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REACTION OF PHOSPHORUS TRIFLUORIDE AND THIOPHOSPHORYL FLUORIDE WITH IODINE MONOCHLORIDE AND OXIDATION OF PHOSPHORUS TRIFLUORIDE WITH NITRYL CHLORIDE, IODIC ACID, PERIODIC ACID, SODIUM NITRITE AND POTASSIUM NITRITE

H.P. Sampath Kumar* and D.K. Padma**

Department of Inorganic and Physical Chemistry
Indian Institute of Science, Bangalore-560 012 (India)

SUMMARY

Phosphorus trifluoride and thiophosphoryl fluoride both react smoothly with iodine monochloride at room temperature to form dichlorotrifluorophosphorane. The oxidants, nitryl chloride, iodic acid and periodic acid undergo reduction to nitrosyl chloride and iodine respectively, oxidising the phosphorus trifluoride to phosphoryl fluoride. The nitrite salts of sodium and potassium also undergo reduction at elevated temperatures(200°C) with phosphorus trifluoride and then react further with the formed phosphoryl fluoride to yield the corresponding monofluorophosphates of sodium and potassium.

* Current address: P.O.Box 870336, Department of Chemistry, The University of Alabama, Tuscaloosa AL 35487, U.S.A.

** Author to whom correspondence should be addressed.

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INTRODUCTION

In continuation of our work on PF_3 oxidations [1,2] we herein report interesting chlorooxidation of both PF_3 and PSF_3. PF_3 undergoes oxidation with nitryl chloride, iodic acid, periodic acid, sodium and potassium nitrites. These oxidations have not previously been reported in the literature. The products have been identified by infrared spectra and have been separated by low temperature fractional distillation in case of gases, and solids have been recrystallized from methanol - water mixtures. The products have been characterized by ir data and chemical analysis after hydrolysis. The reactions have been carried out in strictly anhydrous conditions with dry reagents, as the gases have a tendency for hydrolysis and PSF_3 catches fire when exposed to air and is toxic.

EXPERIMENTAL

Reagents and Methods

Phosphorus trifluoride[3] thiophosphoryl fluoride[4] and nitryl chloride[5] were prepared and stored in previously evacuated glass globes. Iodine monochloride, iodic acid, periodic acid, sodium

nitrite and potassium nitrite (BDH Analar grade) were used without further purification.

The infrared spectra of gaseous compounds were recorded using a 10 cm gas cell, fitted with KBr windows on a PE-599 IR spectrophotometer (Perkin Elmer). The spectra of solid samples were recorded as pellets in vacuum oven dried KBr. The X-ray powder diffractograms of the solid samples were recorded on a Phillips instrument PW 1050/70 diffractometer with Cu-Kα radiation.

Reaction of Phosphorus Trifluoride with Iodine Monochloride

Known amounts of PF_3 (Table 1) were frozen under liquid nitrogen in an evacuated reaction trap fitted with Teflon vacuum stopcocks and g.g. joints. Adequate amounts(Table 1) of iodine monochloride were condensed over it. The reactants were then thawed to room temperature. Crystals of iodine collected on the sides indicate reaction. After an interval of 5-10 minutes, the IR spectrum of the gaseous products were recorded. The spectra indicated completion of reaction as the characteristic absorption peaks of PF_3 [6] were absent. Three very strong absorptions at 925 cm^{-1}, 893 cm^{-1} and 665 cm^{-1} and

TABLE 1

Oxidation of Phosphorus trifluoride with Iodine monochloride

	Sl.No.	Weight of reactants in mg		Mole Ratio PF_3:ICl	Weight of Iodine in mg		Percentage oxidation	Weight of excess Iodine monochloride in mg	
		Phosphorus trifluoride	Iodine monochloride		Calc.	Found		Calc.	Found
Excess Iodine monochloride	1	163.0	750.0	0.40	470.4	466.0	99.06	148	146
	2	158.0	665.0	0.44	456.0	451.0	98.90	81	80
	3	145.0	595.0	0.45	418.5	414.0	98.92	59	58
Excess Phosphorus trifluoride	1	352.7	650.0	1.00	508.0	502.2	98.86	--	--
	2	267.6	490.4	1.01	383.0	379.0	98.95	--	--
	3	160.6	290.0	1.02	226.0	223.6	98.93	--	--

675 cm^{-1} (doublet) could be assigned to dichlorotrifluorophosphorane[7]. In addition there were weak absorptions corresponding to hydrogen chloride[8] [2990 cm^{-1}]and phosphoryl fluoride[9]. These are due to hydrolysis of PF_3Cl_2 with trace amounts of water. At the end of the reaction, the products were separated and the iodine present along with the excess of iodine monochloride in the reaction vessel was extracted with carbon tetrachloride. The solution was shaken with strong hydrochloric acid to carry the iodine monochloride to the acid layer. The iodine in the carbon tetrachloride layer was estimated by titration against potassium iodate solution[10] and the iodine monochloride in the hydrochloric acid layer by titration against hydrazine sulphate solution[11]. A blank experiment was run to confirm nondissociation of iodinemonochloride under these experimental conditions. The results of these analyses are given in Table 1.

The reaction of thiophosphoryl fluoride with iodine monochloride

The experimental set up was similar. In addition to the liberated iodine and dichlorotrifluorophosphorane, a dull yellow white solid, was formed. This solid was identified as elemental sulfur by its reaction with mercury and formation of a red solution with piperidine. When excess of iodine monochloride was present, the sulphur

partly reacted further to form yellow droplets, inside the reaction vessel, identified as disulphur dichloride, by ir spectral data and chemical analysis.

Reaction of phosphorus trifluoride with nitryl chloride (NO_2Cl)

Phosphorus trifluoride(1.793 mmoles) was condensed in the reaction trap, followed by a condensation of an excess of nitryl chloride(2.654 mmoles). The reactants were then thawed to room temperature. At the end of 2 hours, the IR spectrum of the gas product was obtained. The spectrum indicated completion of reaction (absence of PF_3 modes of vibration) and presence of POF_3 [9] (indicating oxidation of PF_3), along with nitrosyl chloride (NOCl) (the reduction product)[12] and excess nitryl chloride [13]. All the three gases were separated by fractional distillation and individually characterized.

Reaction of thiophosphoryl fluoride with nitryl chloride

This reaction does not take place either at room temperature or upto 100°C, though it is thermodynamically favoured to form PCl_2F_3, [ΔG° = -41 kcal mol^{-1}].

Reaction of phosphorus trifluoride with iodic acid and periodic acid

Phosphorus trifluoride (1-2 mmoles) was condensed over an excess of iodic acid/periodic acid(4-5 mmoles) in the reaction vessel along with a magnetic stirrer. The reactants were then thawed to room temperature and the solid agitated. The reaction vessel was protected from light. The reaction proceeded at room temperature as seen from the appearance of iodine vapours. At the end of one hour, the gaseous IR spectrum indicated absence of PF_3 [6] and indicated completion of reaction at room temperature. The other vibrations could be assigned to those of phosphoryl fluoride as well as difluorophosphoric acid, HPO_2F_2, [14] and silicon tetrafluoride [15]. The IR spectra of the solid residue was similar to those of iodic acid/periodic acid indicating that no other solid product was formed.

Reactions of PCl_3 and PBr_3 with iodic acid and periodic acid were carried out similarly. These reactions were found to be violent (accompanied by liberation of heat/flame). However, in the presence of carbon tetrachloride as solvent, the reaction was smooth giving rise to oxyhalides, $POCl_3$ and $POBr_3$, with release of iodine which was estimated.

Reaction of phosphorus trifluoride with sodium nitrite and potassium nitrite

The solid nitrites were dried in vacuum at 100°C for about 2 hours. Equimolar amounts (1-2 mmoles) of the nitrite and phosphorus trifluoride were heated to 200°C (as room temperature reaction was sluggish) for 2 hours. During this period, the PF_3 was consumed as seen from the IR spectrum of the gaseous products. The IR spectrum indicated the presence of nitric oxide(obs. 1875 cm^{-1}, reported [16] 1875 cm^{-1}) and phosphoryl fluoride[9]. If the reaction mixture was heated at 200°C for 4 hours, then the gaseous product was only nitric oxide. The solid left in the reaction vessel contained absorptions due to sodium monofluorophosphate[17] and sodium nitrate[19]. The X-ray powder diffractogram of the solid mixture confirmed the presence of sodium monofluorophosphate, sodium fluoride, sodium nitrite and sodium nitrate. Potassium nitrite underwent similar reaction.

RESULTS AND DISCUSSION

The results in Table 1 indicate that phosphorus trifluoride undergoes easy oxidative chlorine addition at room temperature in presence of iodine monochloride. The overall reaction may be represented as

$$PF_3 + ICl \longrightarrow PF_3Cl_2 + I_2$$

The reaction of thiophosphoryl and iodine monochloride occurs at room temperature. The phosphorus sulphur bond undergoes cleavage and chlorine is inserted to form dichlorotrifluorophosphorane. The cleaved sulphur undergoes partial oxidation at room temperature with iodine monochloride to form sulphur monochloride as has been confirmed in a separate experiment between elemental sulphur and iodine monochloride. In all cases elemental iodine is formed.

Nitryl chloride(NO_2Cl) reacts with phosphorus trifluoride at room temperature by oxidising the P(III) to P(V) and forming phosphoryl chloride and nitrosyl chloride (NOCl). Nitryl chloride does not react with PSF_3.

The interesting reactions of PF_3 with iodic acid and periodic acid lead to the formation of difluorophosphoric acid (HPO_2F_2) and silicon tetrafluoride in addition to the oxidative product POF_3. The water formed in the course of reaction hydrosyles POF_3 and forms the acid and HF. The SiF_4 results from the reaction of HF with glass.

The reactions of PCl_3 and PBr_3 with HIO_3 and H_5IO_6 take place with high exothermicity at room temperature to form phosphoryl halide (chloride, bromide), iodine and water. The water partially hydrolyses the phosphorus halides. Presence of a solvent moderates the reaction.

Sodium nitrite and potassium nitrite oxidise phosphorus trifluoride only at elevated temperatures to form phosphoryl fluoride and nitric oxide. At these temperatures phosphoryl fluoride undergoes partial reaction with the sodium salt to form the more stable sodium/potassium monofluorophosphate.

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