent formation of the stable products. Methylphosphine presumably does not react with NO because of its reduced Lewis basicity.

In this study the fact that ammonia does not react with NO but that an immediate reaction between phosphine (either in the condensed state or in the gaseous state) and NO is evidenced leads to different conclusions. Like NO, phosphine can act as a Lewis base *or* a Lewis acid (through the valence shell *d* orbitals. Ammonia can only act as a Lewis base and thus the reaction between PH_3 and NO most likely occurs with the initial formation of a Lewis acid-base complex with NO acting as a Lewis base. The polymeric material produced in the reaction is most probably formed from the production of the unstable molecule H_3PO.[20] Phosphorus trifluoride, phosphorus difluoride chloride, and phosphorus difluoride bromide do not react with NO in the condensed phase or in the gaseous phase except under the influence of ultraviolet irradiation.[21] With the possibility of backbonding between non-bonding electrons on fluorine and the valence shell *d* orbitals on phosphorus, one could argue that PF_3, PF_2Cl, and PF_2Br should be poorer Lewis acids than PH_3. Apparently ultraviolet irradiation promotes the formation of a complex between the fluorophosphine and NO, and subsequent reaction affords quantitative yields of the fluorophosphine oxide. Iododifluorophosphine, however, reacts without ultraviolet irradiation. Its similarity with PH_3 towards the reaction with NO indicates a gradual increase in acidity of the fluorophosphines from PF_3 to PF_2I.

As in the phosphine reaction, these reactions also produce nitrous oxide and nitrogen. The production of nitrogen in these reactions is further evidence that a different reaction pathway is involved compared to the reactions of organophosphines with NO. The reactions of several trifluoromethylphosphines with NO were reported to yield nitrogen and nitrous oxide.[22] It was suggested in this report that the trifluoromethyl compounds reacted with NO in a manner similar to that proposed for the reaction of triethylphosphite and NO[11] and that the nitrogen was produced by the reduction of N_2O. This mechanism requires nitrogen to be produced as a secondary product. In order to determine whether nitrogen was being generated as a primary or a secondary reaction product in our systems, the interactions between phosphine and trifluorophosphine with N_2O, the interaction of N_2O with NO, and the photolysis of NO[23] were investigated. Under similar experimental conditions, no reactions occurred. It would seem that a different pathway is needed to explain the formation of nitrogen. In the reaction scheme presented here (*vide infra*) the trifluoromethyl-substituted phosphines can easily act as acids. These compounds, in fact, should be slightly better acids than PF_3 since the methyl fluorine nonbonding electron pairs will be unable to participate in any backbonding into the valence shell *d* orbitals of phosphorus. This would allow for the base attack by NO and subsequent formation of the phosphine oxide, nitrous oxide, and nitrogen as primary products.

Consideration of the above factors in postulating one or more reaction pathways must involve NO as a Lewis base and a formation of N_2O and N_2 as stable products. Several pathways are possible and the two most probable pathways are outlined below.

Scheme I:

$$X'X_2P + NO \rightleftharpoons X'X_2PON \tag{1}$$

$$2X'X_2PON \longrightarrow 2X'X_2PO + N_2 \tag{2}$$

$$X'X_2PON + NO \longrightarrow X'X_2PO + N_2O \tag{3}$$

Scheme II:

$$X'X_2P + NO \rightleftharpoons X'X_2PON \tag{4}$$

$$X'X_2PON + NO \rightleftharpoons X'X_2PO_2N_2 \tag{5}$$

$$X'X_2PO_2N_2 + NO \rightleftharpoons X'X_2PO_2N_2 + NO \tag{6}$$

$$X'X_2PO_2N_2 + X'X_2P \longrightarrow X'X_2PO + X'X_2PON_2 \tag{7}$$

$$X'X_2PON_2 \longrightarrow X'X_2P + N_2O \tag{8}$$

$$X'X_2PO_2N_2 + X'X_2P \longrightarrow 2X'X_2PO + N_2 \tag{9}$$

where

$X' = H, F, Cl, Br$ or I

$X = F, H$

In each of the two reaction pathways the initial step is a simple base attack by NO on the phosphorus atom to generate the intermediate, $X'X_2PON$ or $X'X_2PNO$. This adduct can be written as either a nitrogen or oxygen bound species; however, the oxygen bound complex is preferred to explain the reaction products. A low temperature mid-infrared study was performed in an attempt to characterize this intermediate as being either oxygen or nitrogen bound. Several experiments were conducted in hopes of observing the development of new bands from P—N or P—O absorptions or to detect shifts in the frequencies for NO and/or PH_3. In one experiment, PH_3 and NO were condensed separately onto a CsI window at 21°K. The window was allowed to warm slightly and was then cooled again to 21°K before the spectrum was recorded. A second experiment involved allowing the two gases to mix immediately prior to cocondensation. Unfortunately, both experiments were severely hampered by the high vapor pressure of NO which resulted in its migration from the CsI window to colder parts of the cryostatic system. Thus, the spectra which were obtained did not aid in the detection and characterization of the proposed intermediate species.

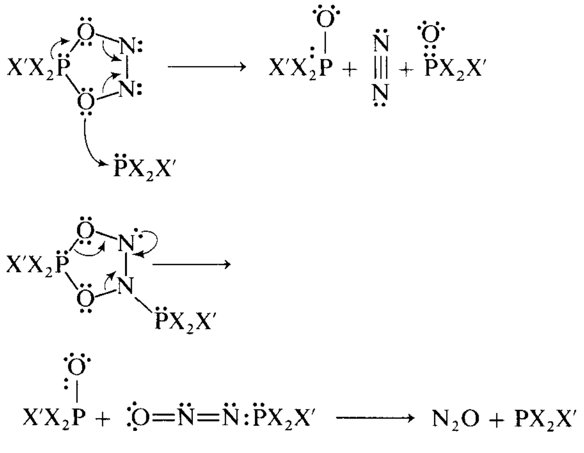
In scheme I, this intermediate reacts with either $X'X_2PON$ to yield N_2 or with NO to yield N_2O. If this pathway is operative, varying the quantity of NO should have a significant effect on the ratio of N_2 to N_2O, i.e., at low concentrations of NO, Eq. (2) will be important while at high concentrations of NO, Eq. (3) will dominate. However, when the concentrations of phosphine and nitric oxide were varied from 1:1 to 1:2 to 1:16, the N_2/N_2O ratio remained constant. This fact would eliminate Scheme I as a plausible pathway.

In Scheme II, Eqs. (4) and (5) are similar to those postulated for the alkylphosphines[11] where a second molecule of NO can add to $X'X_2PON$. This would seem reasonable for the reactions with excess NO where the concentration of NO relative to that of phosphine would be high. In addition, the ability of phosphorus to become pentavalent would enable two molecules of NO to bind to it. The equilibrium established in Eq. (6) is an important aspect of these reactions. It simply states that with excess nitric oxide, the intermediate is most likely to encounter another NO molecule; however, this interaction is unproductive and does not result in the observed products. A steady state concentration develops until a phosphine molecule interacts with the intermediate to form the observed products. This attack can occur in two different ways as outlined in Eqs. (7-9). Once again, the production of N_2O and 1 mole of phosphine oxide would be similar to that proposed for alkylphosphines while step (9) generates N_2 and 2 moles of the phosphine oxide. To better understand how N_2 and N_2O are formed in these steps, it is helpful to describe the likely configuration of the intermediate, $X'X_2PO_2N_2$. Considering the abilities of phosphorus to become five-coordinate and NO to dimerize, a cyclic structure

$X'X_2\overline{PONNO}$,

is possible. Also, an equilibrium between a cyclic and an open structure, NOPON, is not unreasonable. When the intermediate is cyclic, N_2 or N_2O will be produced depending on whether the phosphine interacts with the oxygen or nitrogen as shown in Scheme III.

This pathway appears to adequately explain the formation of N_2O and N_2; however, it should also be able to predict the relative quantities of products. The oxygen should be the preferred position for interaction with the phosphine, remembering that the phosphine is acting as an acid. This would suggest that the ratio of N_2 to N_2O would be greater than 1. The N_2/N_2O ratios for PH_3, PF_3, PF_2Cl, PF_2Br, and PF_2I with nitric oxide are 1.4, 12.8, 4.3, 3.0 and 3.0, respectively. The higher ratios for the fluorophosphine reactions can be attributed to the effects of the electronegative fluorines on phosphorus which withdraw electron density from the ring system. This effect would tend to enhance the Lewis basicity of the oxygen relative to the nitrogen, thereby making the oxygen more susceptible to interaction with a Lewis acid. The observed decrease in the ratio of N_2/N_2O as X varies from



Scheme III

F to I (and H) can be attributed to the electronegativity trends of the X substituent. This trend would predict the highest ratio of N_2/N_2O for trifluorophosphine and the lowest for iododifluorophosphine and difluorophosphine. The abrupt change which occurs between PF_3 and the other fluorophosphines arises from the effects of both electronegativity and backbonding. Phosphorus trifluoride would maximize these effects and clearly would produce the largest ratio of N_2/N_2O.

The preceding discussion has been mainly concerned with the reaction of halodifluorophosphines with nitric oxide. When HPF_2 and NO react, nitrogen is not consistently obtained. In terms of Scheme II, a weaker acid than the halodifluorophosphines would be expected to cause a decrease in the ratio of N_2/N_2O. In this reaction the quantity of nitrogen varies from 0.9 to 0 mmoles. The smaller value is expected for the increased basicity observed for HPF_2 in other studies[26–28] *versus* other fluorophosphines. The fact that in some reactions no nitrogen is produced suggests HPF_2 may be a borderline case between the halodifluorophosphines and the organophosphines. The factors which cause this effect to be observed are not understood and deserve further study.

The formation of the phosphorus containing compounds in the reactions of HPF_2 and P_2F_4 with NO can be attributed to decompositive processes and secondary reactions. From the product isolated in the reaction of P_2F_4 with NO, it is apparent that the reaction involves multiple steps to produce high molecular weight phosphorylfluorides. The fragmentation pattern obtained in the mass spectra of these molecules suggests that the building units are OPF_2 and O_2PF_2. Obviously, additional work will be necessary to fully understand the mechanisms of these reactions and to establish the identity of these high molecular weight compounds.

In conclusion, the pathway described above explains the interactions of PH_3 and PF_2X ($X = F$, Cl, Br, I) with NO and adequately accounts for the products and their relative abundance. However, other plausible reaction schemes are possible and, indeed, more complex ones can be envisioned. In several experiments it was necessary to duplicate exactly the experimental conditions to obtain consistent results. The total pressure of the system and the mixing procedure of the two gases appeared to be important. In this connection, the reaction between $P_2(CF_3)_4$ and NO has been reported to yield two different products depending on the mixing procedure.[22] When $P_2(CF_3)_4$ and NO are slowly warmed, a high yield of pure $[(CF_3)_2PO]_2O$ is obtained; however, $P_2(CF_3)_4$ vapor at 50° is converted by NO to pure $(CF_3)_2POP(O)(CF_3)_2$. These factors imply a more complex situation, possibly involving surface effects. Finally, it has been demonstrated that, contrary to a previous report, PH_3 reacts with NO both in the condensed state and in the gas phase. In addition, PF_3, $ClPF_2$ and $BrPF_2$ react with NO under the influence of ultraviolet irradiation to quantitatively yield $P(O)F_3$. $ClP(O)F_2$, and $BrP(O)F_2$, respectively. Iododifluorophosphine, as with PH_3, reacts immediately with NO to yield an unstable oxide, $IP(O)F_2$. It seems that these phosphines react by the same pathway which is complex and different from that in the reactions of organophosphines with NO. Lastly, difluorophosphine and tetrafluorodiphosphine also react with NO to yield a complex mixture of phosphorus containing compounds. These reactions are apparently complicated by decomposition processes and secondary reactions. Additional work will be necessary to understand the pathway for these two fluorophosphines.

EXPERIMENTAL

Materials

The preparation and purification of all compounds was accomplished using standard high vacuum techniques in all-glass vacuum system employing greaseless stopcocks.[12] Ammonia (Matheson), trifluorophosphine (Ozark-Mahoning) and nitric oxide (Matheson) were obtained commercially. Trifluorophosphine was purified by passage through a trap held at −160° (isopentane-liquid nitrogen slush). The commercial nitric oxide was found to be contaminated with other nitrogen oxides which were effectively removed by several passages through three consecutive traps held at −160°, Phosphine,[13] chloro-, bromo-, and iododifluorophosphine,[14] difluorphosphine,[15] tetrafluorodiphosphine[15] and nitrous oxide[16] were prepared as previously described. The purity of all compounds was monitored by vapor pressure, infrared and/or mass spectral measurements.

Instrumental

Nuclear magnetic spectra (^{19}F, 94.1 MHz; ^{31}P, 40.5 MHz) were obtained on a Varian Associates XL-100-15 spectrometer operating in the Fourier transform mode. Chemical shifts were measured relative to external 85% o-H_3PO_4 (^{31}P) and $CFCl_3$ (^{19}F). A negative sign (−) denotes increased shielding. Mass spectra were obtained at 70 eV on a Perkin-Elmer RMU-6 spectrometer. Exact masses were obtained on an AEI MS902 spectrometer. Infrared spectra of compounds in the gas phase were obtained in a 10 cm cell fitted with KBr optics on a Perkin-Elmer 337 grating infrared spectrometer. A low temperature mid-infrared experiment with PH_3 and NO was performed by condensing the reactants onto a CsI window at 21°K in a Cryogenics Technology, Inc. Spectrim cryostat equipped with a Lake Shore Cryotronics model DTL-500 high precision temperature controller. The mid-infrared spectra were recorded with a Perkin–Elmer model 621 spectrophotometer. The instrument housing was purged with dry nitrogen in order to eliminate CO_2 and water vapor.

Reactions

1) NH_3 and NO Ammonia (2.5 mmoles) and nitric oxide (5.1 mmoles) were condensed at $-196°$ into an evacuated 200 ml tube fitted with a greaseless stopcock. The tube was isolated from the vacuum system and allowed to warm to room temperature. After 5 hr there was no visible sign of reaction and all volatile materials from the tube were reintroduced into the vacuum system and fractionated using cold traps held at $-131°$ (liquid nitrogen-*n*-pentane slush), $-160°$, and $-196°$. The starting materials were recovered quantitatively and thus no reaction occurred.

2) PH_3 and NO Several sets of reaction conditions were employed for these reactants. In the most typical reaction, PH_3 (2.4 mmoles) and NO (4.8 mmoles) were condensed at $-196°$ into an evacuated 200 ml vessel fitted with a greaseless stopcock. The vessel was isolated from the vacuum system and the liquid nitrogen dewar was removed. Visual examination of the reaction vessel indicated that NO vaporized almost immediately and reaction ensued as the PH_3 vaporized. Reaction was easily recognized by the formation of white clouds in the vessel which appeared to rapidly settle on the walls as a nonvolatile yellow solid. The tube was allowed to warm to ambient temperature and remain at that temperature for approximately 2 hr. At that time the tube was reopened to the vacuum system and the volatile components fractionated to yield N_2 (1.3 mmoles measured on a calibrated system employing a Toepler pump), N_2O (0.9 mmoles), unreacted PH_3 (1.0 mmoles), and unreacted NO (0.1 mmoles). The fractionation of N_2O, PH_3, and NO required a special procedure because of their volatility. After removing the N_2 by a Toepler pump, the entire mixture of volatile materials was condensed into a trap on the vacuum system without using dynamic vacuum. The total number of mmoles of volatiles was then measured and the materials were recondensed with liquid nitrogen. Because NO has a vapor pressure at $-196°$ (5×10^{-3} torr),[17] the liquid nitrogen trap was then subjected to dynamic vacuum and the pressure was monitored with a thermocouple gauge. When there was no residual pressure on the gauge, the volatile materials were measured and the difference (in mmoles) was the amount of unreacted NO recovered from the reaction. The PH_3 and N_2O were then passed into a $-160°$ slush which was situated directly at the entrance to a low temperature fractionation column being held at a temperature of less than $-160°$. The pressure of gas exciting the column was monitored with a thermocouple gauge and, as soon as a pressure lowering was observed on the gauge, a stopcock at the top of the column was used to isolate the two fractions. The material which exited the column was shown by IR and mass spectrometry to be pure PH_3 and the material which remained on the column was shown to be pure N_2O. The yellow residue produced in this reaction was insoluble in hydrocarbon solvents (CH_2Cl_2 and $CHCl_3$). Upon exposure to air, it slowly produced a clear liquid which was acidic (tested with litmus paper). ^{31}P NMR spectra of the neat liquid and a 10% solution of the liquid were identical and the ^{31}P chemical shifts corresponded to those of H_3PO_3 and H_3PO_4.[18] Using the same conditions and the same reaction volume, a 1:1 mole ratio of PH_3 and NO produced the same products in the same ratio as the 1:2 mole ratio reaction. Another reaction in which the two reactants were in a 1:2 mole ratio but both were in the gas phase at ambient temperature was performed. When the valve connecting the vessels containing the gaseous PH_3 and NO was opened, reaction was visible immediately. The same products were obtained in the same ratio. A further reaction was performed with both reactants in the gas phase but with a PH_3:NO mole ratio of 1:16. In this reaction a 200 ml bulb containing NO (39.0 mmoles) was attached via a greaseless stop-cock to a 1000 ml bulb containing PH_3 (2.5 mmoles). At ambient temperature the valve connecting the bulbs was opened and the reactants appeared to be well mixed due to the large pressure differential (4.7 atm). The formation of a white cloud was observed immediately in the larger bulb and a non-volatile clear solid deposited on the walls of the vessel. Fractionation of the volatile materials yielded N_2 (2.7 mmoles), N_2O (2.0 mmoles), and unreacted NO (33.3 mmoles). The clear solid slowly turned yellow and the ^{31}P NMR spectrum of an aqueous solution of this material indicated that the phosphorus containing material consisted of H_3PO_3 and H_3PO_4.

3) PH_3 and N_2O Phosphine (2.5 mmoles) and nitrous oxide (5.0 mmoles) were condensed into an evacuated 200 ml tube fitted with a greaseless stopcock. The tube was isolated from the vacuum system and allowed to stand at room temperature for 3 hr. At the end of this time the volatile materials were reintroduced into the system and fractionated using a $-160°$ trap and a low temperature vacuum distillation column which was held below $-160°$. Quantitative recovery of both reactants was achieved and thus no reaction had occurred.

4) PF_3 and NO This reaction was investigated using several methods. The first method involved condensing PF_3 (2.5 mmoles) and NO (5.0 mmoles) into an evacuated 200 ml vessel fitted with a greaseless stopcock. The vessel was then isolated from the vacuum system, warmed to ambient temperature, and allowed to stand for 7 hr. At the end of this time volatile materials were reintroduced to the vacuum system. Efficient fractionation of PF_3 and NO cannot be achieved by low temperature fractional distillation and the same procedure was used as has been previously described for PH_3 and NO (*vide supra*) in order to determine the relative amounts of unreacted reactants. Quantitative recovery of these materials was achieved and thus no reaction had occurred. The second method involved the condensation of PF_3 (2.5 mmoles) and NO (5.0 mmoles) into an evacuated 200 ml quartz vessel fitted with a greaseless stopcock. The vessel was isolated from the vacuum system, allowed to warm to room temperature, and irradiated for 7 hr using a Hanovia medium pressure 450 watt mercury lamp. At the end of this time the tube was reattached to the system and volatile materials were removed. Nitrogen (1.3 mmoles) was removed by a Toepler pump. The remaining materials were fractionated and identified as unreacted NO (2.3 mmoles), N_2O (0.1 mmoles), and $P(O)F_3$ (2.5 mmoles). Trifluorophosphine oxide was identified by its vapor pressure (465 torr at $-45°$),[12] mass spectrum, IR spectrum, and ^{19}F and ^{31}P NMR spectra.[18,19] A third method involved condensing PF_3 (3.0 mmoles) and NO (45.9 mmoles) into a reaction vessel consisting of a 1000 ml Pyrex bulb and a 250 ml quartz bulb connected via a greaseless stopcock. This apparatus was used in order to duplicate the total pressure of reactants which had been used in previous experiments. The quartz vessel was irradiated for 7 hrs using a

Hanovia medium pressure 450 watt mercury lamp. During this time the contents were circulated by hourly free-thaw cycles. After 7 hrs, the vessel was attached to the vacuum system and the volatile materials were isolated. Nitrogen (0.5 mmoles) was removed by a Toepler pump. Other volatile components which were fractionated and characterized were unreacted NO (42.6 mmoles), $P(O)F_3$ (0.7 mmoles), and unreacted PF_3 (2.3 mmoles). A third reaction method was performed in which PF_3 (4.0 mmoles) and NO (8.0 mmoles) were condensed into a 500 ml reaction vessel equipped with a break seal. The bulb was sealed from the vacuum system and placed into an oven held at 155°. After 9 hr the volatile components were removed and fractionated. Nitrogen (0.2 mmoles) was removed by a Toepler pump. Unreacted NO (6.0 mmoles), unreacted PF_3 (3.8 mmoles), and $P(O)F_3$ (0.2 mmoles) were also isolated and identified. A trace of N_2O_3 was also observed.

5) PF_3 and N_2O Two methods were used for these materials. In the first experiment, PF_3 (2.5 mmoles) and N_2O (5.0 mmoles) were held at ambient temperature in a 200 ml tube for 5 hr. At the end of this time quantitative recovery of the starting materials was achieved. In the second experiment, PF_3 (2.7 mmoles) and N_2O (5.2 mmoles) were irradiated with ultraviolet for 5 hr at ambient temperature using a Hanovia medium pressure 1000 watt mercury lamp. Quantitative recovery of the starting materials was achieved and thus no reaction occurred under these conditions.

6) $ClPF_2$ and NO This reaction was investigated using two methods. The first method involved condensing $ClPF_2$ (2.5 mmoles) and NO (5.2 mmoles) into an evacuated 200 ml vessel fitted with a greaseless stopcock. The vessel was isolated from the vacuum system and warmed to ambient temperature. After 8 hr all volatile materials were reintroduced to the vacuum system and fractionated in a static vacuum through traps held at −126° (methylcyclohexane-liquid nitrogen slush), −160°, and −196°. No volatile materials were obtained in the −126° trap. The trap held at −160° contained $ClPF_2$ (2.5 mmoles) which was identified by its vapor pressure (121 torr at −83.6°),[12] mass spectrum, and IR spectrum. Nitric oxide (5.1 mmoles) was obtained in the −196° trap. Since a quantitative recovery of these materials was achieved, no reaction had occurred. The second method involved the condensation of $ClPF_2$ (2.6 mmoles) and NO (5.2 mmoles) into an evacuated 200 ml quartz vessel fitted with a greaseless stopcock. The vessel was isolated from the vacuum system, warmed to ambient temperature, and irradiated for 8 hr using a Hanovia medium pressure 450 watt mercury lamp. At the end of this time the vessel was reattached to the vacuum system and all volatile materials were removed. Nitrogen (1.3 mmoles) was removed by a Toepler pump. The remaining volatile materials were fractionated and identified as unreacted NO (1.5 mmoles). N_2O (0.3 mmoles), and $P(O)F_2Cl$ (2.6 mmoles). Phosphorylchloride difluoride was characterized by its vapor pressure (672 torr at 0°),[12] mass spectrum, IR spectrum, and ^{19}F and ^{31}P NMR spectra.[18,19]

7) $BrPF_2$ and NO Two methods were used for these materials. The first method involved condensing $BrPF_2$ (2.5 mmoles) and NO (5.1 mmoles) into an evacuated 200 ml vessel equipped with a greaseless stopcock. The tube was isolated from the system and held at ambient temperature for 7 hr. At the end of this time the volatile materials were reintroduced to the vacuum system and fractionated. Quantitative recovery of these materials was obtained and thus no reaction had occurred. The second method involved condensing $BrPF_2$ (2.6 mmoles) and NO (5.2 mmoles) into an evacuated 200 ml quartz vessel fitted with a greaseless stopcock. The bulb was removed from the system, warmed to ambient temperature and irradiated using a Hanovia medium pressure 450 watt mercury lamp. After 7 hr all volatile materials were removed and fractionated Nitrogen (1.2 mmoles) was removed by a Toepler pump. The remaining volatile materials were fractionated and identified as unreacted NO (1.6 mmoles), N_2O (0.4 mmoles), and $P(O)F_2Br$ (2.6 mmoles). A trace of Br_2 was also detected. Phosphorylbromide difluoride was characterized by its vapor pressure (199 torr at 0°),[12] mass spectrum, IR spectrum, and ^{19}F and ^{31}P NMR spectra.[18,19]

8) IPF_2 and NO Iododifluorophosphine (2.4 mmoles) and NO (4.9 mmoles) were condensed into an evacuated 200 ml vessel equipped with a greaseless stopcock. The bulb was removed from the vacuum system. Upon warming to ambient temperature, a reaction was evidenced by the formation of a violet colored cloud. The reaction appeared to be complete after several minutes. The vessel was reattached to the vacuum system and all volatile materials removed. Nitrogen (1.2 mmoles) was removed by a Toepler pump. The remaining volatiles were fractionated on a low temperature distillation column and identified as unreacted NO (1.2 mmoles), N_2O (0.4 mmoles), $P(O)F_2I$ (~0.4 mmoles), $P_2O_3F_4$ (~0.2 mmoles), and I_2 (0.8 mmoles). The bulb also contained a nonvolatile material which was not characterized. μ-Oxobisphosphoryldifluoride was identified by its mass spectrum, IR spectrum, and ^{19}F and ^{31}P NMR spectra.[18,19] The phosphoryldifluoride iodide could not be obtained pure since it readily decomposed upon warming to ambient temperature. Its decomposition yielded I_2, $P_2O_3F_4$ and a nonvolatile material. It was characterized by its mass spectrum (m/e (intensity), ion): 212 (100.0), $P(O)F_2I^+$; 193 (4.1), $P(O)FI^+$; 186 (2.0), $P_2O_3F_4^+$; 127 (42.8), I^+; 85 (67.3), $P(O)F_2^+$; 69 (28.6), PF_2^+; 66 (10.2), OPF^+; 50 (6.1), PF^+; 47 (12.2), PO^+. The ^{19}F NMR spectrum at −20° consisted of a doublet ($\delta_{^{19}F} = -6.4$ ppm) with $J_{PF} = 1263.8$ Hz, and the ^{31}P NMR spectrum at −20° consisted of a triplet ($\delta_{^{31}P} = -29.0$ ppm).

9) HPF_2 and NO In a typical experiment, HPF_2 (2.5 mmoles) and NO (5.1 mmoles) were condensed into a 200 ml vessel equipped with a greaseless stopcock. The bulb was removed from the vacuum system and warmed to ambient temperature. After 2 hr the volatile components were removed and fractionated. Nitrogen (0.9 mmoles) was removed by a Toepler pump. Other volatile compounds included unreacted NO (1.9 mmoles), N_2O (0.8 mmoles), PF_3 (0.3 mmoles), $(PF_2)_2O$ (0.2 mmoles), $P(O)F_3$ (0.1 mmoles), and a yellow residue. A trace quantity of $P(O)F_2OH$ was identified. The yellow solid was not characterized. Each product was identified by its IR and mass spectra as well as by its ^{19}F and ^{31}P NMR spectra. In another experiment HPF_2 (2.6 mmoles) and NO (5.3 mmoles) were condensed into a 200 ml vessel equipped with a greaseless stopcock. The bulb was removed from the vacuum system and warmed to ambient temperature for 2 hr under the exact conditions as above. At this time the volatile materials were reintroduced to the system and fractionated. No nitrogen was obtained. The volatile compounds included unreacted NO (3.1 mmoles), N_2O (0.6 mmoles), PF_3 (0.7 mmoles), unreacted HPF_2 (0.2 mmoles), $(PF_2)_2O$ (0.1 mmoles), $P(O)F_3$ (0.7 mmoles), $P(O)F_2H$ (0.4 mmoles), and a yellow residue.

10) P_2F_4 and NO In a typical reaction P_2F_4 (2.5 mmoles) and NO (5.0 mmoles) were condensed into an evacuated 200 ml vessel equipped with a greaseless stopcock. The bulb was isolated

from the vacuum system and warmed to ambient temperature. A reaction was evidenced by the formation of a white cloud which rapidly deposited a yellow residue. After 1 hr the volatile components were removed and fractionated. Nitrogen (0.7 mmoles) was removed by a Toepler pump. Other volatiles included unreacted NO (1.7 mmoles), N_2O (0.4 mmoles), PF_3 (0.6 mmoles), $(PF_2)_2O$ (0.5 mmoles), and a trace of $P(O)F_3$. These compounds were characterized by their vapor pressure,[12] IR spectra, mass spectra, and/or ^{19}F and ^{31}P NMR spectra.[18,19] Two additional compounds of unknown composition were also isolated (named unknowns 1 and 2). Both compounds were materials of low volatility. Unknown 1 was thermally unstable and decomposed at ambient temperature with the deposition of a yellow residue. A high resolution mass spectral analysis of this compound yielded an exact mass of the highest observable mass peak of 414.8709. The low resolution mass spectrum exhibited peaks at m/e (intensity) values of 69 (100.0), 85 (16.0), 154 (24.0), 231 (34.0), 250 (96.0), 313 (8.0), 332 (24.0), 396 (1.0), and 415 (4.8). The ^{31}P NMR spectrum consisted of an intense triplet ($J_{PF} = 1365$ Hz; $\delta = +103.6$ ppm) and a weak doublet ($J_{PF} = 1370$ Hz; $\delta = +103.0$ ppm). The ^{19}F NMR spectrum exhibited a single doublet at -31.6 ppm. A high resolution mass spectrum of unknown 2 indicated an exact mass of the highest observable peak to be 663.8002. Fragmentation of this compound produced peaks with the following m/e values: 69 (100.0), 85 (19.2), 88 (23.1), 135 (3.1), 154 (23.1), 170 (34.6), 187 (19.2), 230 (6.5), 315 (11.2), 334 (3.5), 396 (3.5), 415 (3.8), 476 (5.8), 498 (3.5), 581 (3.1), and 664 (0.7). An exact mass determination was performed on the 581 peak and was 580.8176.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support by the National Science Foundation (Grant No. 77-08310). This work was initiated while one of us (JDO) was a fellow of the Alexander von Humboldt Foundation at the University of Stuttgart, West Germany. Fruitful discussions and kind hospitality were provided by Professor Ekkehard Fluck and are gratefully acknowledged.

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