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High-Pressure Reactions of Small Covalent Molecules. 10. The Reaction of PF_3 with H_2S and SO_2[1]

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Phosphorus trifluoride reacts with sulfur dioxide and hydrogen sulfide at increased pressure. The reaction yields within 24 h are greatly influenced by pressure. The sulfur dioxide reaction forms sulfur and OPF_3 in a 4% yield at 150 °C (670 atm) and 84% yield at 150 °C (4000 atm). The hydrogen sulfide interaction leads to a 3% yield of SPF_3 and hydrogen at 200 °C (1350 atm) and a 35% yield at 200 °C (4000 atm). When longer reaction times are used, both reactions become nearly quantitative which indicates pressure is changing the rate of the reaction. This rate increase supports a mechanism in which the rate-determining step involves a bond formation rather than an initial decomposition of sulfur dioxide or hydrogen sulfide.

Phosphorus trifluoride has been shown to react at increased pressure with sulfides and oxides.[2-4] For example, when PF_3 was combined with nickel(II) oxide, $Ni(PF_3)_4$ and OPF_3 were obtained, and when it reacted with carbon dioxide, OPF_3 and C or CO were formed. In this investigation, phosphorus trifluoride has been found to react with sulfur dioxide at 130 °C (3000 atm) and with hydrogen sulfide at 150 °C (4000 atm).

Results and Discussion

Tables I and II summarize the experimental results when the samples are at the given conditions for 24 h. When the reaction period is longer, the quantity of material reacting increases and the reactions become essentially quantitative. Therefore the temperature and pressure changes are indicative of a rate change rather than a shift in equilibrium.

Sulfur dioxide is a well-known reducing agent. It has also been shown to oxidize $(CH_3)_3P$, $(C_6H_5)_3P$, and PBr_3 at 185 °C in sealed silica tubes[5] and PCl_3 at 550 °C in a flow reactor.[6] In this study sulfur dioxide was found (Table I) to oxidize PF_3 at the minimum conditions 130 °C (3000 atm), 150 °C (670 atm), and 200 °C (335 atm) forming OPF_3 and sulfur:

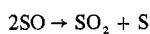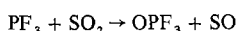$$2PF_3 + SO_2 \rightarrow 2OPF_3 + S$$
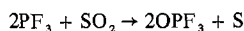
The lack of SPF_3 in all of the experiments was surprising, since phosphorus trifluoride readily reacts with sulfur at increased pressure[2] to form SPF_3. The relative amounts of SO_2 and PF_3 were varied in experiments additional to those listed in Table I at pressures up to 4000 atm and at temperatures up to 500 °C in an attempt to isolate SPF_3, but none was detected. It was found, however, at the mildest conditions where SO_2 and PF_3 interact, SPF_3 reacts with SO_2 to form OPF_3 and sulfur:

$$2SPF_3 + SO_2 \rightarrow 2OPF_3 + 3S$$
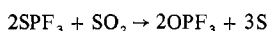
The lack of SPF_3 can therefore be explained if the rate of its reaction with SO_2 is greater than the rate of the reaction of PF_3 with sulfur.

It is reasonable to postulate that the overall reaction of PF_3 with SO_2 is a two-step process:

$$PF_3 + SO_2 \rightarrow OPF_3 + SO$$
$$2SO \rightarrow SO_2 + S$$

Since this reaction shows pressure dependence at relatively low

Table I. Sulfur Dioxide Reactions

P, atm	T, °C	% conversion[a]	Amt of reactants, mmol		Amt of material out,[b] mmol		
			PF_3	SO_2	PF_3	SO_2	OPF_3
4000	100		0.81	0.75	0.80	0.74	
2000	130		0.81	0.82	0.80	0.80	
3000	130	14	0.83	0.84	0.71	0.78	0.12
4000	130	14	0.84	0.83	0.72	0.77	0.12
335	150		0.84	0.85	0.83	0.83	
670	150	4	0.91	0.89	0.87	0.87	0.04
1350	150	10	0.87	0.85	0.78	0.82	0.09
4000	150	84	0.83	0.84	0.13	0.49	0.70
335	200	6	0.82	0.82	0.77	0.80	0.05
2670	200	80	1.13	0.90	0.23	0.54	0.90
4000	200	88	0.82	0.86	0.10	0.48	0.72

[a] Based on mmol of PF_3 consumed. All experiments were for 24 h. [b] The amount of sulfur can be calculated from the material balance.

Table II. Hydrogen Sulfide Reactions

P atm	T, °C	% conversion[a]	Amt of reactants, mmol		Amt of material out,[b] mmol		
			PF_3	H_2S	PF_3	H_2S	SPF_3
2000	150		0.66	0.65	0.65	0.64	
4000	150	3	0.74	0.78	0.72	0.76	0.02
670	200		0.92	0.91	0.92	0.91	
1350	200	3	0.87	0.84	0.84	0.81	0.03
4000	200	35	0.75	0.77	0.49	0.49	0.28
670	500	32	1.11	1.19	0.75	0.85	0.34
3300	500	40	0.86	0.87	0.52	0.52	0.35

[a] Based on mmol of PF_3 consumed. All experiments were for 24 h. [b] The amount of hydrogen can be calculated from the material balance.

pressures and temperatures and since we have no evidence for any thermal decomposition of the SO_2 at the same conditions, it is most reasonable that the reaction takes place via a coordinated intermediate rather than by an initial thermal decomposition of sulfur dioxide.

The reactions with H_2S are summarized in Table II. At conditions above 150 °C (4000 atm) or 200 °C (1350 atm) the reaction is

$$PF_3 + H_2S \rightarrow H_2 + SPF_3$$
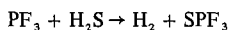
The series of reactions at 200 °C (670, 1350, and 4000 atm) shows the effect of pressure on this reaction. The reaction most likely takes place by a direct reaction of H_2S with PF_3 since there is no evidence for any uncombined sulfur in the reaction ampoule. For example, no sulfur or hydrogen was obtained when hydrogen sulfide was heated at the same conditions as given in Table II in the absence of PF_3. In addition, no sulfanes (H_2S_n) were noted in any experiments even though they would have been expected from the reaction of liquid sulfur and hydrogen sulfide.[7]

It is not unreasonable that a S–P-bonded intermediate forms in this reaction. This intermediate would be analogous to the known complex π-$C_5H_5(CO)_2Mn(SH_2)$[8] which has limited stability at room temperature. In addition, this step would agree with the generally accepted hypothesis that insoluble sulfides of ions of high field strength (e.g., Hg^{2+}, Ag^+) are formed by an initial coordination of H_2S followed by the removal of the protons.[9]

The influence of pressure on these reactions is shown by the data in Tables I and II. While precise kinetic data are difficult to obtain for these reaction systems, it is obvious that an increase in pressure increases the rate of reaction. It is not reasonable to assume that the only role of the applied pressure is to increase the concentration of the gaseous reactants. Consider the data at 150 °C for the sulfur dioxide reactions (Table I). No reaction is observed at 335 atm, but a measurable amount of material is obtained at pressures in excess of 670 atm. Since the concentration of the reacting fluids would be expected to change little upon going from 335 to 670 atm as compared to the change from 1 to 335 atm, the dramatic rate increase must come from a change in the rate constant.

The rate change therefore can be explained by postulating a mechanism which has a negative activation volume:

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

Such a mechanism could have a transition state which involves a bond formation as has been postulated for these reactions.

Experimental Section

All work was carried out in a borosilicate glass vacuum system constructed with Teflon stopcocks (Fischer & Porter Co., Warminster, Pa., No. 795-005-0004). High pressures were generated using a gas pressure booster manufactured by High Pressure Equipment Co., Erie, Pa. The samples were contained in sealed ampules made from 3-mm diameter thin-walled gold tubing which were placed in a high-pressure microreactor (Autoclave Engineers, Erie, Pa.). Nitrogen gas was used to generate the desired pressure. At the end of a reaction period the microreactor was cooled to –196 °C before the pressure was released. Then the frozen ampule was placed in an opening device attached to the vacuum line. Water and other condensable materials on the surface of the gold tubing were removed and then transferred directly into the vacuum line. Infrared spectra were recorded on a Beckman Model IR-10 double-beam grating spectrophotometer. Volatile materials were confined at reduced pressure in a 10-cm cell fitted with KBr or AgCl windows sealed with rubber O-rings. Mass spectra were taken at 70-eV energies on a Hitachi Perkin-Elmer RMU-6E mass spectrometer at 150 °C. The purity and identification of all materials were determined by two or more criteria including the above instrumental methods in addition to gas-phase molecular weight determinations and vapor pressure and melting point measurements.

Specific Procedure. Phosphorus trifluoride (74 mg, 0.84 mmol) and SO_2 (53 mg, 0.83 mmol) were condensed into a gold tube. The tube was sealed and held at 130 °C (4000 atm) for 24 h and then opened into the vacuum system. The volatile material was passed through a trap cooled to –126 °C (methylcyclohexane slush) into a trap at –196 °C. The former trap contained OPF_3 (12 mg, 0.12 mmol) and SO_2 (49 mg, 0.77 mmol) and the latter contained PF_3 (63 mg, 0.72 mmol); these were identified by their infrared spectra and confirmed by their mass spectra. Approximately 2 mg of sulfur remained in the gold tube. Additional experiments are summarized in Table I.

In a series of related experiments PF_3 and H_2S were combined. The yield and stoichiometry of the reactions were determined by measuring the total amount of material recovered. The experiments are summarized in Table II.

Registry No. PF_3, 7783-55-3; SO_2, 7446-09-5; H_2S, 7783-06-4; OPF_3, 13478-20-1; SPF_3, 2404-52-6.

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