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High-Pressure Interaction of Phosphorus Trifluoride with Carbon Dioxide, Carbon Disulfide, and Carbonyl Sulfide[1]

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Phosphorus trifluoride has been found to react with CO_2, CS_2, and COS. At a minimum of 400° (680 atm) or 500° (340 atm) CO_2 reacted forming OPF_3 and CO. When the conditions of 500° (4000 atm) were reached, a 93% conversion of PF_3 was attained. Carbon disulfide reacted at 300° (1350 atm) or 500° (680 atm) forming carbon and SPF_3. The maximum conversion of 70% was obtained at 500° (4000 atm). Carbonyl sulfide reacted in the range 260° (680 atm)–300° (540 atm) forming CO and SPF_3. When the pressure was increased to 3000 atm at 300°, OPF_3 was also formed. The maximum conversion was obtained at 300° (3000 atm) with no appreciable change when more rigorous conditions were employed.

This communication describes the reaction chemistry of PF_3 when combined with CO_2, CS_2, and COS at conditions up to 500° (4000 atm). The previously described interactions[2,3] of PF_3 with O_2, S, Se, and Te indicated that other systems for which PF_3 would be expected to act as a reducing agent[4] should be pressure favored where a coordination complex intermediate could be postulated.[5] Such an intermediate would give rise to a transition state of smaller volume than the isolated reactants which should cause the reaction to be pressure favored.

Experimental Section

All experiments were conducted under conditions at which the compounds were relatively thermally stable to minimize extraneous reactions. When an interaction was not observed at or near ambient conditions, the system was then examined at elevated conditions.

All work at reduced pressures was carried out in a borosilicate glass vacuum system constructed with Teflon stopcocks (Fisher & Porter Co., Warminster, Pa.). High pressures were generated using a gas pressure booster (High Pressure Equipment Co., Erie, Pa.) attached to a high-pressure–high-temperature hydrothermal research unit (Model HB-1B-4, Tem-Press Research, State College, Pa.). The samples were contained in sealed ampoules made from 3-mm diameter thin-walled gold tubing which was placed in a high-pressure reactor. Nitrogen gas was used to generate the desired pressure. At the end of a reaction period the reactor was cooled to −196° before releasing the pressure. The ampoule was removed and placed into an opening device attached to the vacuum line. After warming to room temperature, water, CO_2, and other condensable materials on the surface of the gold tubing were pumped away. The opening device and vacuum line were pretreated with Me_3SiCl or SF_4 to remove any remaining traces of H_2O, and then the ampoule was opened. The substances which volatilized were transferred directly into the vacuum line. Solid material was removed from the ampoule in a glove bag under a N_2 or Ar atmosphere.

All reaction mixtures were separated by using standard vacuum-line fractionation techniques. All yields are based on the amount of PF_3 consumed. All products were identified and confirmed by two or more techniques including infrared spectroscopy, mass spectroscopy, vapor pressure measurements, melting point determinations, and elemental analysis.

All reagents were commercially available and were vacuum distilled just prior to use. Phosphorus trifluoride,[6,7] CO_2,[8] and COS[9] were purified by distilling the sample through a trap cooled to −95° (toluene slush) to remove impurities of low volatility and then retaining the material which stopped in a trap cooled to −160° (isopentane slush). The same procedure was used to purify CS_2[10] using a −78° bath (Dry Ice–acetone mixture) and a −95° bath. All of the reagents were checked for purity by infrared and mass spectroscopy.

Instrumentation. Infrared absorption spectra were obtained in the 4000–300-cm^{-1} region using a Beckman Model IR-10 double-beam, grating spectrophotometer. Volatile materials were confined in a 100-mm gas cell fitted with KBr windows sealed with rubber O rings at reduced pressure. The instrument was calibrated using polystyrene.

The mass spectra were obtained using a Hitachi Perkin-Elmer RMU-7E mass spectrometer with an ionizing potential of 70 eV, a current of 50 μA, an ion source temperature of 150°, an accelerating potential of 3600 V, and a pressure of between 10^{-6} and 5×10^{-5} Torr as measured by the unit's gauge.

Table I. PF_3 and CO_2 System[a]

Pressure, atm	Temp, °C	Conversion, %[b]	Products
4000	350		No reaction
680	400		No reaction
1000	400	12	OPF_3, CO
1350	400	11	OPF_3, CO
4000	400	41	OPF_3, CO
340	500	71	OPF_3, CO, C
4000	500	93	OPF_3, CO, C

[a] Approximately equimolar amounts of each reactant for a total of 1.5–2.5 mmol of reactants. [b] Percent of PF_3 consumed.

Table II. PF_3 and CS_2 System[a]

Pressure, atm	Temp, °C	Conversion, %[b]	Products
4000	290		No reaction
1000	300		No reaction
1350	300	6	SPF_3, C
4000	300	6	SPF_3, C
4000	400	15	SPF_3, C
680	500	53	SPF_3, C
4000	500	70	SPF_3, C

[a] Approximately equimolar amounts of each reactant for a total of 1.5–2.5 mmol of reactants. [b] Percent of PF_3 consumed.

Reaction of PF_3 and CO_2. Phosphorus trifluoride (97.7 mg, 1.11 mmol) and CO_2 (47.1 mg, 1.07 mmol) were condensed into a gold tube at −196°. The tube was sealed and held at 400° (4000 atm) for 24 hr. The gold ampoule was opened and carbon monoxide (~0.4 mmol; identified by infrared spectrum[8]) was recovered as a noncondensable gas. The material which condensed at −196° was passed through a −145° trap (isopentane–pentane slush) into a trap at −196°. The former trap contained OPF_3[9] and CO_2 (83.8 mg, 1.25 mmol) and the latter trap contained PF_3 (42 mg, 0.48 mmol).

Additional experiments are summarized in Table I.

Reaction of PF_3 and CO. Phosphorus trifluoride (88.9 mg, 1.01 mmol) and CO (41 mg, 0.94 mmol) were condensed into a gold tube at −196°. The tube was sealed and held at 500° (270 atm) for 24 hr. The gold tube was opened and the noncondensable material pumped away through a trap cooled to −196°. The trap contained OPF_3 and PF_3 (89 mg, 0.98 mmol; about a 5% reaction based on an analysis of the mass and infrared spectral data).

Reaction of PF_3 and CS_2. Phosphorus trifluoride (76 mg, 0.86 mmol) and CS_2 (59 mg, 0.78 mmol) were condensed into a gold tube at −196°. The tube was sealed and held at 400° (4000 atm) for 24 hr. The gold ampoule was opened and all of the volatile material condensed at −196°. The volatile material was passed through traps cooled to −95 and −145° into a trap at −196°. The first trap contained CS_2 (54 mg, 0.72 mmol), the −145° trap contained SPF_3 (15 mg, 0.13 mmol), and the −196° trap contained PF_3 (64 mg, 0.73 mmol). Carbon remained in the gold tube.

Additional experiments are summarized in Table II.

Reaction of PF_3 and COS. Phosphorus trifluoride (77 mg, 0.87

Table III. PF_3 and COS System[a]

Pressure, atm	Temp, °C	Conversion, %[b]	Products
340	260		No reaction
680	260	1	SPF_3, CO
4000	260	7	SPF_3, CO
135	300	6	SPF_3, CO
270	300	5	SPF_3, CO
540	300	23	SPF_3, CO
3000	300	55	SPF_3, OPF_3, CO, CS_2, C
4000	300	27	SPF_3, OPF_3, CO, CS_2, C
4000	400	52	SPF_3, OPF_3, CO, CS_2, C
340	500	55	SPF_3, OPF_3, CO, CS_2, C
3000	500	50	SPF_3, OPF_3, CO, CS_2, C

[a] Approximately equimolar amounts of each reactant for a total of 1.5–2.5 mmol of reactants. [b] Percent of PF_3 consumed.

mmol) and COS (52 mg, 0.87 mmol) were condensed into a gold tube at −196°. The tube was sealed and held at 400° (4000 atm) for 24 hr. The gold ampoule was opened and a small amount of CO was recovered as a noncondensable gas (~0.3 mmol). The remaining volatile material was passed through traps cooled to −95 and −145° into a trap at −196°. The −95° trap contained a trace of CS_2, the −145° trap contained a mixture of COS, OPF_3, and SPF_3, and the −196° fraction contained PF_3 (37 mg, 0.42 mmol). The gold tube contained carbon.

Additional experiments are summarized in Table III.

Thermal Decomposition of CS_2. Carbon disulfide (120 mg, 1.58 mmol) was condensed into a gold tube at −196°. The tube was sealed and held at 500° (275 atm) for 24 hr. The gold tube was opened and all of the volatile material collected at −196°. This trap contained CS_2 (59 mg, 0.77 mmol). The solid material in the gold tube was washed with CS_2. The soluble portion contained sulfur and the residue was sulfur-free carbon.

In similar experiments no decomposition was observed at 250° (4000 atm) and 40% decomposition took place at 500° (4000 atm).

Attempted Reactions. The following substances were found not to undergo any reaction or decomposition at the indicated conditions: COS [500° (170 atm), 500° (270 atm), 500° (4000 atm)], COS and CS_2 [500° (4000 atm)], CO_2 and CS_2 [450° (4000 atm)].

Results and Discussion

The normal lack of reactivity of PF_3 with CO_2, CS_2, and COS must be due to unfavorable kinetic factors, since the reactions observed in this study are by thermodynamic calculations favored at room temperature and 1 atm pressure. It is postulated for the reactants in this study that the use of high pressure brings about the formation of the weak adduct or intermediate complex required for a bimolecular reaction, thus causing favorable changes in the reaction kinetics. The formation of this complex would cause a reduction in volume of the system causing an increase in the rate of reaction since the rate constant would be expected to change according to the expression

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = -\frac{\Delta V^*}{RT}$$

where the activation volume (ΔV^*) represents the difference in the partial molar volumes of the transition state and the reactants. Therefore when the volume of the transition state is less than the volume of the reactants, ΔV^* will be negative and the rate constant increases.[2]

It has been established that PF_3 can act as either a Lewis base or a Lewis acid. Examples of Lewis base behavior would include PF_3 transition metal complexes[4] or $PF_3 \cdot BH_3$ addition complexes.[12] Phosphorus trifluoride is a very weak Lewis acid; however it interacts strongly with liquid hydrogen sulfide forming the postulated PF_3SH^- intermediate

$$PF_3 + SH^- \rightarrow PF_3SH^-$$

which spectral data indicates may rearrange to $HPSF_3^-$.[13] In addition a weak adduct with trimethylamine has been reported.[14]

The system PF_3–CO_2 is summarized in Table I. It should be noted that below 400°, pressure alone does not change the system enough for any reaction to take place. However, at 400° the influence of pressure is clearly demonstrated by the increase in amount of reaction forming OPF_3 and CO as the pressure is increased from 680 to 4000 atm.

$$PF_3(g) + CO_2(g) \rightarrow OPF_3(g) + CO(g)$$

When the system is heated to 500°, a more complex reaction takes place which is best described by the overall equation

$$3PF_3(g) + 2CO_2(g) \rightarrow 3OPF_3(g) + CO(g) + C(s)$$

which describes the process as observed in this study.

The formation of C can be explained by the reaction

$$PF_3(g) + CO(g) \rightarrow OPF_3(g) + C(s)$$

which is observed at 500° (270 atm). The overall reaction is therefore most likely a two-step process

$$PF_3(g) + CO_2(g) \rightarrow OPF_3(g) + CO(g)$$

$$PF_3(g) + CO(g) \rightarrow OPF_3(g) + C(s)$$

If the reactions are carried out with a sufficient amount of PF_3, all of the CO is then consumed.

The interaction of CS_2 with PF_3 is similar to that of CO_2; however, it is complicated by the thermal decomposition of CS_2. This decomposition is not seen at 250° (4000 atm) and it should also be noted that the amount of thermal decomposition to carbon and sulfur is reduced at 500° when increasing the pressure from 275 to 4000 atm. Polymeric $(CS_2)_n$ has been synthesized at temperatures over 175° and at pressures with an excess of 10,000 atm; however, none of this material was observed in this study.[15-17] In addition no evidence exists for the formation of $(CS)_n$, even though free sulfur was observed.[18] No thermal decomposition of CS_2 is observed at 450° (4000 atm) in the presence of CO_2 or at 500° (4000 atm) when mixed with COS.

No interaction between PF_3 and CS_2 is observed below 290° (4000 atm). At 300° no interaction takes place at 1000 atm, but at 1350 atm reaction is observed, viz.

$$2PF_3(g) + CS_2(g) \rightarrow 2SPF_3(g) + C(s)$$

Interestingly, no further increase in yield is noted up to 300° (4000 atm). At 400° (4000 atm) a 15% conversion is obtained with a 70% yield being realized at 500° (4000 atm). The effect of temperature is noted by the 53% conversion at 500° (680 atm) as compared to the need for higher pressures for a reasonable yield at lower temperatures.

There appears to be the possibility of two reaction routes. First, a reaction which is initiated by the thermal decomposition of CS_2 to CS and S or to C and S

$$CS_2(g) \rightarrow CS(g) + S(s)$$

$$CS_2(g) \rightarrow C(s) + 2S(s)$$

$$CS(g) + PF_3(g) \rightarrow C(s) + SPF_3(g)$$

$$S(s) + PF_3(g) \rightarrow SPF_3(g)$$

The last reaction is most reasonable since in an earlier study[2] it was shown that at 300° (4000 atm) S and PF_3 reacted nearly quantitatively and at 300° (800 atm) a 50% conversion was obtained.

Second, at higher pressures a complex reaction intermediate could form between CS_2 and PF_3, viz.

$$CS_2(g) + PF_3(g) \rightarrow SCS \cdot PF_3(g)$$

The intermediate can then decompose forming SPF_3 and CS

$$CS_2(g) + PF_3(g) \rightarrow CS(g) + SPF_3(g)$$

$$CS(g) + PF_3(g) \rightarrow C(s) + SPF_3(g)$$

The reactions of PF_3 with COS are observed at less rigorous conditions than for the PF_3 reactions with CO_2 or CS_2. Previous workers[19] have shown that COS thermally decomposes via two independent simultaneous equilibria

$$2COS(g) \rightleftarrows CO_2(g) + CS_2(g)$$

$$COS(g) \rightleftarrows CO(g) + S(s)$$

It has been noted that these reactions were sensitive to the vessel used for reaction. For example, more decomposition was noted when "Jena" glass vessels were used or when silica was placed in a "Pyrex" vessel than for a clean Pyrex reaction. In this study no decomposition is noted at 500° and at 170, 270, or 4000 atm or for a mixture of COS and CS_2 at 500° (4000 atm).

Table III summarizes these most interesting experiments. If excess PF_3 is employed at the given conditions, complete reactions are observed. The reported experiments show the range of products which are obtained.

No reaction of any kind is observed below 260° (680 atm); however, at these conditions small amounts of CO and SPF_3 are recovered

$$PF_3(g) + COS(g) \rightarrow CO(g) + SPF_3(g)$$

The amount of reaction increases with more rigorous conditions until a 23% conversion is obtained at 300° (540 atm).

When the pressure is increased to 3000 atm at 300°, more than 50% of the PF_3 is consumed, with no apparent change in the amount of conversion at 4000 atm. When a large excess of PF_3 is not employed, the products include SPF_3, OPF_3, CS_2, CO, and carbon. At 500° and a minimum pressure of 340 atm the same products are obtained.

The products can all be rationalized by postulating an initial complex between the carbonyl sulfide and phosphorus trifluoride. There actually are two possible intermediates which fit the experimental data, $OCS{\cdot}PF_3$ and $SCO{\cdot}PF_3$. The complex decomposes forming CO and SPF_3 or CS and OPF_3. The former would appear to explain the reactions at lower temperatures and pressures. Both interactions may take place at increased pressure or temperature. The following reaction sequence may be postulated for the formation of CS_2

$$COS(g) + PF_3(g) \rightarrow SPF_3(g) + CO(g)$$

$$COS(g) + PF_3(g) \rightarrow OPF_3(g) + CS(g)$$

$$COS(g) + CS(g) \rightarrow CO(g) + CS_2(g)$$

The carbon can then be formed by the reaction

$$CO(g) + PF_3(g) \rightarrow OPF_3(g) + C(s)$$

The formation of a complex where PF_3 acts as a Lewis acid can be used to explain all of the observed initial reactions of CO_2, CS_2, and COS with PF_3. In this study the products at even the lowest set of physical conditions can be postulated as arising from the abstraction of a chalcogen atom by PF_3. Consider COS as a Lewis base

$$:\ddot{O}{=}C{=}\ddot{S}:$$

interacting with the expanded octet of PF_3, viz.

$$\underset{\cdot\cdot}{\ddot{O}}{=}C{=}\ddot{S}\rightarrow\ddot{P}F_3$$

The complex will then decompose forming SPF_3 and CO.

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Registry No. PF_3, 7783-55-3; CO_2, 124-38-9; CS_2, 75-15-0; COS, 463-58-1; OPF_3, 13478-20-1; SPF_3, 2404-52-6.

References and Notes

(1) This report is based on portions of a dissertation submitted by B. W. Callaway to the Graduate College of The University of Oklahoma in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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Enthalpy of Formation of Neodymium Dichloride and Thulium Dichloride

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Well-characterized samples of $NdCl_{2.06}$ and $TmCl_2$ were allowed to react in a solution microcalorimeter with HCl(aq). From measured heats of solution and from related thermochemical data, the enthalpies of formation of $NdCl_2(c)$ and $TmCl_2(c)$ have been calculated to be -706.9 ± 4.2 and -709.1 ± 4.2 kJ mol^{-1}. The energetics of oxidation and hydration of all the dipositive lanthanide ions have been calculated and correlated; in particular, $\Delta H_f°(Nd^{2+}(aq))$ and $\Delta H_f°(Tm^{2+}(aq))$ are estimated to be -402 and -442 kJ mol^{-1}.

Introduction

The dihalides of samarium, europium, and ytterbium have been known since the beginning of this century. However, only in 1959 was it reported by Druding and Corbett that certain other lanthanide metals were sufficiently soluble in the corresponding molten trihalides that stoichiometric dihalides could be identified on phase diagrams and isolated from the solid solutions.[1] Many of these halides are saline, and the phase diagrams and physical properties of most dihalides were reviewed by Brown in 1968.[2] More recently, Corbett has published an extensive review of the preparation and stabilities of reduced rare earth halides.[3]

Although the reasons for the stability of lanthanide dihalides with respect to the disproportionation reaction

$$3MX_2(c) = 2MX_3(c) + M(c) \qquad (1)$$

are well known,[3-5] very few studies of the stability of the