

Received: December 28, 1983; accepted: February 29, 1984

## REACTION OF THIOPHOSPHORYL FLUORIDE WITH SULPHUR TRIOXIDE

H.P.SAMPATH KUMAR, D.K.PADMA AND A.R.VASUDEVA MURTHY

Department of Inorganic and Physical Chemistry  
Indian Institute of Science, Bangalore-560012 (India)

### SUMMARY

Thiophosphoryl fluoride is observed to undergo a facile reaction with sulphur trioxide forming phosphoryl fluoride, sulphur dioxide and elemental sulphur in quantitative yields. In the presence of excess of sulphur trioxide, however, the elemental sulphur released combines with it to form sulphur sesquioxide which subsequently decomposes and gives off sulphur dioxide. Similar observations are made with oleum.

### INTRODUCTION

We have reported [1] that phosphorus trifluoride undergoes oxidation to phosphoryl fluoride with sulphur trioxide or freshly prepared oleum liberating equimolar amounts of sulphur dioxide. It was of interest to study the reaction between sulphur trioxide and thiophosphoryl fluoride. Preliminary trials indicated that when the two reagents were allowed to mix, the reaction set in immediately resulting in the formation of phosphoryl fluoride, sulphur dioxide and elemental sulphur in quantitative yields. However, in the presence of excess of sulphur trioxide the elemental sulphur released combined with it to form greenish blue sulphur sesquioxide which subsequently decomposed to give off sulphur dioxide. Similar results were observed when thiophosphoryl fluoride reacted with oleum. The details of this investigation are described in this paper.

**EXPERIMENTAL****Reagents****Thiophosphoryl fluoride**

A pure sample of thiophosphoryl fluoride was prepared by the fluorination of thiophosphoryl chloride using sodium fluoride in boiling acetonitrile [2] and stored in a previously evacuated glass globe provided with stopcocks lubricated with KEL-F grease.

**Sulphur trioxide**

Sulphur trioxide was prepared by the distillation of a commercial sample of oleum (25%) in vacuo [3] and purified by repeated distillations (4 times) over phosphorus pentoxide and stored as above.

The sulphur trioxide content of the oleum sample employed for the reaction was estimated by a standard titrimetric method [4].

**Reaction(A) Thiophosphoryl fluoride (in excess) and sulphur trioxide**

A known amount of thiophosphoryl fluoride was taken in a glass reaction tube, ( $T_1$ ) fitted with appropriate stopcocks and attached to a vacuum line. The tube  $T_1$  was cooled with liquid nitrogen and a known amount of sulphur trioxide was condensed into it. The cooling bath was removed and the tube ( $T_1$ ) was allowed to attain room temperature ( $25^\circ\text{C}$ ) over 10 to 15 minutes. During this interval, the reagents were observed to react as indicated by a series of colour changes from orange yellow to brown. The vapours condensed into coloured droplets which gradually evaporated off leaving behind a colourless residue on the walls of the reaction tube during the course of about two hours. An examination of the IR spectrum of the gaseous mixture revealed the presence of

unreacted thiophosphoryl fluoride (IR absorptions at 402(m), 435(m), 695(m), 942(vs), 980(vs), 1670(w) and 1880(w)  $\text{cm}^{-1}$ , recorded with KBr windows Ref [5] ) along with phosphoryl fluoride (absorptions at 473(s), 493(ms), 873(ms), 990(vs) and 1415(ms)  $\text{cm}^{-1}$  [6] ) and sulphur dioxide (absorptions at 520(s), 1150(s) and 1360(s)  $\text{cm}^{-1}$  [7] ). The gaseous products of the reaction were isolated by fractional distillation and estimated [8].

The experimental results are presented in Table I.

It is well known [9] that a blue/bluish green colour is developed when elemental sulphur reacts with sulphur trioxide or when the former is dissolved in oleum. Such a colouration is attributed to the formation of sulphur sesquioxide ( $\text{S}_2\text{O}_3$ ). However, the coloured product is not stable. It gives off sulphur dioxide until all the sulphur is consumed in the presence of excess of sulphur trioxide. It was, therefore, of interest to study the reaction of thiophosphoryl fluoride with excess of sulphur trioxide to investigate the behaviour of elemental sulphur released during the reaction.

#### Reaction (B) Thiophosphoryl fluoride and sulphur trioxide (in excess)

A known excess of sulphur trioxide was condensed into a reaction tube ( $T_1$ ) containing a known amount of thiophosphoryl fluoride. When the tube  $T_1$  was allowed to attain room temperature ( $25^\circ\text{C}$ ), a vigorous reaction set in with the formation of yellow clouds followed by a series of colour changes from orange yellow to brown, green to bluish green over 10 to 15 minutes. The IR spectrum of the gaseous products (recorded using sodium chloride windows) showed the presence of sulphur dioxide and phosphoryl fluoride only, indicating that thiophosphoryl fluoride is completely consumed in the reaction. The absorptions due to sulphur trioxide merged with those due to sulphur dioxide [10]. The tube  $T_1$  was warmed in a boiling water bath to decompose the coloured residue. The products of the reaction were isolated and estimated.

TABLE I

## Reaction of thiophosphoryl fluoride with sulphur trioxide

Reagent taken in excess	Expt. No.	Amounts of reagents taken*		Amount of sulphur dioxide*		Amount of sulphur*	
		Thiophosphoryl fluoride	Sulphur trioxide	Expt.	Percentage	Expt.	Percentage
PSF <sub>3</sub> (A)	1	2.5625	1.2213	1.2063	98.80	1.2094	98.60
	2	1.7408	1.5413	1.4928	96.80	1.5250	99.00
	3	1.8267	1.0625	1.0313	96.99	1.0469	98.50
SO <sub>3</sub> (B)	1	1.6600	16.2788	4.9781	74.97	0.5050	91.10
	2	1.6400	17.7250	4.9172	74.96	0.4931	90.02
Oleum	1	1.6300	17.2800	3.6203	55.52	0.8800	91.10
	2	1.5433	25.9200	3.0500	49.40	0.9900	95.10

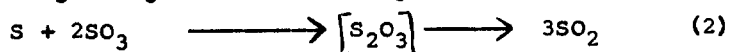
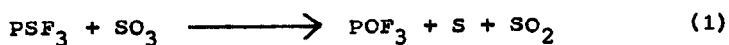
\* Quantities are expressed in m moles

Reaction (C) Thiophosphoryl fluoride and sulphur trioxide  
(in oleum)

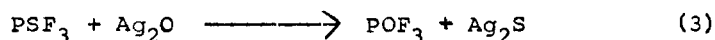
A known amount of thiophosphoryl fluoride was condensed into a reaction tube ( $T_1$ ) cooled in liquid nitrogen and in which oleum holding an excess of sulphur trioxide was taken. As the tube attained room temperature ( $25^\circ\text{C}$ ) a yellow/dull white solid formed near the liquid surface. The solid slowly dissolved in oleum imparting a dark green colour. During an interval of 2 hours the colour of the liquid gradually darkened. The IR spectrum of the volatile products evolved at room temperature during a period of 4 hours was recorded at frequent intervals. The spectrum recorded at the end of 4 hours indicated the presence of phosphoryl fluoride and sulphur dioxide indicating the complete consumption of thiophosphoryl fluoride in the reaction. The absorptions due to sulphur trioxide merged with those due to sulphur dioxide. The tube was kept for a further period of 4 hours and warmed to decompose the coloured residue. The products were separated and estimated.

RESULTS AND DISCUSSION

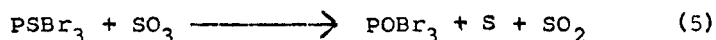
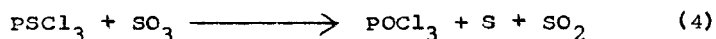
The experimental results observed during the present study indicate that one mole each of sulphur dioxide and elemental sulphur are produced during the reaction between sulphur trioxide and thiophosphoryl fluoride in excess. In the presence of excess of sulphur trioxide (either free or in solution) the elemental sulphur released is oxidised by residual sulphur trioxide and gives off sulphur dioxide via the formation of sulphur sesquioxide,  $\text{S}_2\text{O}_3$ . These reactions may be represented in terms of the equations:



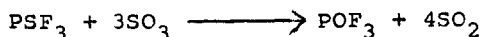
The phosphorus-sulphur bond in thiophosphoryl fluoride is the primary point of attack by oxidising agents. It is easy to visualise the replacement of sulphur by oxygen with the formation of more stable phosphoryl linkage. The oxidation of thiophosphoryl fluoride with oxides of nitrogen [11] or silver oxide [12] follows the same initial pattern. For instance, the reaction with silver oxide may be represented as



It is of interest to point out that similar replacement of sulphur by oxygen is observed to take place when sulphur trioxide reacts with thiophosphoryl chloride [13] or thiophosphoryl bromide [14].



Three moles of sulphur trioxide are necessary to oxidise all the sulphur in thiophosphoryl fluoride and give off sulphur dioxide in quantitative yield in terms of the equation :



The analytical results in sections B and C of Table 1 indicate that in spite of a large excess of sulphur trioxide, the amount of sulphur dioxide evolved is considerably less than the theoretical expectation. While it is about 75% with sulphur trioxide it decreases to 50% with oleum. It is easy to compute the amount of unreacted sulphur assuming that a gram atom of sulphur is formed along with a gram mole of sulphur dioxide for every gram mole of thiophosphoryl fluoride taken for the reaction. On this basis it is calculated that about 70% of elemental sulphur is oxidised by sulphur trioxide while only about 45% is oxidised by oleum.

## REFERENCES

- 1 H.P. Sampath Kumar, D.K. Padma and A.R.Vasudeva Murthy, Indian J. Chem., accepted for publication.
- 2 D.K. Padma, S.K. Vijayalakshmi and A.R.Vasudeva Murthy, J. Fluorine Chem. 8 (1976) 461.
- 3 R.J. Lovejoy, J.H. Colwell, D.F.Eggers and G.D.Halsey, J. Chem. Phys. 36 (1962) 612.
- 4 J. Rosin, Reagent Chemicals and Standards, 5th Edn., D. Van Nostrand Co. (1967) 510.
- 5 J.R. Durig and J.W. Clark, J. Chem. Phys. 46 (1967) 3057.
- 6 H.S. Gutowsky and A.D. Liehr, Ibid., 20 (1952) 1652.
- 7 R.D. Shelton, A.H. Nielson and W.H. Fletcher, Ibid., 21 (1953) 2178.
- 8 A.R.Vasudeva Murthy, V.A. Narayan and M.R.A. Rao, Analyst, 81 (1956) 373.
- 9 Vogel and J.R. Partington, J. Chem. Soc. 127 (1925) 1514.
- 10 See 3 above,
- 11 R.G. Kalbandkeri, D.K. Padma and A.R. Vasudeva Murthy, Annual Convention of Chemists, December 26-27 (1981) India.
- 12 D.K.Padma, S.K. Vijayalakshmi and A.R.Vasudeva Murthy, J. Fluorine Chem. 10 (1977) 173.
- 13 W. Van der Veer and F. Jellinck, Rec. Trav. Chim. 87 (1968) 365 - 374.
- 14 W. Van der Veer and F. Jellinck, ibid. 89 (1970) 833.