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INVESTIGATIONS ON THE PREPARATION, OXIDATION AND REDUCTION REACTIONS OF
THIOPHOSPHORYL FLUORIDE

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SUMMARY

Pure thiophosphoryl fluoride has been prepared by the fluorination of thiophosphoryl chloride by sodium fluoride in acetonitrile medium. Oxidation of this phosphoryl fluoride by acidified chloramine-T ruptures the phosphorus-sulphur bond and oxidises the sulphur present to the hexavalent state. Anhydrous hydrogen iodide reduces the sulphur to hydrogen sulphide and phosphorus to the trivalent state.

INTRODUCTION

Thiophosphoryl fluoride is one of the most reactive compounds. The manufacturing process is invariably covered in patent literature without giving experimental details [1]. In the laboratory it is generally prepared by fluorination of phosphorus sulphide or thiophosphoryl chloride [2, 3, 4]. In the latter procedure the thiophosphoryl fluoride (PSF_3) is contaminated heavily with other chlorofluorides of phosphorus. In the present investigation a method has been standardised for the preparation of a pure sample of thiophosphoryl fluoride by fluorinating thiophosphoryl chloride in acetonitrile medium with sodium fluoride. With this pure sample, oxidation reduction behaviour of thiophosphoryl fluoride has been investigated making use of chloramine-T and hydrogen iodide respectively. Experimental results are presented in this paper.

EXPERIMENTAL

A. Preparation of pure thiophosphoryl fluoride

A 500 ml tree necked flask with ground glass joints is provided with a dropping funnel equipped with a pressure equalising side tube, an efficient reflux condensor containing ice cold water and a nitrogen inlet. The ground glass connections are lubricated with Kel-F halocarbon stopcock grease. The top of the reflux condenser is connected to two traps, one cooled to -40°C and the other by liquid nitrogen. The apparatus is thoroughly dried before use and is protected from moisture during the preparation. The flask is heated with the help of an isomantle. 10 grams of dry sodium fluoride and 100 ml of acetonitrile are taken in the flask. 3 ml of thiophosphoryl chloride dissolved in 25 ml of acetonitrile are placed in the dropping funnel. A stream of nitrogen is passed through the apparatus throughout the experiment. The contents of the flask are refluxed for 10 minutes. The thiophosphoryl chloride solution is then added slowly dropwise to the suspension of sodium fluoride in boiling acetonitrile during a period of one hour. The liberated gas is swept in a current of nitrogen. The issuing gaseous mixture is cooled and condensed in the two traps. Escaping vapours of acetonitrile are condensed in the trap (I) at -40°C and thiophosphoryl fluoride condenses in the trap (II) cooled by liquid air. When evolution of gas ceases (about 90 min) the heating is put off. The nitrogen stream is stopped. The trap (II) containing thiophosphoryl fluoride is disconnected from this unit and connected to the vacuum line to remove any uncondensable gas. The gaseous residue is then allowed to sublime into a previously evacuated globe (1 litre). The pressure inside the globe indicated the amount of gas collected.

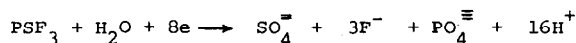
The purity of the gas thus prepared is checked by i.r. spectroscopy, chemical analysis after hydrolysis with alkali and density measurements. The i.r. spectra of the gaseous sample recorded on a UR-10 (Carl zeiss) showed peaks at 990, 980, 973, 951, 944, 702, 694, 685, 447, 430 cm^{-1} . Reported [5]: 989, 981, 973, 952, 945, 703, 695, 686, 448, 431 cm^{-1} , 402, and 284 cm^{-1} . The absence of other peaks indicated that chlorofluoro compounds are not present. An aliquot of the gaseous sample is hydrolysed with alkali (2N) and the amount of sulphur, phosphorus and fluorine are estimated by standard methods (Sulphur: Calcd. 26.71% found 26.68%, Phosphorus: Calcd. 25.83% found 25.78%, Fluorine: Calcd. 47.51% found 47.35%). The above ana-

lytical results indicate that the sample of thiophosphoryl fluoride prepared is over 99.8% pure. On this basis the yield of thiophosphoryl fluoride is found to be 80%. The purity is further checked by measuring the relative density of the gas. (Reported [6]: 5.210 g/l at N.T.P.; found: 5.20 g/l at N.T.P.).

B. Oxidation of thiophosphoryl chloride by chloramine-T.

Chloramine-T is observed to rupture the phosphorus-sulphur bond in a variety of compounds under suitable experimental conditions and oxidise the sulphur present to sulphuric acid [7, 8]. It is of interest to investigate this oxidation reaction with thiophosphoryl fluoride also.

A known excess of acidified chloramine-T is sucked into a flask containing a known amount of thiophosphoryl fluoride. The reaction is allowed to take place for 2 h and excess chloramine-T is estimated iodometrically. It is possible to calculate from the titre values the number of equivalents of the oxidising agent required for 1 mole of thiophosphoryl fluoride for complete oxidation. Stoichiometry of the reaction can be represented by the equation



The products of the reaction namely sulphate, fluoride and phosphate could be identified by standard methods and checked by quantitative analysis. The results of a few representative experiments are presented in Table 1.

TABLE 1

Oxidation of thiophosphoryl fluoride by chloramine-T

Expt. No.	PSF ₃ taken moles x 10 ⁻⁴	Equivalents of chloramine-T consumed x 10 ⁻⁴	Equivalents of chloramine-T consumed per mole of PSF ₃
1	0.783	6.28	7.87
2	1.625	12.79	7.88
3	1.750	13.80	7.88
4	2.925	23.00	7.88

It is evident from the analytical results that eight equivalents of chloramine-T are required for every mole of thiophosphoryl fluoride and corresponds to the stoichiometric expectations.

C. Reaction of thiophosphoryl fluoride with anhydrous hydrogen iodide

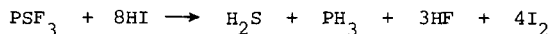
Anhydrous hydrogen iodide is observed to bring the fission of the phosphorus-sulphur bond in thiophosphoryl chloride [7] and reduces sulphur to hydrogen sulphide and phosphorus to trivalent state. It is of interest to investigate whether anhydrous hydrogen iodide would bring about similar reduction in thiophosphoryl fluoride also. A known amount of thiophosphoryl fluoride is taken in a reaction vessel and treated with excess anhydrous hydrogen iodide. In a few instances an inert solvent like carbon tetrachloride is also introduced. As the reaction is found to be slow, the reactants are left overnight for completion. Iodine is found deposited on the walls of the reaction vessel. The gaseous products are then swept in a current of nitrogen and passed through a bubbler (1) containing chilled (0°C) carbon tetrachloride (to remove any iodine that might sublime in the flushing stream), bubbler (2) containing a suspension of cadmium hydroxide in alkali (to absorb hydrogen sulphide) and then through a bubbler (III) containing a solution of silver nitrate (1%), to remove any phosphorus compound. The hydrogen sulphide trapped in the second trap as cadmium sulphide is estimated iodometrically. Iodine found in the reaction vessel and carbon tetrachloride medium is estimated by titrating against standard sodium thiosulphate. The results are given in Table 2.

TABLE 2

Reduction of thiophosphoryl fluoride by anhydrous hydrogen iodide

Expt. No.	Medium	PSF ₃ taken moles x 10 ⁻⁴	H ₂ S formed moles x 10 ⁻⁴	Iodine liberated per mole of PSF ₃
1	gas phase	4.464	4.447	1.46
2	gas phase	5.353	5.350	1.51
3	CCl ₄	4.464	4.451	1.52
4	CCl ₄	8.316	8.294	1.48

From the analytical results it is found that for every mole of thiophosphoryl fluoride taken for reaction one mole of hydrogen sulphide is liberated. The reaction may be represented by the equation



The amount of iodine estimated is found to be rather low compared to the amount expected from the stoichiometry of the equation. This may be attributed to the oxidation of trivalent phosphorus and formation of phosphorus iodides.

The foregoing experimental results indicate that the phosphorus-sulphur bond in thiophosphoryl fluoride could be ruptured by oxidation and reduction.

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